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

**Suggested citation for the entire volume:**

**Suggested citation for an individual paper:**

---

**Volume 1**
Advances in understanding hydrothermal processes

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

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

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

---

This publication cannot be reproduced in whole or in part without the permission of The Society for Geology Applied to Mineral Deposits (SGA).

A digital version of theses volumes is available from the SGA website at www.e-sga.org
KEYNOTE: Andean Arc and Backarc Magmatic and Tectonic Processes and the Formation of Giant Cu, Au and Ag Porphyry Deposits. Suzanne Mahlburg Kay

Links between tectonics, magmatism, and mineralization in the formation of Late Cretaceous porphyry systems in the Yukon-Tanana upland, Alaska, USA. Douglas C. Kreiner, James V. Jones III, Erin Todd, Chris Holm-Denoma, Jonathan Saul Caine, Jeff Benowitz

Structural control and tectonic environment of the Cenozoic giant Kadjaran porphyry Cu-Mo and epithermal system, southern Armenia, Lesser Caucasus. Samvel Hovakimyan, Robert Moritz, Hervé Rezeau, Marianna Harutunyan, Arshavir Hovhannisyan, Rafael Melkonyan, Rodrik Tayan Gevorg Iskandaryan

Cenozoic porphyry and epithermal systems in the South Armenian Block, Lesser Caucasus, Armenia: new temporal, geochemical and petrogenetic constraints. Marion Grosjean, Robert Moritz, Samvel Hovakimyan, Massimo Chiaradia, Richard Spikings, Hervé Rezeau, Alexey Ulyanov, Jorge Spangenberg, Rafael Melkonyan


Revised model of porphyry-Cu formation: ore forms at the porphyry to epithermal transition, overprinting barren stockwork veining and potassic alteration. Thomas Driesner, Christoph A. Heinrich

Fertilisation of porphyry magmas by Cu-Au sulfide melt mobilisation in the lower crust. David Holwell, Thomas Knott, Daryl Blanks, Marco Fiorentini, Iain McDonald, Cam McCuaig

Recycling of metal-fertilized lower continental crust: Origin of non-arc Au-rich porphyry deposits at cratonic edges. Zeng-Qian Hou, Rui Wang, Ye Zhou


Platinum-group elements as a tracer of sulphide saturation in evolving magmas: application to the Río Blanco Cu-porphyry deposit, central Chile. Yamila Cajal, Ian H.Campbell
The nature of fluid exsolution and migration in porphyry systems – evidence from the Yerington District, Nevada

Lawrence C. Carter, Ben J. Williamson, Robin N. Armstrong, Simon R. Tapster

INVITED: “Chlorimetry” of porphyry copper forming magmas, why does it matter?.....

Cyril Chelle-Michou

KEYNOTE: Fertility Assessment in Porphyry Copper Exploration – An Industry Perspective

Christian Ihlenfeld

Zircon-Hosted Apatite Inclusions at La Granja Cu-Mo Porphyry: Implications for the Use of Apatite as a Probe of Magma Petrogenesis

Emily Brugge, Jamie J. Wilkinson, Yannick Buret, Andrew J. Miles

Using PGE geochemistry to assess magma fertility in the Polo Sur and Penacho Blanco Cu-porphyry deposits, Centinela District, Northern Chile

Carlos I. Carrasco-Godoy, Ian H. Campbell

Titanite petrology and chemistry from the Strontian Igneous Complex

Tom Matthews, Jamie Wilkinson, Matthew Loader

Magma fertility related to porphyry copper mineralization potential in Sangilo, Baguio Mineral District, Philippines


Role of breccias in porphyry copper formation

Richard H. Sillitoe

The hypogene evolution of the Spence porphyry copper system, northern Chile


Ore genesis of the Devonian superimposed Yulekenhalasu porphyry Cu-Mo deposit in CAOB: Insights from paragenesis and fluid inclusions

Chao Wu, Huayong Chen

Relative timing of sulfide precipitation at the Batu Hijau porphyry Cu-Au deposit, Sumbawa, Indonesia

Michael Schirra, Thomas Driesner, Christoph A. Heinrich

Magnetite alteration and formation of porphyry Cu (Au) deposits

Huaying Liang, Wenting Huang, Weidong Sun, Long Ren

Chlorite alteration in porphyry Cu systems: New insights from mineralogy and mineral chemistry

Bing Xiao, Huayong Chen, Yuzhou Feng, Pete Hollings, Yu Zhang

Porphyry Cu(Mo) deposits of the Urals: insights from molybdenite trace element geochemistry

Olga Y. Plotinskaya, Vera D. Abramova, Dmitry Bondar, Reimar Seltmann, John Spratt

Identifying a superimposed porphyry-epithermal system based on alteration mapping: example from the Cretaceous Dongnan Cu deposit, Zijinshan ore district (SE China)

Gan Duan, Huayong Chen
The Ryabinovoe Cu-Au-Porphyry Deposit (Southern Yakutia, Russia): Geology, Wallrock Alteration, Noble Gases Isotope Systematics and Isotopic Dating of Ore-Forming Processes………………………………………………………………………………………………………..1073
Shatova N.V., Shatov V.V., Molchanov A.V., Terekhov A.V., Sergeev S.A., Prasolov E.M., Dvornik G.P., Leontev V.I.,

Geological position and structural control of ore mineralization of the Manukuyu-Varchatinsky ore cluster (the Polar Urals, Russia)..........................................................................................................................................................................................1077
Julia N. Ivanova, Roman I. Vyhirstenko, Ilya V. Vikentyev

Mineralisation in the K1 vein-system, Kencana Epithermal Deposit, Gosowong Goldfield.........................................................................................................................................................................................................................................................1081
Thomas Tindell, Kotaro Yonezu, Syafrizal,

The new discovered Tasikmadu porphyry copper-(gold) prospect in Watulimo sub-district, Southern Trenggalek, Java Island, Indonesia: Characteristics and exploration challenges..........................................................................................................................................................................................1085
Arifudin Idrus, Trifatama Rahmalia, Kresna Kustrianugroho

Contributions to the mineralogical and geochemical characterization of Fe-Sn-Zn-Cu-In skarn-type mineralization in the Schwarzenberg mining district, Germany.................................................................................................................................1089
Malte Stoltnow, Thomas Seifert, Tilman J. Jeske, Sabine Gilbracht, Joachim Krause

Transition from porphyry to epithermal Cu-Au environments in Sardinia – Italy..................1093
Sandro Fadda, Maddalena Fiori, Carlo Matzuzzi

Geological setting and lithological controls of breccia-hosted Cu-Au ore at the Late Cretaceous Kvemo Bolnisi prospect, Bolnisi, Lesser Caucasus, Georgia.................................................................1097
Nino Popkhadze, Greg Corbett, Jason Cunliffe, James Royall, Simon Cleghorn, Mikheil Chokhonelidze, Jack Davies, Ryan Hampton, John Newman, Leqso Gelashvili, Koba Khmaladze, Tariel Tedliashvili, Robert Moritz

Regional-scale mapping of mineral potential for porphyry Cu-Au deposits in southeastern Europe ..................................................................................................................................................................................1101
Felix Camenzuli and Hartwig E. Frimmel, Adam Wooldridge

Mineralogical characterization of Te-Au porphyry- epithermal California prospect in Tolima, Colombia..................................................................................................................................................................................................................................................1105
Iván Mateo Espinel Pachón, Andrés Felipe González Durán, Juan Carlos Molano Mendoza, Juan David Alarcón Rodriguez, Mónica Ágreda López

Geology setting and metallogenesis of the Alta Floresta Province, southern Amazon Craton (Brazil)................................................................................................................................................................................................................................................................................1109
Veronica Trevisan, Roberto Xavier, Steffen Hagemann, Anthony Kemp, Robert Loucks, Jian-Feng Gao

Trace element variation in ore minerals from the Iron Cap (KMS) deposit, British Columbia, Canada: Implications for fluid evolution in porphyry-epithermal gold systems..........................1113
Hugh Graham, Daniel Morgan, Robert Chapman, David Banks
An Integrated Accessory Mineral Approach to Understanding Post-Subduction Magmatism and Mineralisation

Jessica Berry, Andrew J. Miles, David A. Holwell, Shaun Graham, Lane, Cambridge, C. Johan Lissenberg, Chiara M. Petrone

Trace element chemistry, polytypes, isotopic composition and Re-Os dates of molybdenite from the Bingham Canyon Cu-Au-Mo porphyry deposit, Utah

Simon Kocher, Jamie J. Wilkinson, Robin N. Armstrong, Iain McDonald, Mark Rehkaemper, Robert A. Creaser, Jens Najorka

Salinity of magmatic fluid: experiments, phase equilibrium models, and implications for ore formation

David Dolejš

---

New discoveries – new views: Advances in the Science of Mineral Exploration

The critical role of architecture in constraining fluid flow and sustain chemical gradients in Late Archean Gold Systems, eastern Yilgarn Craton

Adam B. Bath, John L. Walshe

Critical mineral systems under cover: insights from magnetic, gravity, and magnetotelluric 3D inversion models, Southern Midcontinent, USA

A.E. McCafferty, P.A. Bedrosian, J.D. Phillips

Automated facies classification and gold grade prediction using machine learning algorithms

Glen T. Nwaila, Steven E. Zhan, Hartwig E. Frimmel

Comparisons of Metallogenesis within the Pyrenees-Alps-Zagros-Himalaya collisional orogens

Hongrui Zhang, Zengqian Hou

500 Myrs in the making: Control of Gondwana margin assembly on Carboniferous orogenic gold in Peru

Daniel Wiemer, Steffen G. Hagemann, Nicolas Thébaud, Carlos Villanes

Geodynamic and metallogenetic reconstruction of the Neoarchean Qingyuan greenstone belt: Evidence from petrogeochemistry and U-Pb geochronology

Zidong Peng, Lianchang Zhang, Changle Wang, Xiaoxue Tong

Crustal architecture of the south-east Superior Craton

David R. Mole, Jeffrey H. Marsh, Phil Thurston, John A. Ayer, Balz S. Kamber
KEYNOTE: Isotopic and geochemical indicators on volcanic-hosted massive sulfide prospectivity: a review
David L Huston, David C Champion, Michael P Doublier

Does heat matter? Magmatism and metallogeny in the IPB: assessment of future mineral exploration vectors
André Cravinho, Jorge MRS Relvas, Rita Solá, Igor Mora, Luis Albardeiro, João X Matos, Rute Salgueiro, Daniel de Oliveira, Nelson Pacheco

Unravelling the geochemistry of dark-grey to black metapelites in the Iberian Pyrite Belt (Portugal): the relation to massive sulphide ores
Filipa Luz, António Mateus

Diagenetic evaluation of a possible redbed source for anomalous Cu in the Paleozoic-hosted Cornwallis Zn district, NU
Mathieu, J., Turner, E.C

Hot, deep-sourced, hydrothermal Cu-Ag-Au-PGE-polymetallic deposits of the Zechstein Kupferschiefer age
Volker Spieth, Hans-Joachim Massonn, Jürgen C. Kopp, Tillmann Viefhaus, Michael Trinkler, Heinz-Jürgen Bernhardt, Stanley B. Keith, Jan C. Rasmussen

Permeability network, alteration and mineralization of the Spitfire basement-hosted uranium prospect, Western Athabasca, Canada
Maher Abdelrazek, Antonio Benedicto, Mostafa Fayek, Cameron Mackay, Darren Slugoski, Olivier Gerbeaud, Patrick Ledru

The Mineral System concept applied to unconformity-related uranium deposits of the Athabasca Basin (Canada)
Patrick Ledru

KEYNOTE: Mineral Systems to Exploration Systems to Research Roadmaps
T. Campbell McCuaig, Stephen Busuttil, Keenan Jennings, Elizabeth R. Sharman, Jean des Rivières

Evaluating the role of the mantle as a source of metals for magmatic-hydrothermal ores in arc systems
José María González Jiménez, Fernando Gervilla, Claudio Marchesi, Juan José Rovira, Fernando Torns, Rubén Piña, Vanessa Colás, Edward Saunders, Graham C. Begg

The metal budget above subduction zones: Evidence from pyroxenite xenoliths
Hannah S. R. Hughes, Magdalena M. Matusiak-Małe, Iain McDonald

Crustal-scale controls on zinc-lead-silver deposits of the North Australian Zinc Belt: evidence from lead isotope geochemistry and surface wave tomography
David L Huston, David C Champion, Karol Czarnota, Mark Hoggard, Fred Richards, George M Gibson, Bryant Ware, Svetlana Tesselina, Graham Carr
Mapping Pb isotope variations across Ireland: from terrane delineation to deposit-scale fluid flow

Steven P. Hollis, Aileen L. Doran, Julian F. Menuge, J. Stephen Daly, John Güven, Stephen J. Piercey, Mark Cooper, Oakley Turner, Richard Unitt

Correlated petrographic and isotopic studies (S, Pb) of carbonate-hosted Zn-Pb mineralization: the formation of the high-grade Island Pod, Lisheen

Aileen L. Doran, Julian F. Menuge, John Güven, Steven P. Hollis, Adrian J. Boyce, Stephen J. Piercey

Preliminary Results: The Tara Deep Zn-Pb Deposit, Navan, Co. Meath, Ireland

Drummond, D.A., Boyce, A. J., Yesares, L., Blakeman, R. J., Ashton, J. H., Blakeman, R. J., Ashton, J. H.

Structural modification and associated remobilization of the San Vicente MVT deposit during the Andean Orogeny

Helen B. McFarlane, Steffen Hagemann, Jorge Palacios, Nancy Tuanama, Carlos Flores

Pre-metamorphic oxidation of the Broken Hill deposit at Aggeneys (South Africa) revealed by Cu isotopes

Stefan Höhn, Hartwig E. Frimmel, Vinciane Debaille

GIS-based mineral system approach for prospectivity mapping of iron-oxide apatite-bearing mineralisation in Bergslagen, Sweden

Martiya Sadeghi, Mehrdad Bastani, Stefan Luth, Alireza Malehmir, Emma Bäckström, Paul Marsden

Defining an alkaline igneous-associated REE-HFSE mineral system: a foundation to map plays, uncertainty and risks to project value

Graham J. Banks, Benjamin F. Walter, Michael A.W. Marks, Pete R. Siegfried

Late-orogenic W-Sn vein-type mineralization at Minas da Panasqueira (Portugal): a structural and in-situ Rb-Sr geochronological study

Dominique Jacques, Philippe Muchez, Manuel Sintubin, Thomas Zack

Stream sediment geochemistry for regional prospectivity analysis: Tin, cesium, tantalum and tungsten anomalies in Leinster, southeast Ireland

David Kaeter, Julian F. Menuge, John Harrop

Impact of subduction zone seismotectonics on magmatic systems and porphyry deposits

Alex Jenkins, Juliet Biggs, Alison Rust, Rosa Jara Torres

Metallogenic controls of mantle plumes on platinum-group elements and precious metals

Jordan J. Lindsay, Hannah S. R. Hughes, Jens C. Ø. Andersen, Iain McDonald

Mantle metasomatism in SCLM under the Grib Kimberlite pipe, Arkhangelsk province, Russia

Nataliya M. Lebedeva, Anna A. Nosova, Alexey V. Kargin, Yulia O. Larionova, Yana S. Tikhomirova
Petrography, geochemistry and geochronology of rocks related to rare elements (RE) outcropping in southeastern Colombia

Héctor Ricardo Campos Rodríguez, José Alejandro Franco Victoria, Alejandro Piraquive, Jimmy Alejandro Muñoz, Thomas Cramer, Amed Bonilla Pérez, Zeze Amaya Perea

Nb-rutile: A reference mineral for timing of Sn, Nb-Ta, U-Th and REE mineralization at NW part of the Amazonian Craton

Jose A. Franco, Thomas Cramer, Amed Bonilla, Alejandro Piraquive, Héctor Campos

Sulphide-sulpharsenide Re-Os geochronology and the wide-angle lens on Earth’s history - emerging views for new discoveries in ore deposit research

Nicolas J. Saintilan, Robert A. Creaser, David Selby

Elvira: a new shale-hosted VMS deposit in the Iberian Pyrite Belt

Guillem Gisbert, Emma Losantos, Fernando Tornos, Juan Manuel Pons, Juan Carlos Videira

Why magnesite, talc, and MVT ore deposits are associated with burial dolostones. Serpentinization provides the magnesium

Enrique Merino, Àngels Canals

Fluid histories and controlling factors on mineralisation in the Cornwallis Zn-Pb district, Arctic Canada

Mathieu J., Turner E.C., Kontak D.J., Fayek M.

Geochemical characterization of felsic metavolcanic rocks hosting the Archean Taivaljärvi Ag-Zn-Pb-Au deposit in the Tipasjärvi greenstone belt, Finland

Axel Cima, Eero Hanski, Erkki Kuronen, Tapio Halkoaho

New Techniques for ore discovery

KEYNOTE: How will technology facilitate Agile Discovery?

James S Cleverley

A comparison of random forests and cluster analysis to identify ore deposits type Using LA-ICPMS analysis of pyrite

Daniel D. Gregory, Chao Liu, Shaunna M. Morrison, Robert M. Hazen, Mathew J. Cracknell, Ross R. Large, Peter McGoldrick, Stephen Kuhn, Michael J. Baker, Nathan Fox, Ivan Belousov, Jeffery A. Steadman

3D ore prediction by MLAs based on computational modeling in maturely explored area: A case study in Anqing orefield, China

Liu Liangming, Qin Yaozhu
Building 3D geomodels using XRF-XRT-generated drill core data: The Lovisa-Håkansboda base metal- and Stråssa-Blanka iron deposits in Bergslagen, Sweden
Stefan Luth, Fredrik Sahlström, Nils Jansson, Johan Jönberger, Stefan Sädbom, Eric Landström, Mikael Bergqvist, Nikolaos Arvanitidis, Ronald Arvidsson

INVITED: Isotope geochemistry of groundwaters in mineral exploration – the tip of the iceberg
James Kidder, Matthew I. Leybourne, Alexandre Voinot, Daniel Layton-Matthews

Sonic Drilling coupled with on-line-on-mine-analyses: first tests at the Villeveyrac bauxite deposit (Southern France)

Application of non-destructive, micro-focus X-ray computed tomographic analyses on gold occurrence and distribution in drill-core samples
Thomas Stapley, Gillian R. Drennan, Asinne Tshibubudze, Glen T. Nwaila, Lunga C. Bam, Jason D. Kirk

Determination of Re-Os isotopes, PGEs by isotope dilution, and trace elements from single aliquots of geological materials of economic interest
Bryant Ware, Svetlana Tessalina, Vitor Barrote

Mineral trace element chemistry in the exploration for magmatic sulfide deposits
Marek Locmelis, Jonathan Obrist-Farner, Andreas Eckert, Marco L. Fiorentini, Stephen J. Barnes, Eero J. Hanski, Alan F. Kobussen, Ricardo D. Arevalo Jr., Igor S. Puchtel

KEYNOTE: To make better exploration tools, we first need to better understand ore deposits
Tim Ireland, Robert Siewwright, Adam Bath, Elitsa Stefanova, Janharm Godfroid

INVITED: Hydrothermal Apatite as an Indicator of Porphyry Cu Deposit Fertility
Matthew A. Loader, Jamie J. Wilkinson, Robin N. Armstrong

Porphyry Copper Indicator Minerals (PCIM) in stream sediment samples: Application at the Taurus deposit with comparison to other exploration techniques
Karen D. Kelley, Garth E. Graham, Douglas C. Kreiner, Katharina Pfaff

Titanite geochronology and chlorite chemistry resolve multiple phases of propylitic alteration in the Oyu Tolgoi district, Mongolia
Lisa Hart, Jamie J. Wilkinson, Robin Armstrong

Hyperspectral image analysis of Aguas Teñidas, Magdalena, Sotiel and Majada deposits: towards a drill-core scan in the Iberian Pyrite Belt
Pedro S.T. Mendes, Pierre Barnabé, Eric Pirard, Juan Manuel Pons, Juan Carlos V. Vasquez, Carlos G. Piña

High-resolution short-wave infrared hyperspectral characterization of alteration at the Sadiola Hill gold deposit, Mali, Western Africa
Semyon Martynenko, Pekka Tuisku, Frank J.A. van Ruitenbeek, Kim A.A. Hein
Application of ASTER Data for Exploration of Porphyry Cu-Au Deposits in the Neoproterozoic Arabian–Nubian Shield: a Case Study from Egypt

Hamdy El Desouky

1329

Structural-geochemical vectors for cost-effective targeting of unconformity-type uranium mineralization: the Maverick uranium deposit case study

Ranee E. Joshi, Irvine R. Annesley, Gautier Laurent, Christine L. McKechnie, Zoltan Hajnal

1333

Geophysical imaging of iron-oxide apatite deposits in the eastern Adirondacks, northern New York

A.K. Shah, R.D. Taylor, G.J. Walsh

1337

New methodology of application of historical geophysical materials for the exploration of mineral deposits, as presented for Nowa Sól area

Stanislaw Speczik, Lidia Dziewińska, Andrzej Pepel, Waldemar Jóźwiak, Krzysztof Zieiński

1341

Implicit model creation for the application of geophysical inversion and forward modelling; drill target generation for undercover ore deposits

Daniel Gerger, Patrick Ledru, Dwayne Kinar, Grant Harrison, Gabriel Courrioux, Charles Gumiaux

1345

Prospecting strategy for deep sediment-hosted Cu-Ag ore deposits in Poland

Alicja Pietrzela, Stanisław Speczik, Tomasz Bieńko, Krzysztof Zieiński

1349

Miniaturised Gravity Sensors for Geophysical Monitoring


1353

Low volume solution ICP-MS: achieving high-precision geochemical analysis of small amounts of sample

Lewis A. Banks, Simon R. Tapster, Matthew S.A. Horstwood, Simon R. Chenery, Daniel J. Smith, Tiffany L. Barry

1356

Biogeochemical surveys for epithermal Au-Ag exploration in New Zealand

Anthony B. Christie, Colin E. Dunn

1359

Troubleshooting hydrogeochemical sampling in grassroots mineral exploration: a Case Study from Central Australia’s Western Amadeus basin

Jennifer A. Roskowski, Nathan Reid, James Kidder, Ryan R.P. Noble

1363

Application of synchrotron X-rays to ore geology research

Bjorn P. von der Heyden

1367

Garnierite characterization for open data bases for nickel laterite exploration

Nicolas Maubec, Pierre Gilles Blaineau, Cédric Duée, Anthony Da Silva Alves, Xavier Bourrat, Guillaume Wille, Beate Orberger, Monique Le Guen, Cristina Villanova-de-Benavent

1370

It’s not easy being green – detecting arc-related mineral system fingerprints using mineral chemistry in ‘propylitic alteration’ in a Cambrian arc terrane Victoria, Australia

Rob Duncan, David Taylor, Sébastien Meffre, Ivan Belousov, Leonid Danyushevsky, David Cooke

1374
Remote sensing based geological mapping and mineral exploration of the area of North Waziristan Pakistan..........................................................................................................1378
Adil Nawaz, Janusz Magiera

Lithium prediction using reflectance spectroscopy in Jiajika area of western Sichuan province, China..........................................................................................................1381
Jingjing Dai, Denghong Wang, Hongzhang Dai

Soil magnetic susceptibility mapping as a vectoring tool for mineral exploration: an example from southern New Zealand.........................................................1385
Adam P. Martin, Christian Ohneiser, Rose E. Turnbull, Delia T. Strong, Philip Rieger

The new approach for kimberlite pipes exploration based on passive seismic and radiometric methods (the example of the Arkhangelsk province).........................................................1389
Konstantin Danilov, Evgenii Iakovlev, Nikita Afonin

Delineation of the permissive tract using computational mineral prospectivity modelling......1393
Johanna Torppa, Kalevi Rasilainen
Magmatic hydrothermal systems: from Porphyry to Epithermal

Andean arc and backarc magmatic and tectonic processes and the formation of giant Cu, Au and Ag porphyry deposits

Suzanne Mahlburg Kay
Cornell University, USA

Abstract. A long-standing question has been the relation between Andean arc and backarc magmatic and tectonic processes and the formation of giant Andean Cu, Au, Ag, Zn and Sn deposits. Integrating geochemical, geophysical and structural studies provides insights into some possible links in the Neogene Andes of Chile, Argentina and Bolivia. The relation of Andean tectonic processes and ore deposits are explored in two examples. The first involves the role of shallowing subduction zones related to aseismic ridge collision, crustal thickening and forearc subduction erosion in setting the stage for generating the giant Miocene-Pliocene Cu-Au porphyries in the largely igneous crust of the Chilean flatslab and surrounding region of Chile and Argentina. The second involves the role of a steepening subduction zone, a peak in extreme crustal thickening related to compressional deformation and lower crustal flow, and the incorporation of crust and lithosphere removed by delamination into the mantle wedge in generating the giant Ag-Sn-Zn deposits in the more sediment-rich crust and older Precambrian basement of the Andean backarc in the Bolivian Altiplano.

1 Introduction

A number of studies in the past 20 years have addressed the relation of subduction zone arc and continental magmatic and tectonic processes to the formation of giant Andean arc and backarc Cu, Au, Ag and Sn porphyry deposits. While general mechanisms for driving the related magmatism are relatively well-established, specific subduction-related parameters linking episodes of ore formation to particular tectonic environments are less clear. Virtually all proposals link the formation of the large and giant Andean ore deposits to arc subduction processes. A number of papers have suggested a relationship of giant Cu, Au and Ag deposits to episodes of shallowing or steepening subduction zones and crustal thickening associated with contractional deformation (e.g. Kay et al. 1999; Kay and Mpodozis 2001, 2002; Cooke et al. 2005). More recently in a general analyses of the settings of giant Andean porphyry Cu deposits, Butterworth et al. (2016) have pointed to a coincidence of rapid convergence rates (~100 km/Myr), a subduction zone obliquity of ~15°, a subducting plate age of ~25–70 Myr, and a location along a trench more than 2000 km from the edge of the plate boundary as common features in the formation of giant Andean porphyries.

On a more local magmatic scale, the general mechanisms of porphyry formation seem to be relatively well established. As summarized in recent papers such as those of Richards (2018) and Gilmer et al. (2018), porphyry deposits are concentrated in the shallow upper crustal parts of arc magmatic systems whose ultimate roots are in the mantle wedge above the subducting slab. In detail, these porphyries reflect the end products of mantle magmas that intrude and evolve in lower crustal MASH (melting, assimilation, storage & homogenization) zones. The melts extracted from this zone are then further processed as they rise through the lower to middle crust and accumulate in the mid-crust from where they are periodically transferred into upper crustal batholiths at depths of 5 to 10 km. The formation of the large porphyries is rare and takes place rapidly (~0.1 Myr) as hydrous volatiles are exsolved from the underlying batholiths and channeled into structurally controlled cupolas at depths of 2–5 km. Richards (2018) speculates on specific mechanisms that could explain their sporadic emplacement and suggests that sudden volatile release could be triggered by large sector volcanic collapses or earthquakes.

Outstanding questions are how arc magmatic and tectonic processes like shallowing and steepening subduction zones, crustal thickening, lower crustal flow, delamination of dense overthickened lower crust with the underlying lithospheric mantle, forearc subduction erosion and the composition of the crust and mantle lithosphere factor into the character and formation of giant Andean Cu, Au and Ag arc and backarc porphyries. Two regional examples are explored below. The first involves the relation of aseismic ridge subduction and the shallowing of the subducting oceanic plate, crustal thickening, and forearc subduction erosion in creating the giant Miocene-Pliocene Cu and Au porphyries in and on the margins of the modern Chilean flatslab region. The second addresses the role of a steepening subduction zone, crustal thickening and lower crustal flow that includes incorporating continental sediments into the lower crust and delamination of crustal and mantle lithosphere in the generation of giant Ag-Sn-Zn deposits in the Cerro Rico region of the Bolivian Altiplano.
2 Discussion

2.1 Case study 1. Maricunga-El Indio/Pascua-El Teniente region Cu-Au porphyries: Ridge subduction, crustal thickening and forearc subduction erosion

The evolving magmatic history of the Central Andean Chilean margin reflects the motion of the South America plate relative to the Nazca plate and the overriding mantle, and the subduction of anomalies on the Nazca plate. Below, we examine the Neogene magmatic history of the arc and near backarc region in and surrounding the Chilean-Pampean flatslab region from 26°S to 35°S as the Juan Fernandez Ridge arrives and subducts on the Nazca plate. This history can be viewed in terms of the evolution of the crustal and mantle lithosphere beneath the arc (e.g. Kay and Mpodozis, 2002), the relative rate of westward drift (hinge motion) of the South American plate relative to the Nazca plate, the collision of the Juan Fernandez ridge (e.g. Yáñez et al. 2001) and the possible effects of forearc subduction erosion.

The region of interest includes the late Oligocene to Miocene Maricunga magmatic arc (26°-28°S) and the southernmost late Pliocene to Recent Central Volcanic Zone (CVZ) arc that terminates with the Bonete Complex near 28°S, the region of the current Chilean-Pampean flatslab from 28° to 33°S and region of the northernmost Southern Volcanic Zone (SVZ) at 33° to 35°S (Figs. 1 and 2). The period coincides with the approach and arrival of the Juan Fernandez Ridge on the subducting Nazca plate, the shallowing of the subducting plate under the flatslab region that is accompanied by the expansion of the volcanic arc and deformation front far to the east, the thickening of the crust and the cessation of flatslab magmatism as the frontal arc moves into the foreland to the north (Goss et al. 2013) and south (Kay et al. 2005). The magmatic history of the region can further be broken into temporal stages in which common times of change can be traced from north to south (e.g. Kay and Mpodozis, 2002). These periods appear related to variable convergence rates caused by increases and decreases in the westward hinge motion of South America leading to events such as the Andes going from extension to compression around 18 Ma (see discussion in Kay and Coira 2009).

The history of the subduction of the Juan Fernandez Ridge is an important part of the evolution of the region and appears associated with porphyry mineralization. Following the ridge reconstruction of Yáñez et al. (2001), the northern end of a ~45-50° NE-oriented Juan Fernandez Ridge segment that formed after a N-S oriented segment was intersecting the Andean margin at 21°-22°S in the early Miocene. At this time, the southern end of this segment was still far to the east of the margin near 26-28°S and any relation with the ~23-19 Ma Maricunga gold belt is tenuous. However, this picture had changed by ~14 Ma as the southern end of the NE-trending Juan Fernandez Ridge segment approached the margin at this latitude and was crossing below the region by 13-10 Ma (Fig. 1a) as gold porphyry mineralization was occurring in the Maricunga belt (e.g. Mpodozis et al. 1995). At the same time, the next younger Juan Fernandez Ridge segment with a nearly E-W orientation was approaching to the south and arriving beneath the El Indio-Pascua region (Figs. 1b & c) as gold mineralization occurred from ~9.4 to 6.2 Ma (see Holly et al. 2016). In the larger picture, the timing of this mineralization coincides with shallowing of the subducting slab under the foreland in the Chilean-Pampean flatslab region to the east. This flattening was accompanied by minor mineralization as late Miocene compressional deformation drove crustal thicknesses up to 55-60 km as far as 450-500 km east of the trench and subduction-related magmatism reached the Pocho volcanic field ~700 km east of the trench at ~7.8-4.6 Ma. What just preceded and coincided with mineralization under the arc region was the crustal thickening that is reflected in the trace element chemistry, which was driven by crustal shortening to the east (e.g. Kay and Mpodozis, 2002). The continued southward advance of the E-W trending segment of the Juan Fernandez Ridge as the intersection migrated more slowly to the south shut-off magmatism across the flatslab region, while beginning to play a larger role in the region of the giant El Teniente Cu deposit to the south (Figs. 1c & d).

Figure 1. Maps showing subducting Juan Fernandez ridge (thick line) relative to evolving continental margin in purple based on reconstructions in Yáñez et al. (2001) and discussion in Kay and Mpodozis (2002). Regions of Ag, Au and Cu mineralization (ellipses) are schematically shown along with selected coeval active volcanic centers (red and black circles). Purple wedge highlights events at 27°-29°S at intersection of the Central Volcanic Zone arc and Chilean flatslab. See discussion in text.

The arrival of the E-W segment of the Juan Fernandez Ridge at ~11-10 Ma also set the stage for the possible removal of up to ~40-50 km of the Chilean forearc margin from ~27° to 34°S by forearc subduction erosion at 9-8 to 4-3 Ma. The argument for forearc subduction erosion comes from the ~40-50 km eastward displacement of the volcanic arc in the southernmost CVZ (Goss et al. 2013) and the northernmost SVZ (Kay et al. 2005) as the arc disappeared in the connecting region through the Uspallata-Calingasta Valley across the flatslab (Fig. 2). The calculated removal rate below further assumes that
the late Miocene arc front (blue line) was ~ 300 km from the trench as it is now for the modern CVZ and SVZ arc front (red line). Based on this arc migration, the implied forearc subduction erosion rate across the region is ~190 km³/my/km for 5-6 Ma from ~8 to 3 Ma (see Goss et al. 2013). This requires forearc crust and lithosphere to be entering the magma source as magmatism slowed in the migrating arc front and Au and Cu mineralization occurred in the Indio-Pascua and Rio Blanco-El Teniente belts. Such a setting would also generate extensive earthquakes, possibly facilitating an earthquake trigger for porphyry formation as suggested by Richards (2018).

2.2 Case study 2. Puna-Altiplano and Cerro Rico de Potosi Ag-Pb-Sn deposits: Delamination and lower crustal flow

The eruption history and evolving major and trace element and O-Sr-Nd isotopic characteristics of Neogene Cerro Rico–Los Frailes region magmatic rocks record the crustal thickening and delamination events under the southern Altiplano as a formerly shallow subduction zone steepened after the passing of the Juan Fernandez ridge (Fig. 1a). The temporal changes in these mafic to rhyodacitic magmas complement a crustal shortening and uplift history inferred from balanced cross-sections, surface uplift indicators and seismic studies by Garzione et al. (2017). Together, these factors provide a context in which to view the origin of the Cerro Rico de Potosi and Porco Ag-Zn-Sn porphyries.

Importantly, the strongly peraluminous chemistry (Al/Ca+K+Na = 0.05-1.35), high δ¹⁸O values (+9.73-11.09‰ in quartz), changing initial ⁸⁷Sr/⁸⁶Sr (0.707-0.7125) and ¹⁴⁴Nd/¹⁴³Nd (0.51231-0.51215) ratios and variably steep REE patterns (La/Yb up to 100) in the erupted magmas implicate a role for metapelitic contaminants that facilitate Ag-Pb-Sn mineralization. Support for deep crustal or mantle incorporation of these metapelitic components comes from steep to extremely steep “adakitic” HREE patterns (Sm/Yb = 3-14, Fig. 3) and high Sr contents (400-650 ppm) in the erupted magmas. A deep crustal source for the peraluminous components is in line with seismic data supporting a relatively silicic middle to lower crust. The transfer of upper crust components to depth is best explained by a contractional structural regime facilitated by crustal flow.

Assimilation-fractional crystallization (AFC) modelling of O-Sr-Nd isotopes and trace element in Kato et al. (2014) further suggest the erupted magmas being ~50:50 mixtures of enriched mantle basalt (⁸⁷Sr/⁸⁶Sr = 0.7055, 500-950 ppm; ¹⁴⁴Nd/¹⁴³Nd = 0.51260, 25-30 ppm; δ¹⁸O = +5.8‰) and variably peraluminous crustal melts (δ¹⁸O = +13-16‰, ⁸⁷Sr/⁸⁶Sr = 0.730-0.750, 95-160 ppm; ¹⁴⁴Nd/¹⁴³Nd = 0.51190, 25-40 ppm). Negative Eu/Eu* (0.6-0.9) anomalies in the erupted rocks require magma storage and feldspar fractionation in the middle to upper crust, and low pressure crystal cargos (+ cordierite) indicate pre-eruption crystallization in the upper crust.

The plot of temporal trends in REE ratios in the volcanic rocks of the region in Figure 3 shows that Sm/Yb ratios increased from ~4 at ~19 Ma to ~11 at ~12 Ma requiring increasing amounts of garnet in a thickening crust in line with concurrent uplift and thrusting in the Eastern Cordillera. Subsequently, Sm/Yb ratios drop to ~5-6 in the 8-7 Ma ignimbrites as brittle deformation shifts into the Subandean belt and a major surface uplift event is in accord with a crustal delamination event between 12 and 8 Ma. A post 12 Ma shift to higher ⁸⁷Sr/⁸⁶Sr ratios supports exposure of mantle melts to more isotopically evolved silicic crust in the lower crust as the lowermost crust is delaminated in the mantle wedge. A decreasing in ¹⁴⁴Nd/¹⁴³Nd (0.5123-0.5122) at nearly constant ⁸⁷Sr/⁸⁶Sr (~0.710) ratios in the mafic lavas at the same time supports incorporation of Brazilian lithosphere into the site of magma evolution. Significantly, the giant Ag-Zn-Sn mineralization event in the Potosi region occurs at ~14-12 Ma at the peak of crustal thickening and the beginning of the inferred delamination event. Lower crustal flow of the hot crust can explain a subsequent increase in crustal thickness and the return to higher
Sm/Yb at ~4-2 Ma. The voluminous ~1.5 Ma Los Frailes Ignimbrites erupted as the crust thickened above a thinned lithosphere.

2.3 Giant Neogene Andean porphyries and the angles of subducted aseismic ridges

Another tectonic regional factor to possibly consider in the formation of ore deposits is the obliquity of linear aseismic ridges with the trench as they are subducted beneath the margin. In this regard, Butterworth et al. (2016) considered the obliquity of the subduction angle to the trench and showed that giant Andean porphyry deposits tended to occur where the obliquity was ~15°, but did not consider the obliquity of ridge intersections. Approximately 15° is also the angle at which the Juan Fernandez Ridge has been subducting beneath the Nazca plate since the replacement of the Maricunga belt gold porphyries at 13-10 Ma. Given, the Yáñez et al. (2001) reconstruction, the ~14 Ma Cerro Rico de Potosi Ag deposit north was emplaced at a time that the Juan Fernandez ridge was subducting more parallel to the trench at 22°S (Fig. 1a). What is notable is that late Miocene giant porphyries are unknown between ~21°S and 26°S where the Juan Fernandez ridge was subducting at an angle near 45° to the margin between these times. Instead, this is where the large Altiplano-Puna ignimbrites occur (e.g. Kay et al. 2010, de Silva and Kay SM (2018) Turning up the heat: high-flux magmatism in the Central Andes. Elements 14:245-250.


3 Conclusions

Giant Andean Neogene porphyry deposits appear to variously correlate in time with shallowing and steepening of subducting oceanic slabs related to subduction of aseismic ridges on the incoming oceanic plate, peaks in crustal thickening and crustal flow related to contraction influenced by the relative rate of westward drift of South America over the Nazca plate and delamination of the lower crust and lithosphere. A potentially important source of metals is associated with forearc subduction erosion, which removes and subducts continental crust and lithosphere into the mantle wedge where it becomes a potential source for recycling metals into porphyries and other ore deposits, although this might reflect their erosion level.

Acknowledgements

This study would not have been possible without the long-term collaboration of Constantino Mpodozis, Beatriz Coira, Paula Cornejo, Víctor A. Ramos, Moyra Gardeweg, Nestor Jimenez and other South American colleagues. Funding has been provided by the US National Science Foundation, the Chilean FONDECYT and SERNAGEOMIN, CODELCO, and the Argentine Agencia Nacional de Promoción Científica y Tecnológica. Butterworth N, Steinberg D, Müller RD, Williams S, Merdith AS Hardy S (2016). Tectonic environments of South American porphyry copper magmatism through time revealed by spatio-temporal data mining. Tectonics 35:2847-2862.


References
Links between tectonics, magmatism, and mineralization in the formation of Late Cretaceous porphyry systems in the Yukon-Tanana upland, eastern Alaska, USA

Douglas C. Kreiner, James V. Jones III, Erin Todd
U.S. Geological Survey, Alaska Science Center, Anchorage, AK, USA

Chris Holm-Denoma, Jonathan Saul Caine
U.S. Geological Survey, Geology, Geophysics, and Geochemistry Science Center, Denver, CO, USA

Jeff Benowitz
University of Alaska-Fairbanks, Fairbanks, AK, USA

Abstract. Cretaceous-Paleocene porphyry Cu(±Mo±Au) occurrences are scattered throughout the Yukon-Tanana upland in eastern Alaska. Known occurrences in eastern Alaska are poorly characterized, despite a resurgence in exploration. Porphyry deposits in the upland are emplaced into structurally complex metamorphic rocks representing a variety of tectonic environments, resulting in diverse alteration and mineralization assemblages. New mapping, drill core logging, petrography, geochemistry, geochronology, and structural analysis allow improved characterization of the parameters of porphyry systems and identify key linkages to regional tectonic and magmatic events. New sericite 40Ar/39Ar and zircon U/Pb dates constrain porphyry systems to the Late Cretaceous-earliest Paleocene (ca. 71-63 Ma). Zircon Hf-isotope ratios and Ce and Eu concentrations indicate that Late Cretaceous-Paleocene intrusions emplaced into basement dominated by Triassic and Jurassic plutons are more isotopically juvenile and more oxidized reflecting wallrock controls. In contrast, intrusions emplaced into basement dominated by mid-Cretaceous plutons are more reduced with crustal geochemical-affinity.

Diversity in mineral assemblages in contrasting systems may reflect emplacement into crustal domains of varying compositions and oxidation states. Porphyries formed within a domain containing more-oxidized Triassic and Jurassic plutons are molybdenite-rich and apparently lack gold. In contrast, systems formed within domains dominated by more reduced mid-Cretaceous plutons contain lower-sulfidation state mineral assemblages with reported gold.

1 Regional Geology

Eastern Alaska represents the boundary between allochthonous terranes and rift-modified ancestral North American basement, geographically coinciding with the Alaska-Yukon border (Fig. 1). The geometry of the boundary is complicated by extensive polyphase, amphibolite facies metamorphism associated with multiple contractional and extensional deformation events and a protracted igneous evolution in the region. The Yukon-Tanana terrane (YTT) rifted off the western margin of North America in the Late Devonian, resulting in the formation of an ocean basin (Nelson et al. 2013). Multiple magmatic events occurred during the Paleozoic in the YTT, whereas magmatism along the rifted continental margin ceased around 360 Ma (Dusel-Bacon et al. 2006). During the Permian, closing of the ocean basin occurred as the allochthonous terrane was accreted back to the rift-modified North American margin.

Post-accretion magmatism active from the Triassic through Eocene is expressed as multiple pulses within assemblages of the allochthonous YTT and ancestral North America. Triassic and Jurassic magmatism is more mafic on average and spatially restricted compared to Cretaceous magmatism (Fig. 1; Dusel-Bacon et al. 2006). Mid Cretaceous magmatism is volumetrically substantial, whereas the Late Cretaceous to earliest Paleocene magmatism is volumetrically minor and more diffuse (Fig. 1).

Mesozoic plutons were emplaced into siliciclastic schists, paragneisses, and orthogneisses of the allochthonous and parautochthonous (e.g., ancestral North America) assemblages across eastern Alaska (Fig. 1). Jurassic and Triassic plutons are predominantly emplaced into the allochthonous terrane, whereas volumetrically extensive mid Cretaceous plutons are primarily emplaced into the parautochthonous assemblages (Fig. 1). Late Cretaceous plutonism is widely distributed, yet volumetrically minor, and manifested as small stocks, dike swarms, and caldera-associated tuffs (Fig. 1). The presence of the tuffs suggests preservation of the Late Cretaceous paleosurface, and consequently the uppermost crust, across eastern Alaska (Dusel-Bacon et al. 2006).
Late Cretaceous porphyry systems

Porphyry systems in the eastern Yukon-Tanana upland exhibit diverse mineral assemblages and alteration styles. This paper will focus primarily on systems located in the Kechumstuck and Sixtymile-Pika areas (Fig. 1).

2.1 Kechumstuck area porphyry occurrences

Kechumstuck area porphyry occurrences, including Oscar and Mitchell, are associated with porphyritic igneous stocks and dikes of granodiorite to granite composition emplaced into oxidized granitic Jurassic and Triassic plutons, siliciclastic and carbonate rocks of the allochthonous Yukon-Tanana terrane (Dusel-Bacon et al. 2006). Resulting mineral occurrences are characterized by skarn and manto-style base-metal mineralization in wall rocks, roof pendants, and stoped blocks. Additionally, porphyry Mo, and porphyry Cu-Mo systems associated with more alkaline monzonite and granite (e.g., Little Enchilada and Mosquito occurrences) are located in the Kechumstuck region.

The Oscar occurrence is poorly characterized but recent work indicates skarn mineralization assemblages are hosted in inter-layered marble lenses and reduced Paleozoic siliciclastic rocks and weakly foliated and altered Jurassic (ca. 190.5 Ma, U/Pb) diorite. Calcic-potassic alteration characterized by calcite-epidote-biotite (-sericite-magnetite) cuts K-feldspar-biotite, porphyritic Late Cretaceous (68.4-69.0 Ma, U/Pb) dikes. Mineralization is characterized by multiple generations of garnet, calcic amphiboles, pyroxene, biotite, epidote and chlorite. Sulfide assemblages consist of more reduced pyrrhotite-magnetite-chalcopyrite mineral assemblages as a function of the reduced nature of the host rocks.

The Mitchell occurrence is characterized by calc-silicate dominated skarn and endoskarn associated with plagioclase-hornblende porphyritic dikes emplaced into a Jurassic (ca. 199 Ma, U/Pb) diorite pluton and associated carbonate-dominant roof pendants or stoped blocks of Paleozoic Fortymile River assemblage rocks. Alteration is characterized by epidote-garnet-calcite-quartz(-magnetite) associations. Mineralization is manifested as bornite with later chalcopyrite replacement associated with garnet. This mineral assemblage is commonly indicative of intermediate- to high-sulfidation states (Einaudi et al., 2003).

2.2 Sixtymile-Pika area porphyry occurrences

Porphyry occurrences in the Sixtymile area are associated with Late Cretaceous alkaline to calc-alkaline porphyry stocks and dike swarms emplaced into upper crustal, moderately reduced mid Cretaceous granite to monzogranite. Mineralized systems in the Taurus district and further south at the Road Metal prospect are characterized by porphyry Cu-Mo(-Au) styles of mineralization, and are commonly weakly to highly anomalous in As.

The Taurus district (Fig. 2) consists of a series of prospects such as, West Taurus, East Taurus, Bluff, Dennison and Pushbush. East and West Taurus, Bluff, and Dennison are all porphyry occurrences whereas Pushbush appears to be epithermal. The district is characterized by at least three discrete, mappable, porphyry systems (Fig. 2) representative of multiple pulses of mineralization spanning approximately 6 million years. Bluff and Taurus are the oldest, with Taurus emplaced between ca. 69.8-71.5 Ma (U/Pb zircon LA-ICP-MS), and Bluff at ca. 71.4-71.6 Ma (Allan et al. 2013). Dennison is younger with altered quartz porphyry dikes emplaced at 67.8±0.5 Ma (U/Pb zircon LA-ICP-MS) with overprinting hydrothermal sericite-tourmaline-pyrite at ca. 65.8±0.8 Ma (40Ar/39Ar, sericite). Mineralization is associated with porphyritic quartz-monzonite, equigranular quartz-monzonite, and quartz-eye granite porphyry dike swarms. Tourmaline-quartz breccias are present across the prospects (Fig. 2). Alteration assemblages in these systems are dominated by hydrolytic assemblages, local proximal potassic zones, and abundant magnetite-chlorite-alkaline and chlorite-epidote dominant assemblages (Fig. 2). Mineralization assemblages are characterized by pyrite-dominant, pyrrhotite-bearing, and chalcopyrite-molybdenite with weak Au. Distally, galena-zonspalerite is present, with associated epidote-chlorite-sericite(-magnetite) assemblages.

Pushbush is located about 14 km south of the Taurus, Bluff, and Dennison occurrences. The prospect is
characterized by molybdenum-base metal mineralization hosted in sericitically altered volcanic rocks. Nearby, the volcanic rocks have been dated at ~57 Ma (U/Pb, zircon).

The Road Metal prospect, to the south of the greater Taurus district, is characterized by overlapping, but distinct mineralization assemblages. To the east, Au-As-Bi assemblages with coarse, muscovite-tourmaline-pyrite alteration are associated with Au- and As-rich quartz veins. Classic porphyry-style Cu-Mo(-Au) mineralization is located to the west. Porphyry assemblages are characterized by quartz-pyrite-chalcopyrite-(pyrrhotite) veins with K-feldspar and biotite selvages. Both mineralization styles are hosted within the mid Cretaceous monzonite, sparse Late Cretaceous (?) biotite-hornblende granodiorite, and granite porphyry dikes. Hydrothermal sericite in both porphyry Cu, and Au-rich alteration assemblages has yielded overlapping dates ranging from ca. 64.4-66.8 Ma (ca. 59.8-66.5 from illite-rich vein alteration halos) (40Ar/39Ar).

Some Au-rich quartz veins distal to the main zones of mineralization at Road Metal show evidence for syn- to post-vein emplacement brittle strain. Strain is marked by polished and striated slip surfaces along the vein margins and within the associated hydrothermal alteration halos consisting of clay minerals (e.g. illite). The veins are steeply dipping north-south and northeast-southwest striking with dextral and sinistral subhorizontal slickenlines. Such kinematic indicators are consistent with a regional, subhorizontal northeast directed shortening direction that links stress, strain, Au mineralization, and permeability creation in the latest Late Cretaceous or earliest Paleocene.

Exhibit Mo-rich, As-poor signatures and intermediate to high sulfidation state mineral assemblages. In contrast, Late Cretaceous porphyry systems emplaced into mid-Cretaceous, pluton-dominated basement are Au-bearing, commonly Mo poor, anomalous in As, and exhibit intermediate to low sulfidation states. Igneous zircon rare earth element (REE) geochemistry differs for Late Cretaceous plutons depending on the tectonic history of the basement. Because the magnitude of concentration anomalies of multivalent REEs (e.g. Ce, Eu) negatively correlates with relative oxygen fugacity, zircon REE concentration anomalies may be used to approximate relative redox conditions (Burnham and Berry 2012). Plutons emplaced into Triassic-Jurassic upper crust (Fig. 3) within the allochthonous YTT crystallized under more oxidizing magmas whereas plutons emplaced into upper crust dominated by mid Cretaceous plutons within parautochthonous North American assemblages, crystallized under more less oxidized magmas. These patterns are indicated by the distinct relative oxidation states recorded by igneous zircons in mid Cretaceous and Triassic-Jurassic plutons (Fig. 3); mid Cretaceous plutons tend to be more reduced than Triassic-Jurassic plutons. Moreover, zircon trace element systematics (U/Yb vs Nb/Yb; Fig. 4) differentiate between more juvenile (Triassic-Jurassic) and more continental (mid Cretaceous) affinity of basement plutons. Mineralization styles seem to depend on these basement regimes; porphyry-style mineralization is strongly associated with

### Figure 2

*Geologic and alteration sketch map of the greater Taurus-Bluff porphyry district. Three mappable edges of decreasing alteration highlight the presence of at least three mineralizing systems.*

### Figure 3

*Average Ce/Ce* (a) and Eu/Eu* (b) zircon data for eastern Alaska igneous rocks. Averages calculated from all data points analyzed on zircons from each sample. Late Cretaceous samples highlighted by magenta ovals are emplaced into mid-Cretaceous plutons and those highlighted in green are emplaced into Jurassic-Triassic plutons.*

### 3 Links between tectonics, magmatism and mineralization

Porphyry occurrences, such as Oscar, Mosquito, and Little Enchilada (not discussed here) formed in the Triassic-Jurassic pluton-dominated upper crust that
the crust characterized by more juvenile plutons in the Late Cretaceous, whereas no known mineralization is associated with crust dominated by mid Cretaceous (least-juvenile) host plutons in eastern Alaska. In short, the precursor tectonic and magmatic events impart a strong signature on the superimposed porphyry systems which correlates to the mineral assemblages observed in the systems in eastern Alaska.

Figure 4. Tectonic discrimination diagram for zircon trace element compositions from plutons in eastern Alaska. Mid Cretaceous plutons exhibit a more enriched (relative to mantle), “crustal” tectonic signature whereas Triassic-Jurassic plutons exhibit a more “juvenile” signature. Late Cretaceous pluton tectonic affinity correlates to dominant basement types, and porphyry-style mineralization is only present with the more juvenile plutons. (after Barth et al., 2017).

4 Summary

Eastern Alaska is a geologically complex region with multiple superimposed tectonic, magmatic and metallogenic events. A shift in the tectonic setting occurred between ~90 and 75 Ma from a more crustal collisional-granite setting to a more juvenile arc environment. Porphyry systems formed in the Late Cretaceous and are associated with calc-alkaline arc plutons that exhibit juvenile, chemistries. Across eastern Alaska, porphyry systems exhibit varying mineralization assemblages which record different evolutionary trends. Porphyry systems formed in upper crust dominated by Triassic-Jurassic plutonic units exhibit As-poor, Mo-rich, intermediate- to high-sulfidation state assemblages. In contrast, those emplaced into upper crust dominated by mid Cretaceous plutons exhibit intermediate- to low-sulfidation states with Au-bearing, As-rich assemblages. Zircon geochemistry in Late Cretaceous plutons mimics that of the upper crustal plutons, with a more reduced signature exhibited by those plutons emplaced into mid Cretaceous upper crust and more oxidized signatures recorded in Late Cretaceous plutons emplaced into Triassic-Jurassic upper crust.

Acknowledgements

The authors would like to acknowledge Kenorland Minerals and Doyon Regional Native Corporation who have provided access to land, data, and drill core. Alaska Division of Geological and Geophysical Surveys has provided observations and insight in support of collaborative ongoing regional mapping efforts. Thoughtful reviews by Garth Graham, Karen Kelley, and Dave Stevenson have greatly improved this manuscript. U.S. Geological Survey Mineral Resources Program has provided funding for field and analytical work in support of the broader geologic framework project attempting to better characterize the relations among tectonics, magmatism and metallogeny in eastern Alaska. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

References


Abstract. In this contribution, we focus on the Oligocene to Miocene structural evolution of the giant Kadjaran porphyry Cu-Mo deposit and its epithermal overprint. This evolution was controlled by long-lived regional faults during the Cenozoic tectonic and magmatic evolution of the Meghri-Ordubad composite pluton located in the southernmost Lesser Caucasus. We discuss the ore-bearing fracture network characteristics related with the deposit-scale ore-controlling structures in the frame of regional strike-slip faults. Stereonets summarizing the orientations of different generations of mineralized veins allow us to constrain the favorable fracture network environment for ore-formation at the giant Kadjaran deposit. During the middle-late Oligocene, NNE-oriented shortening created the major ~N-S- and NE-oriented steeply dipping ore-controlling deposit-scale faults under dextral strike-slip tectonics. The gently to moderately dipping NE-, ~N-S- and ~E-W-oriented fracture networks along the steeply dipping deposit-scale faults were the most important structural control for the emplacement of the main porphyry stockwork mineralization. These deposit-scale ore-controlling faults were reactivated during the early Miocene under WNW-oriented shortening and NNE-oriented extension. The progressive anticlockwise rotation of paleostress orientations from middle-late Oligocene to early Miocene was linked to re-organization of tectonic plates during Arabia-Eurasia collision.

Introduction

The giant Kadjaran porphyry Cu-Mo deposit and its epithermal overprint (2244 Mt @ 0.23% Cu, 0.033% Mo, 0.02 g/t Au) is located in southern Armenia, in the southernmost Lesser Caucasus and belongs to the Central segment of the Tethyan metallogenic belt. The Kadjaran deposit is hosted by the Cenozoic Meghri-Ordubad composite pluton (Karamyan and Faramazyan 1960; Mkrtchyan et al. 1969; Tayan 1984; Hovakimyan et al. 2015; Moritz et al. 2016; Rezeau et al. 2016).

Recent structural investigations of the southernmost Lesser Caucasus emphasize the fundamental role of regional dextral strike-slip tectonics controlling the emplacement of porphyry Cu-Mo and epithermal deposits and prospects and the associated magmatism of the Meghri-Ordubad pluton (Hovakimyan at al. in press). This contribution is focused on the local fracture network characteristics of the Kadjaran deposit. Our aim is to understand the favorable structural conditions leading to the emplacement of this giant porphyry deposit and its epithermal overprint. This study is based on detailed district and deposit-scale structural mapping and data collected during the past 30 years, during the progressive development and mining of the deposit. The data set consists in thousands of measurements of different mineralized veins and fractures, crosscutting relationships of dikes and mineralized veins, and the kinematic analysis of the main ore-controlling structures. This data set allows us to constrain the Oligocene to Miocene structural evolution of the Kadjaran deposit, controlled by long-lived regional faults, which were active during the Cenozoic tectonic and magmatic evolution of the Meghri-Ordubad composite pluton.

2 Geological setting

The Kadjaran deposit formed at the intersection of the regional NNW-oriented Tashtun oblique-slip fault and the E-W-oriented Voghji sinistral strike-slip fault. It is hosted by monzonite and quartz-monzonite belonging to the composite Cenozoic Meghri-Ordubad pluton dated at 28.3 - 28.1 Ma (Rezeau et al. 2016).

The Kadjaran deposit is the result of two successive magmatic-hydrothermal events dated at 27.3 - 26.4 Ma and 22.2 - 20.5 Ma (Rezeau et al. in press), which can be associated with two distinct tectonic environments (Hovakimyan et al. in press). The structural framework of the deposit consists of an orthogonal system of steeply dipping (65-85°) ~E-W~, ~N-S~ and NE-oriented sub-parallel deposit-scale ore controlling faults (Tayan 1984). They were formed during an early Oligocene dextral strike-slip tectonic environment, under a NE-oriented compressive regime, in a collisional setting, and were reactivated in a sinistral strike-slip tectonic regime during the early Miocene (Hovakimyan et al. in press).
Figure 1. Lower-hemisphere, equal-area stereographic projections (Schmidt net) of the orientations of mineralized veinlets and veins in different parts of the Kadjaran open pit. The numbers on the picture represent the locations of the field measurements reported by the stereonets, which include data from the present-day open pit and data collected from the same area on historical mining levels. The porphyry deposit occupies the predominant and central part of the open pit, and the epithermal overprint consists of the 6th vein zone and Schlorkut in the eastern part of the open pit.

3 Geometry of veinlets and veins

The main porphyry Cu-Mo ore consists of a ~N-S-elongated stockwork confined to a more than 3.5 km-long and about 2 km-wide corridor, and subsidiary isolated veins (Tayan 1984). The majority of the porphyry ore-bearing stockwork zones contain gently dipping (25-40º), sub-parallel sets of mm- up to 5 cm-thick mineralized veins (Tayan 1984; Hovakimyan et al. in press). The relatively larger subsidiary, isolated porphyry Cu-Mo veins are hosted by ~N-S- and ~E-W-oriented structures. The main porphyry stockwork consists of gently dipping thin, veinlet systems. Crosscutting and displacement relationships of the mineralized fractures and detailed studies of the age relationship between different paragenetic mineral associations were the criteria for distinction of ten stages of mineralization at the Kadjaran deposit (Karamyan and Faramazyan 1960).

The stereonets summarizing the data of the different mineralized veins and veinlets show significant variations in orientations at the different historical mining levels of the open pit (Fig. 1). In the central part of the open pit, the majority of the ore-bearing fractures are NE-oriented with a moderate dip to the NW. The porphyry ore consists of quartz-molybdenite, quartz-molybdenite-chalcopyrite and quartz-chalcopyrite veinlets hosted by NE-oriented extension fractures dipping gently to moderately to the SE and ~E-W-oriented extension fractures dipping 15-25º to the south, and 60º to the north (Fig. 1: stereonets 3, 5, 6 and 7). The other dominant orientation of quartz-molybdenite veinlets in the central part of the open pit consists of ~N-S-oriented subparallel extension fractures gently dipping to the W (20-35º) (Fig. 1: stereonets 2 and 3), and ~N-S-oriented ore-bearing fractures, steeply dipping to the W (75-80º). This structure also hosts isolated thick veins having the same ~N-S-strike.

In the central part of the open pit, at the historical mining level 1965m (not shown in Fig. 1), ~N-S-oriented fractures hosting quartz-polymetallic veinlets overprint thick quartz-molybdenite veins within the gently dipping fracture systems, dipping 20-40º to the W (Tayan 1984). They also host late carbonate and chalcedony veins.

In the northeastern part of the deposit, the ore type is...
significantly different from the central part of the open pit. The ore-controlling structures of this part are mainly NE-oriented, strike-slip deposit-scale faults dipping 55-70° to NW. The ore is mainly composed of quartz-chalcopyrite veins (Fig. 1: stereonet 4). Single, isolated quartz-molybdenite veins are scarce. Late mineralization stages, consisting of quartz-pyrite, quartz-sphalerite-galena, quartz-carbonate and chalcedony veins are abundant (Tayan 1984). They are hosted by NE-oriented fracture systems, steeply dipping to the NW and SE. The thick, isolated veins are confined within the NE-oriented structures. In the NE part of the deposit (Fig. 1: stereonet 4), there are also NE-oriented reverse structures, steeply dipping to the NW have the same strike. E-W-oriented thrusts steeply dip (80°) to the south. Epithermal veins in the 6th vein zone are emplaced along ~E-W-oriented fractures zones (Fig. 1; Rezeau et al. in press).

The southeastern part of the open pit in the Schlorkut area mainly contains quartz-chalcopyrite veins, and only subsidiary quartz-molybdenite and quartz-pyrite veins. The epithermal overprint is controlled by subvertical N-S-oriented structures (Hovakimyan et al. 2015).

4 Kinematic analyses of the ore-controlling structures

Kinematics along the deposit-scale ore-controlling faults varies consistently with orientation: ~N-S- and NE-oriented structures record dextral strike-slip kinematics during the late Oligocene. The displacement pattern is kinematically coherent, and consistent with NNE-oriented shortening (Fig. 2). The geometry and dominant NE- and ~N-S-orientation of porphyry veinlets and veins are consistent with dextral strike-slip kinematics along the ~N-S and NE-oriented steeply dipping structures in the central and northern parts of the open pit, formed under a NNE-oriented shortening (Peacock and Sanderson 2018) (Fig. 2a).

Many of the steeply dipping ore-controlling structures in Kadjaran record reverse kinematics, favorable for the opening of gently dipping extension fractures (Fig. 3a).

The major ~E-W-oriented deposit-scale faults in the central and northeastern part of the open pit are dipping to the north (75-80°) and record sinistral strike-slip kinematics and repeated reactivation. We recognize different mineralization events along the same structures. Younger ~E-W- to WNW-oriented porphyritic granodiorite dikes (22.2 Ma; Mortiz et al. 2016; Rezeau et al. 2016) are also related with the early Miocene sinistral reactivation of ~E-W-oriented strike-slip structures, which is consistent with the re-orientation of the tectonic plate kinematics and re-organization of the Arabia-Eurasia collision during the early Miocene.

5 Paleostress reconstructions and evolution in time

Paleostress orientation analysis in middle to late Oligocene host monzonite and monzodiorite indicates NNE-oriented shortening direction and WNW-oriented extension (Fig. 2a) during Arabia-Eurasia collision (Hovakimyan et al. in press). The same shortening direction is indicated by the kinematics analyses of quartz-molybdenite porphyry veins (Fig. 2b).

In late Oligocene rocks dated at 24.5 Ma (Rezeau et al. 2016), paleostress reconstructions document N-S-oriented shortening and E-W-oriented extension (Fig. 2c). In early Miocene porphyritic granite dated at 22.6 Ma (Moritz et al. 2016; Rezeau et al. 2016), paleostress reconstructions indicate WNW-ESE-oriented shortening and NNE-oriented extension (Fig. 2d).

6 Discussion and conclusions

6.1 Middle to late Oligocene ore controls and tectonic regime

Paleostress reconstructions indicate two main tectonic events in the Kadjaran mining district. They are consistent with progressive anticlockwise rotation of paleostress orientations from the middle - late Oligocene to the early Miocene (Fig. 2), which was linked to the re-organization of the tectonic plates during Arabia-Eurasia collision (Hovakimyan et al. in press). During the middle to late Oligocene, NNE-oriented shortening and WNW-oriented extension initiated the major N-S- and NE-oriented ore-controlling structures under dextral strike-slip tectonics. This regime is compatible with the emplacement of N- to NE-oriented fine-grained porphyritic granodioritic and lamprophyre dikes (Tayan et al. 1984; Harutunyan et al. 2002) dated between 26.6 and 24.5 Ma (Rezeau et al. 2016) and dominantly NE- and N-S-oriented porphyry veins and veins dated at 27.3 to 26.4 Ma (Moritz et al. 2016; Rezeau et al. 2016). During the NNE-oriented shortening regime (Fig. 2c), many E-W-oriented deposit-scale faults behaved as thrust faults, which was favorable for the opening of gently dipping extension fractures (Fig. 3a). This fracture network...
resulted in high permeability around the steeply dipping deposit-scale faults and was the most important structural control for the emplacement of stockwork mineralization, which consists predominantly of gently to moderately dipping veinlets (Fig. 1).

![Diagrams of stress orientations](image)

**Figure 3.** Models for the relationship among extension fractures, faults and principal stresses: (a) reverse (thrust) faulting, (b) normal dip-slip faulting (Mikhailov 1984; Blenkinsop 2008).

### 6.2 Early Miocene reactivation of pre-existing ore-controlling structures

During the early Miocene event, WNW-oriented shortening and NNE-oriented extension resulted in reactivation of pre-existing structures in a sinistral strike-slip tectonic regime (Hovakimyan et al. in press). This setting played an important role in controlling the emplacement of the early Miocene ~E-W-oriented coarse-grained porphyritic granodioritic dikes dated at 22.2 to 21.2 Ma (Rezeau et al. 2016), which represent the youngest dike generation in the district (Tayan et al. 1984; Harutunyan et al. 2002). This paleostress setting controlled the emplacement of an epithermal overprint at the Kadjaran deposit. The available structural data allow us to conclude that the fracture and plumbing systems were formed continuously during the entire life span of the formation of the Kadjaran deposit. The structural data allow us to conclude that the fracture and plumbing systems were formed continuously during the entire life span of the formation of the Kadjaran deposit. N-S-, NE and E-W-oriented deposit-scale faults, characterized by different kinematics, controlled ore formation under a regional dextral strike-slip tectonic regime.

This study was financially supported by the National Academy of Sciences of Republic of Armenia, the SCOPES projects IB7620-118901 and IZ7320-128324 and the Swiss National Science Foundation projects 200020-138130, 200020-155928 and 200020-168996. S. Hovakimyan has been funded by the Swiss Government Excellence Postdoctoral Scholarship, Foundation Ernst et Lucie Schmidheiny (University of Geneva), Foundation Azad and the Swiss Chapter of the Armenian General Benevolent Union (Taline Avakian). We thank Marion Grosjean for participation in fieldwork, and the staff of the Zangezur Copper-Molybdenum Combine for access to the Kadjaran mine and for logistical help.

### References


### Acknowledgements

We thank Marion Grosjean for participation in fieldwork, and the staff of the Zangezur Copper-Molybdenum Combine for access to the Kadjaran mine and for logistical help.
Cenozoic porphyry and epithermal systems in the South Armenian Block, Lesser Caucasus, Armenia: new temporal geochemical and petrogenetic constraints

Marion Grosjean, Robert Moritz, Samvel Hovakimyan, Massimo Chiaradia, Richard Spikings
Department of Earth Sciences, University of Geneva, Geneva, Switzerland

Hervé Rezeau
Department of Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, USA

Alexey Ulyanov
Institute of Earth Sciences, University of Lausanne, Lausanne, Switzerland

Jorge Spangenberg
Institute of Earth Surface Dynamics, University of Lausanne, Lausanne, Switzerland

Rafael Melkonyan
Institute of Geological Sciences, National Academy of Sciences, Yerevan, Armenia

Abstract. The South Armenian Block (SAB) of the Lesser Caucasus is characterized by abundant Cenozoic magmatism and hosts important Au, Cu and Mo ore deposits. Their emplacement was controlled by dextral strike-slip tectonics initiated during the collision between the Arabian and Eurasian plates. This regional study focuses on the Meghradzor and Amulsar mining districts, hosting epithermal Au deposits, located in the northern and central parts of the SAB, respectively. New geochemical and geochronological results for these sites combined with previous data published for the southernmost Lesser Caucasus aim at providing regional petrogenetic constraints. Based on Hf, Sr and Nd isotope systematics, the magmatism in the Lesser Caucasus is predominantly juvenile with limited crustal contamination. Zircon U-Pb ages range from 48.9 to 21.2 Ma in southernmost Armenia, and from 43.2 to 28.4 Ma in the central to northern part of Armenia. The magmatic rocks exposed in the different mining districts display variable geochemical compositions reflecting various magmatic differentiation and source processes. However, each magmatic series is temporally and spatially associated with an ore deposit. The ultimate goal is to characterize the source and crustal differentiation processes to provide new understanding regarding the regional relationship of the diverse magmatic rocks and the associated ore deposits.

1 Introduction

The South Armenian block (SAB) of the Lesser Caucasus orogenic belt is characterized by a long-lived Cenozoic magmatism and associated porphyry Cu-Mo and epithermal Au deposits (Moritz et al. 2016b). The Cenozoic intrusions and related ore deposits are controlled by dextral strike-slip tectonics triggered by the oblique convergence and subsequent collision of the Arabian plate with the Eurasian margin (Agard et al. 2011; Moritz, et al. 2016b; Rezeau et al. 2016, 2017; Hovakimyan et al. in press). In previous studies, Rezeau et al. (2016, 2017, 2018, in press) have documented a 30 m.y.-long incremental assembly of nested intrusions forming the Cenozoic Meghri-Ordubad pluton (MOP) in the southernmost Lesser Caucasus. The magmatic evolution in the MOP is associated with episodic porphyry Cu-Mo events (e.g. the giant Kadjaran deposit; Fig. 1) and subsidiary epithermal systems emplaced during a subduction to post-collisional tectonic evolution.

This follow-up study examines the relationship of Cenozoic magmatism, strike-slip tectonics and ore deposits formation at the scale of the metallogenic belt. Our aim is to characterize the timing of magma crystallization and ore deposit formation, and magma geochemistry, which are key to constrain petrological processes of the Cenozoic magmatic flare-up recognized throughout the SAB. Here we focus on two major Cenozoic mineral districts and associated magmatic rocks, including: (1) the magmatic complex associated with the Meghradzor epithermal Au deposit located in the northern part of the SAB, and (2) the Amulsar intrusion cluster spatially associated with the Amulsar epithermal Au deposit in the central part of the SAB (Fig. 1).

2 Geodynamic context

The Lesser Caucasus is located along the central segment of the Tethyan orogenic belt and encompasses Georgia, Armenia and Azerbaijan. It is subdivided into three main tectonic zones, from NE to SW (Sosson et al. 2010): 1) the magmatic and sedimentary Somkheto-Karabagh belt and the Kapan zone belonging to the southern Eurasian margin, 2) the ophiolitic Amasia-Sevan-Akera suture zone, and 3) the Gondwana-derived SAB. The Lesser Caucasus formed as the result of the successive subduction and closure of the northern and southern branches of the Neothethys ocean during
Mesozoic and Cenozoic times (Rolland et al. 2011). This is characterized by two major collision stages: a Late Cretaceous accretion between the Gondwana-derived SAB and the southern Eurasian margin (Rolland et al. 2009a, b), followed by oblique convergence and final continental collision between the Arabian and the Eurasian plates during the Cenozoic (Agard et al. 2011). The latter initiated regional dextral strike-slip tectonics throughout the Lesser Caucasus as illustrated by the Pambak-Sevan-Sunik and Garni regional faults (Fig. 1; Philip et al. 2001). These faults controlled the emplacement of Cenozoic magmatism and ore deposits (Sossen et al. 2010; Rolland et al. 2011; Moritz et al. 2016a, b).

3 Meghradzor district

3.1 Meghradzor epithermal deposit

Located in the northern part of the SAB, the Meghradzor deposit is defined as an epithermal Au deposit with proven-probable reserves of 0.38 Mt and an Au grade of 12.4 g/t.

The ore field is located at the transition between a southern anticlinorium and a northern synclinorium separated by the Ankavan-Zangezur fault (Kovalenker et al. 1990). Sitting astride on this fault, the Au deposit is largely developed in the synclinorium. The Au ore is associated with sulfide and telluride minerals. The mineralization is hosted in middle Eocene volcaniclastic sedimentary rock sequences intruded by syenite, syenogranite and monzonite, and subsidiary syenite porphyry, monzonite porphyry and lamprophyre dikes (Kovalenker et al. 1990). According to this author, the ore minerals are contained in a fracture network connected to the main northwest-oriented Ankavan-Zangezur regional fault zone. Five stages of mineralization have been described: (i) a pre-ore stage characterized by a quartz-sericite alteration assemblage, ankerite, and pyrite, (ii) an early chalcopyrite-pyrite stage, (iii) a gold-galena-sphalerite stage, (iv) a gold-silver-telluride stage, and (v) post-ore quartz-carbonate veins. The mineralization has been dated by K-Ar on sericite from the hydrothermally altered wall rock at 41.5 ± 1.0 Ma (Bagdasaryan et al. 1969).

3.2 Magmatism of the Meghradzor district

The Meghradzor district is characterized by a wide variety of mafic to differentiated nested intrusions and lavas. Zircons crystallized in these intrusions have been dated by U-Pb LA-ICP-MS geochronology and reveal two distinct magmatic pulses.

The first magmatic pulse spans ~5 m.y. from 43.2 ± 0.4 to 38.8 ± 0.5 Ma (Fig. 1). It is characterized by a large variety of calc-alkaline to alkaline magmatic rocks displaying contrasting mineralogy and geochemistry. The oldest intrusion is a hydrothermally altered granodiorite with a calc-alkaline affinity. It was followed by the emplacement of syenite and monzonite with shoshonitic affinity at 41.2. ± 0.4 Ma and 40.9 ± 0.3 Ma, respectively.

They are crosscut by a large alkaline ring complex, composed of nepheline syenite and phonolite (Sokół et al. 2018) dated in this study at 40.2 ± 1.5 Ma. Finally, a porphyritic syenogranitic intrusion was emplaced at the end of this magmatic series at 38.8 ± 0.5 Ma. This first pulse is temporarily and spatially associated with the Meghradzor epithermal Au deposit.

The second magmatic pulse occurred after a ~10 m.y. gap, with adakitic, porphyritic granodioritic intruding into a Jurassic tonalite at 28.4 ± 0.2 Ma. Both the Jurassic and Cenozoic magmatic rocks are crosscut by quartz-bearing molybdenite veins.

Although the different magmatic rocks are characterized by contrasting mineral assemblage and geochemistry, they have similar whole rock isotopic composition, with 87Sr/86Sr and 143Nd/144Nd ratios ranging from 0.70384 to 0.70434 and from 0.51280 to 0.51284, respectively. In addition, zircon crystallized from the different intrusions display median initial εHf values between +8.6 and +9.7. All together, isotope systematics reveal a homogeneous juvenile, mantle-derived signature with minor crustal contamination.

4 Amulsar district

4.1 Amulsar epithermal deposit

The Amulsar epithermal Au-Ag deposit was discovered in 2006. Located in the central part of the SAB, it is a large tonnage and low grade deposit, with 103 Mt and grades of 0.79 g/t Au and 3.85 g/t Ag (Lydian 2019).

The ore is hosted in an upper, silicified volcanic unit, which is underlain by a lower andesitic unit affected by argillic alteration. Gold-enriched ore bodies contain abundant hematite and are mainly controlled by hydrothermal quartz veinlets and fractures. A subsidiary ore type consists of disseminated gold in the host rocks (Lydian 2019).

Pyrite-alunite assemblages are encountered in drill cores intercepting the mineralized horizons. This study presents new δ34S values of alunite that range between 22 and 26 ‰, whereas pyrite yields low δ34S values of −2.40 ± 0.16 ‰, which is consistent with disproportionation of sulfur in high-sulfidation systems and implying an alunite derived from a magmatic fluid (Rye et al. 1992). 40Ar/39Ar dating was performed on the alunite that yielded a plateau age of 30.5 ± 0.1 Ma.

A complex network of NW-trending faults characterized by fold thrust geometry crosscuts the volcanic host rock units. There is a clear spatial link between these tectonic structures and the location of Au ore bodies (Lydian 2019).

4.2 Magmatism of the Amulsar district

The volcanic host rock sequence is intruded by several shoshonitic intrusions. They range from an alkali-gabbroic to a quartz-monzonitic composition. Zircon U-Pb dating yield a crystallization age between 34.2 ± 0.5 Ma and 34.8 ± 0.5 Ma for the monzonitic–monzodioritic intrusions (Fig.1).
Figure 1: Geological map of the Lesser Caucasus (modified after Mederer et al. 2014). This study focuses on the Cenozoic intrusions (in red on the map). Intrusive bodies are classified according to their whole-rock geochemical affinities. Numbers with errors (e.g. 48.9±0.6 Ma) are U-Pb ages of zircons dated by LA-ICP-MS (1: this study, 2: Rezeau et al. 2016). Deposits have been dated by different methods (1: Ar/Ar in this study, 2: Re-Os by Rezeau et al. (2016), 3: Re-Os by Moritz et al. (2016b), 4: K-Ar by Bagdasaryan et al. (1969). A=Amulsar deposit, BP=Bargushat pluton, DP=Dalidag pluton, K=Kadjaran deposit, M=Meghradzor deposit, MOP=Meghri Ordubad pluton, TP=Tejsar pluton.
The magmatic intrusion U-Pb zircon ages are older than the alunite plateau age of the neighboring Amulsar epithermal deposit. This indicates that the nested intrusions predate the formation of the epithermal deposit. In-situ Hf analyses of magmatic zircons yielded a narrow range of εHf values from +8.1 to +8.5, which overlap with those of the Meghradzor magmatic complex. Thus, we conclude that the Amular district is characterized by juvenile mantle-derived shoshonitic intrusions without any evidence for assimilation of an older crustal.

6 Conclusions

Together with the results acquired in the MOP, our new dataset provides new insights about the origin and the evolution of the Cenozoic magmatism in the SAB and its temporal and spatial relationship with episodic ore forming pulses, and the regional tectonic evolution.

The SAB displays a wide variety of different magmatic rocks with distinct mineral assemblage and geochemistry, but with a dominantly mantle source.

The shoshonitic magmatism appears to be dominant in the SAB and is roughly coeval with epithermal Au and porphyry Cu-Mo deposits. This is consistent with previous studies concluding that alkaline magmas tend to have a high potential to form magmatic-hydrothermal Au deposits (Richards, 2015).

Upcoming investigations will allow us to improve our understanding about magmatic source and crustal differentiation processes in the SAB. These studies will provide new constraints about the relationship of magma evolution and episodic ore formation in the SAB, and will be aimed at providing new decision-making tools for future mineral exploration programs in the region.

Acknowledgements

We thank the Swiss National Science Foundation (grant 200020_168996) for support. Fieldwork was supported by the Augustin Lombard and the Ernst and Lucie Schmidheiny Foundations and a SEG Student Research Grant.

References


Lydian (2019) www.lydianinternational.co.uk/projects/amulsar


The East Sunda Arc, Indonesia – an emerging world-class porphyry Cu-Au province

David R. Cooke1,2, Lejun Zhang1,2, Adi Maryono1,2, Iryanto Rompo3, Rachel L. Harrison1,4, Terence G. Hoschke1,5
1Centre for Ore Deposit and Earth Sciences (CODES), University of Tasmania, Australia
2Transforming the Mining Value Chain, An Australian Research Council Industrial Transformation Research Hub, University of Tasmania, Australia
3PT J Resources Nusantara, Jakarta, Indonesia
4Joglo Pete, Dusun Pete, Majak singi, Borobudur, Magelang, Indonesia
5Alterrex Pty Ltd., Perth, Western Australia

Abstract. The East Sunda arc extends from western Java to Sumbawa in Indonesia and contains at least four world-class porphyry Cu-Au deposits (Batu Hijau, Elang, Tumpangpitu and Sori Onto), along with several porphyry and epithermal prospects. Late Miocene to Pliocene porphyry mineralization was associated with the emplacement of composite tonalite intrusive complexes emplaced into andesitic volcanic and volcaniclastic rocks. The geodynamic setting involved the subduction of the Roo Rise beneath the Sunda arc, with the porphyry deposits forming along the arc segment where the basement transitions from the Sundaland craton beneath eastern Java to oceanic crust beneath Sumbawa. The deposits have mineralized central domains associated with potassic alteration that has been extensively overprinted by intermediate argillic alteration (e.g., Batu Hijau and Elang), and/or advanced argillic alteration (e.g., Tumpangpitu and Sori Onto). High sulfidation epithermal gold mineralization has overprinted the Tumpangpitu porphyry in the Tujuh Bukit district, where an extensive lithocap is well-developed and has overprinted several porphyry deposits and prospects. Lithocaps also define the upper parts of Sori Onto and Elang, where they are superimposed over porphyry mineralization. Only the structural root zones of the Batu Hijau lithocap are preserved due to the greater degree of uplift and exhumation in SW Lombok.

1 Introduction

This paper gives a brief overview of the key characteristics of the porphyry deposits of the east Sunda arc, an emerging major metallogenic belt that is richly endowed with porphyry Cu-Au and high sulfidation epithermal Au-Ag deposits. Indonesia is a collage of oceanic island arc and continental fragments that are caught up between several opposing subduction zones that accommodate oblique convergence of the Indian-Australian, Pacific and Eurasian plates (Fig. 1). There are also several microplates caught up between the larger plates, some of which have undergone significant rotation during oblique convergence (e.g., Borneo). The diversity and complexity of convergent tectonic settings means that the islands of Indonesia have been well-endowed with porphyry and epithermal deposits, providing excellent opportunities for exploration (Fig. 1).

On-going exploration in the east Sunda arc is gradually revealing a spectacularly endowed Late Miocene to Pliocene arc segment associated with northwards-directed subduction of the Australian plate beneath Indonesia (Fig. 2) that has been highly productive in terms of porphyry and epithermal gold mineralization. The discovery of Batu Hijau on the island of Sumbawa by Newmont in 1990 (1.64 Gt @ 0.44% Cu, 0.35 g/t Au) was proof of concept for a greenfields targeting campaign conducted in 1984 that highlighted the region's potential for porphyry deposits (Maula and Levet 1996). Following the discovery of Batu Hijau, a giant porphyry resource at Elang was delineated 15 years after the prospect was initially discovered (2.267 Gt @ 0.36% Cu, 0.46 g/t Au; Maryono et al. 2018). While exploration continued apace in Sumbawa and the adjacent island of Lombok, Placer commenced exploration of the Tujuh Bukit district in East Java in the late 1990s. Placer's drilling identified high sulfidation mineralization but failed to intercept the high-grade giant porphyry Cu-Au resource beneath the high sulfidation ore zones, even though one of Placer's drill holes terminated within 100 m of the ore body (Harrison 2017). Intrepid Mining commenced exploration of the Tujuh Bukit district in 2007, and their discovery of Tumpangpitu in 2008 added a third giant Cu-Au deposit to the mineral endowment of the east Sunda arc. As of December 2017, Tumpangpitu has a porphyry mineral resource of 1.9 Gt @ 0.45% Cu and 0.45 g/t Au and an oxide HS epithermal Au-Ag resource of 106 Mt at 0.73 g/t Au and 24 g/t Ag (http://www.MerdekaCopperGold.com/en/operation). Exploration is on-going in the belt, with Vale currently drilling out the Sori Onto porphyry Cu-Au prospect in the Hu’u district of Sumbawa (1.7 Gt)
Porphyry deposits of the east Sunda arc share several common features, including composite tonalite intrusive complexes, and potassic-altered cores overprinted by late-stage intermediate argillic and/or advanced argillic and silicic alteration, which in most of the systems defines extensive lithocaps that have obscured the porphyry deposits. There is a common pattern of veins in the mineralized core of each deposit, which have been classified by Maryono et al. (2018) as A, B, AB, C and D veins using a version of the classic El Salvador vein nomenclature of Gustafson and Hunt (1975) that has been modified to the local conditions of the east Sunda arc. The following subsections document key aspects of the major deposits.

2.1 Batu Hijau

The geology of Batu Hijau has been documented extensively by Garwin (2000), Garwin et al. (2005) and Maryono et al. (2018). The host rocks are an upwards-fining sequence of volcaniclastic breccias, sandstones and mudstones of basaltic andesite compositions (Wilkinson et al. 2015; Maryono et al. 2015). Cu-Au mineralization was associated with the emplacement of a tonalite intrusive complex from 3.55 ± 0.13 to 3.52 ± 0.14 Ma (Maryono et al. 2018). The highest grades are associated with the early tonalite and its associated quartz vein stockwork. Moderate grade mineralization was added by the intermediate tonalite, and low grades were produced by the young tonalite. The deposit shows a classic sulfide zonation pattern from a bornite-rich core to a medial chalcopyrite-dominant domain and an outer pyrite halo. Alteration is zoned from intense biotite-magnetite alteration in the core, passing outwards to propylitic alteration with subdomains of inner actinolite, medial epidote, and outer chlorite-dominant domains (Garwin et al. 2005). The distal propylitic footprint extends out to 5 km as detected by propylitic mineral chemistry (Wilkinson et al. 2015). Because Batu Hijau is the most deeply eroded of the east Sunda arc porphyry deposits, overprinting phyllic and advanced argillic alteration is restricted mostly to district-scale NW- and NE-trending structures, with only the remnants of a lithocap preserved on a ridgeline to the east of Batu Hijau (Fig. 2a). A late mineralization diatreme crops out NW of Batu Hijau.

The deep erosion level, abundance of magnetite, chalcopryite and bornite in the core of the deposit, and the well-developed pyrite halo means that Batu Hijau has a discrete magnetic anomaly of about 1000nT within a broad zone of high chargeability (Hoschke 2011).
2.2 Elang

Elang is located on the island of Sumbawa, to the east of Batu Hijau (Fig. 1). PT Amman Minerals are planning to commence mining at Elang in 2024. The mineralizing tonalite intrusive complex at Elang was emplaced into andesitic host rocks between $2.51 \pm 0.13$ to $2.38 \pm 0.18$ Ma and a post-mineralization dacite dike intruded at $2.1 \pm 0.11$ Ma (Maryono et al. 2018). Like Batu Hijau, there are three major mineralizing tonalitic intrusive phases, with the earliest (Charlie tonalite) adding the bulk of the grade and the later intrusions (Delta and Echo) adding progressively less grade. Elang is dominated by chalcopyrite in the core of the deposit.

Early actinolite – biotite – magnetite alteration defines the core of Elang, with actinolite more abundant than biotite. Intermediate argillic alteration has overprinted the early potassic assemblage (Maryono et al. 2018). A late-mineralization diatreme crops out to the east of Elang (Fig. 2b). A lithocap is extensively developed at high elevations around Elang and includes high sulfidation state epithermal mineralization at the Ladam prospect (Maryono et al. 2018).

Magnetite associated with the potassic alteration zone produces a discrete magnetic high of about 700nT. This is within argillic alteration that is magnetite destructive, relatively conductive and highly chargeable.

2.3 Tumpangpitu

The Tumpangpitu porphyry Cu-Au deposit in east Java is the oldest of the major porphyry deposits, with syn-to late-mineralization intrusions that range in age from $5.40 \pm 0.46$ to $3.94 \pm 0.69$ Ma (Harrison et al. 2018). The porphyry resource at Tumpangpitu has been extensively overprinted by advanced argillic and phyllic alteration associated with the extensive Tujuh Bukit lithocap (Fig. 2D), which hosts several weathered high sulfidation epithermal ore zones. Additional complications include two diatreme breccia complexes, one with a pre-mineralization timing that crops out to the south of the district (Tanjung Jahe - $8.52 \pm 0.21$ Ma) and a large, late-mineralisation diatreme that disrupted porphyry and epithermal mineralization at Tumpangpitu (Tumpangpitu diatreme - $2.7 \pm 1.0$ Ma; Harrison et al. 2018). Extensive superposition of the high sulfidation environment over the porphyry deposit at Tumpangpitu has created more complex sulfide mineralogies with late covellite and chalcocite after early bornite and chalcopyrite. Early
biotite-magnetite alteration is only preserved in the deepest drill holes, with widespread late stage muscovite-
illite, dickite-pyrophyllite and shallow level alunite alteration overprinting the porphyry system (Maryono et al. 2018).

2.4 Sori Onto

The Hu’u porphyry Cu-Au district is located to the east of Elang on Sumbawa (Fig. 1). Only limited information is available on Hu’u as it is still being assessed by Vale. An extensive lithocap is exposed at higher elevations in the Hu’u district. Several mineralized porphyry centers (Humpaleu, Humpaleu East and Sori Onto) have been discovered in a cluster in the Hu’u district. A large Cu-Au resource has been recently delineated at Sori Onto (1.7 Gt @ 0.90 % Cu and 0.52 g/t Au; Sadikin 2018). The lithocap obscured the location of the deep-seated porphyry deposit, which has early biotite-magnetite alteration and intermediate stage intermediate argillic alteration (Maryono et al. 2018).

2.5 Other prospects

The Brambang porphyry deposit in SW Lombok (Fig. 1) is associated with a late Miocene multiphase intrusive complex (6.65 ± 0.31 Ma; Maryono et al. 2018). The highest grades are associated with an early mineralization tonalite, but only limited intercepts of the early intrusion have been intersected by the limited drilling completed to date. Early potassic alteration is associated with chalcopyrite-bearing quartz veins. These have been overprinted by a small diatreme breccia overprinted by advanced argillic alteration associated with the Brambang lithocap crops out to the north of Brambang (Fig. 2E).

The Selodong prospect in SW Lombok was discovered by Southern Arc Resources. It is a late Miocene porphyry system (7.28 ± 0.31 to 7.04 ± 0.25 Ma) that contains 66.75 Mt @ 0.27 % Cu and 0.43 g/t Au (Maryono et al. 2018). It was disrupted extensively by a large late-stage diatreme and numerous low grade late-stage intrusions (Fig. 2C; Maryono et al. 2018). High grade high sulfidation and intermediate sulfidation stage vein systems crop out to the NW at Pelangan and, Mencangga – they contain 11.78 Mt @ 1.52 g/t Au and 4.58 g/t Ag and are hosted in an extensive lithocap. In recent times, artisanal miners have been exploiting the epithermal veins near Selodong.

3 Conclusions

The east Sunda arc contains several examples of giant porphyry Cu-Au deposits along with several prospects that warrant more detailed exploration. The ore deposits are associated with tonalite intrusive complexes, central domains of quartz stockworks associated with biotite-magnetite alteration, overprinting intermediate argillic alteration, structurally controlled late stage phyllic alteration and in some cases lithocaps are extensively developed and partially overprint and obscure the porphyry deposits (Fig. 2). Diatremes are a common feature of each of the major porphyry systems in the arc. Further exploration success is anticipated.

Acknowledgements

We thank all our colleagues, particularly members of the AMIRA footprints research team, and our industry partners for their strong and sustained support of ongoing research into the east Sunda arc. We also gratefully acknowledge the support of J Resources, Merdeka Copper Gold and PT Amman Minerals.

References


Revised model of porphyry-Cu formation: ore forms at the porphyry to epithermal transition, overprinting barren stockwork veining and potassic alteration

Thomas Driesner and Christoph A. Heinrich
Institute of Geochemistry and Petrology, ETH Zürich, Switzerland

Abstract. Mounting evidence from numerous porphyry-Cu deposits implies that no copper ore minerals precipitated during high temperature stockwork veining and potassic alteration. Rather, the main ore formed at moderate temperatures <400°C, with no or minor quartz, coeval with chloritic to sericitic alteration and sulfide-only ("paint" and C-type) veins, transitional to epithermal conditions. When observed in detail, all textural positions of Cu-sulfides adhere to this scheme: grains and centerlines in A and B stockwork veins are post-quartz infills; disseminated grains in rock are mostly patchy precipitates on thin cracks; and "paint" and C-type veins themselves, which possibly represent thermal contraction-induced jointing. The resulting conundrum of a frequent correlation of stockwork quartz veins / potassic alteration and highest grades can be reconciled by a dynamic process in which the former form inside a hot magmatic fluid plume that is centered on the porphyry stock. The plume top is cooled by a downward migrating magmatic/meteoric fluid interface. Ore minerals precipitate where the magmatic fluid is most strongly cooled, likely prior to the ingestion of meteoric water, and progressively deeper with time, overprinting stockwork veining and potassic alteration. The model is consistent with field observations, petrography, fluid inclusions, oxygen stable isotopes, and heat and mass balance constraints.

1 Introduction

The general idea of how porphyry-Cu deposits are formed from magmatic-hydrothermal systems is well-established (e.g., Dilles 1987; Sillitoe 2010). Metals and fluids are sourced from a deeper, batholithic body of hydrous magma, from which smaller porphyry intrusions emerge on which the deposit is centered. The latter represent sites of failure of country rock overlying the batholith, forming zones of weakness that can act as "overpressure valves" (Sillitoe 2010) focusing magmatic fluid released from the crystallizing batholith. Hydraulic fracturing in response to fluid overpressure and fluid cooling/decompression cause vein formation and ore precipitation.

For many years it seemed clear that the ore-forming Cu-sulfides are linked to early, high-temperature stockwork veining and potassic alteration (see summary in Sillitoe 2010). Deposit-scale correlations as well as macroscopic cross-cutting relations of different vein types and alteration halos hosting the ore minerals seemed to be unambiguous indicators for that. Contrasting observations such as the association of mineralization with phyllic alteration or the occurrence of late, sulfide-only veinlets ("C" and "paint" veins) have often been interpreted as re-mobilization of primary, high-temperature, potassic ore. Examples of associations between the main ore mineralization and sericitic to chloritic alteration (e.g., Hedenquist et al. 1998) have mostly not been considered as typical.

This view was strongly challenged with the first applications of combined cathodoluminescence microscopy and detailed fluid inclusion petrography to porphyry-Cu deposits (Redmond et al. 2004; Rusk and Reed, 2002). At Bingham, this approach demonstrated that Cu-sulfides are interstitial in the early stockwork veinlets and precipitated from a relatively low-temperature fluid (+/-330-380°C) after the main mass of vein quartz had formed at substantially higher (>500°C) temperatures (Redmond et al. 2004). To the best of our knowledge, this and very similar relations have been confirmed for essentially all deposits subsequently studied with this method and unequivocal evidence for significant amounts of Cu-sulfides precipitated during early stockwork veining and potassic alteration has not been reported. Similarly, quite a few studies state that late, sulfide-dominant and quartz-poor to -absent veins may carry a large part or even the main mass of the metal in the respective deposit but almost never have they been the subject of detailed study (e.g., in Grasberg, Pollard et al. 2002 and I. Kavalieris, pers. comm. 2017; at Bingham, Porter et al. 2012) and these observations have received only minor attention in reviews (e.g., Sillitoe 2010). An exception are the studies of Vry et al. (2010) and Spender et al. (2015) who provide a detailed characterization of how main stage mineralization at El Teniente postdates barren veins and commences in veins with only minor associated potassic alteration and/or as infills in pre-existing re-opened veins, then grading into sulfide-dominated veins with phyllic/chloritic alteration that carry the main mass of copper and molybdenum.

The implication of these observations is that Cu ore precipitation and quartz stockwork veining / potassic alteration are genetically decoupled in the process of porphyry-Cu formation. We hypothesize that this may be the rule rather than the exception. However, the deposit-scale spatial correlations between potassic alteration, stockwork veining and high ore grades have remained a major and successful exploration criterion. This conundrum calls for a re-assessment of the existing field criteria and a revision of current models of porphyry-Cu formation.
2 Re-visiting field evidence for the timing of ore precipitation

Re-opening and mineral deposition from successive stages in a single vein is a well-known phenomenon in porphyry-Cu deposits. A single vein can record all stages from early, very high-temperature (>600°C) quartz precipitation to late zeolite and minor quartz precipitation from fluids as cool as 140°C (e.g., Stefanova et al. 2014). In other words, occurrence of Cu-sulfides in a vein or its alteration halo does not imply they formed with the event that formed the main mass of the vein minerals. Therefore, vein cross-cutting relationships alone do not tell the timing of ore mineral formation and different generations of a given mineral derived from macroscopic criteria may in fact belong to a single generation in different textural positions. Re-interpreting the timing of ore mineral precipitation by taking this into account resolves the apparent conundrum.

Sulfides in A-family veins have been demonstrated to postdate the main mass of vein quartz (e.g., Redmond 2004 et al.; Landtwing et al. 2005; Vry et al. 2010). Those in earlier vein types, such as biotite veinlets, may represent an equivalent of this; for example, chalcopyrite overprinting biotite(-actinolite) veinlets was reported by Vry et al. (2010) at El Teniente.

Sulfides as center-lines in B veins, by definition, postdate the quartz. Occurrence of chlorite (e.g., at Batu Hijau, Schirra et al., this conference) that apparently coeval with the sulfides suggests that the latter postdate potassic alteration.

“Paint-type” / C veins are dominantly filled with sulfides, typically with little or no quartz and with thin chloritic to sericitic alteration haloes, and cross-cut A and B veins. At least in Elatsite, Bulgaria, we have seen that paint veins penetrate into B-family veins and then continue as their centerline. From Escondida, El Salvador, and Erdenet we have samples that show paint veins of chalcopyrite +/- pyrite + chlorite cross-cutting hydrothermal anhydrite in vugs in earlier vein types. Paint veins often appear to be joints, i.e., thin tensile cracks. Occasionally, one can find elliptical boundaries of the mineral coating on the crack, suggesting that these are indeed simple tensile cracks or joints with several stages of opening.

Disseminated Cu sulfides in the rock, upon close inspection, can often be demonstrated to sit on very thin cracks with patchy, sparse sulfide precipitation. These appear to belong to the same stage as paint veins - as they can cut through minerals belonging to the potassic stage - and may just be their smallest, poorly mineralized expression.

Large Cu-sulfide grains or blobs in early quartz veins seem to be constrained to open spaces in these veins, post-date anhydrite in them (Erdenet) and pre-date calcite and zeolites (Elatsite).

D veins typically postdate all the above and only rarely appear to be host to significant Cu mineralization (e.g., Erdenet).

We interpret these findings to indicate that - at least for the deposits that we have studied or visited - the Cu sulfides in these very different textural positions represent the same, single stage during which the main mass of the Cu ore minerals were precipitated. At any given point of the orebody, this event postdates and overprints quartz stockwork veining and potassic alteration but adds chlorite/sericite as new alteration minerals in sometimes only minor amounts and no or only subordinate quartz.

3 Published constraints on the ore-forming process

Oxygen and hydrogen stable isotope data of alteration minerals seem to indicate that the potassic to phyllic alteration stages - and possibly parts of the argillic alteration stage - can be linked to a cooling magmatic fluid. Thermodynamic and reaction progress modelling by Reed et al. (2013) suggests that indeed the sequence of reactions and mass balance of subsequent alteration stages can be explained with a single magmatic fluid reacting with host rock. Meteoric overprint as a cause for phyllic alteration was suggested for a number of deposits (see review by Taylor 1979) but is now generally considered unlikely.

A few fluid inclusion studies sampled the distribution of dominant fluid inclusion types across a deposit (Redmond 2004; Zwyer 2010) and/or the evolution of the fluid at a given point in the system (Landtwing et al. 2005; Stefanova et al. 2014). At Bingham, Batu Hijau and Elatsite, high-temperature, intermediate density and low-salinity fluid represents a lithostatically pressured magmatic fluid that is released at depth and is also sampled in the first stages of quartz growth in A family stockwork veins inside the ore body. Entrainment temperatures vary from very high (>640°C) to somewhat lower (<500°C) and this range likely reflects distance from the releasing magma as well as the thermal state of the magmatic fluid plume during entrainment. Inside the ore body in these deposits, the dominant fluid inclusion assemblages are brine+vapor, post-date the intermediate density inclusions, and pre-date the ore minerals. The brine+vapor assemblages record progressive cooling from >600 to <400°C and decompression from lithostatic to hot hydrostatic, sometimes down to pressures of halite+liquid+vapor coexistence and with anhydrite precipitation during the cooler phase. During this process, the dominant vapor phase condenses out a highly saline brine. Ore precipitation happens during a phase in which quartz dissolves or precipitates in only subordinate amounts. Accordingly, associated fluid inclusions are rare and, where present, record temperatures typically in the range of 350-300°C. Ore precipitation is post-dated by aqueous, low-temperature (<200°C) fluid inclusions with a meteoric signature.

4 A revised model of porphyry ore formation

Accepting the overprinting, late character and moderate temperature of porphyry Cu ore precipitation, all of the above cited, field-based observations smoothly fit into a self-consistent process model. The numerical simulations
Magmatic hydrothermal systems: from Porphyry to Epithermal

of Weis et al. (2012) provide a framework with heat and mass balance as well as physically rigorous temperature-pressure-compositional evolution of the fluid phase, within the limits imposed by representing the fluids as H2O-NaCl. Fekete (2017) added quartz precipitation and dissolution as well as oxygen stable isotope fractionation to the simulations.

Following Weis et al. (2012) and the numerous studies that inspired their work, we assume that the process starts with accumulation of magmatic fluids, produced by second boiling due to progressive crystallization of magma, at elevations ("cupolas") in the top of a batholithic magma chamber. Once sufficient fluid pressure has been built up, the overlying host rock fails and a mixture of melt, crystals and overpressured fluid is injected. Melt and crystals consolidate to form a porphyry intrusion while the fluid induces hydrofracturing in both the solidifying porphyry intrusion and host rock.

Within a few hundred to thousand years the released hot fluid establishes a magmatic fluid plume, centered on the porphyry intrusion. This spatial correlation likely reflects that the initial breaching defines this as a zone of weakness, ideally located at a point where fluids in the batholith tend to collect, and through which they can preferentially be released upon further fluid production. The shape of the plume is governed by a dynamic dependence of permeability on temperature, stress, fluid pressure, and depth (Weis et al. 2012).

A key element now is that, in the uppermost crust, permeability is high enough to allow groundwater convection. The convection is driven by heat from the magmatic fluid plume but at the same time provides a negative feedback mechanism and limits further ascent of the plume by providing an efficient cooling mechanism (Fig. 1A). At this boundary, magmatic fluid is entrained into the overlying convecting system and may provide metals for epithermal metal deposit formation. Variations in permeability, rates of meteoric water recharge etc. provide factors that likely influence if and which style of epithermal mineralization may develop. Numerical modeling by Weis et al. (2012) indicates temperatures around 300-350°C just below the magmatic/meteoric fluid interface.

Both the oxygen stable isotope microanalysis of Fekete et al. (2016) and the numerical modeling of Weis et al. (2012) could not resolve if Cu-sulfide precipitation happens from purely magmatic fluid that has been cooled to below 400°C underneath the magmatic/meteoric interface or if actual mixing with meteoric water triggers precipitation. Schirra et al. (this conference) demonstrate that at Batu Hijau a cooled magmatic fluid most likely precipitated the Cu-sulfides. This would agree with the chemical modeling conclusions of Reed et al. (2013). Interestingly, if one accepts temperature of significantly over 500°C for the quartz stockwork veining and potassic stage with subsequent cooling to <350°C, it is a straightforward exercise to demonstrate that thermal stresses are high enough to allow tensile cracking of the rock, in agreement with the field observations on the nature of paint veins.

As the batholith progressively crystallizes, less fluid is produced per successive time increment and the rate of magmatic fluid supply decreases. As a consequence, the magmatic fluid plume will decrease in size and the magmatic/meteoric fluid interface as well as the cooling zone will progressively shift downward (Fig. 1B). Our model therefore predicts that ore formation and different alteration styles are diachronous: the ore body grows incrementally from top to bottom, under chemical conditions favorable for chloritic-sericitic alteration and quartz dissolution with subsequent barren overprint by meteoric water. Simultaneously, but deeper and at higher temperatures, barren potassic alteration and quartz stockwork veining are likely still ongoing until, under
cooling, they become first overprinted by the ore-forming process and then possible meteoric influence. The bottom of the ore body will represent the youngest ore and will cease to grow once the magmatic fluid input diminishes.

5 Discussion and Conclusions

We feel that our model explains numerous observations that have been independently reported from a fast growing number of different deposits and that seem to attest to a recurring theme, namely the "late" nature of Cu-sulfide precipitation. It should, however, be emphasized that "late" refers to textural position and not absolute time during the process of ore formation. Namely, Cu-sulfides would precipitate at early times in the uppermost part of the later ore body and this part would already be under meteoric, non-ore producing influence when the highest grades are accumulating later and further down. The correlation between grade and early stockwork veins / potassic alteration would simply reflect that the early vein types and alteration had more time to accumulate in these deeper, higher grade parts prior to ore deposition.

Many details remain to be investigated, namely if the seemingly broad spectrum of macroscopic evidence for different timing of ore deposition in different styles of porphyry Cu deposits (Sillitoe, 2010) is real or an artifact of relying on macroscopic observations. Furthermore, the actual physico-chemical causes of Cu-sulfide precipitation are still unclear: is it a range of temperature-pressure conditions? Is cooling the main factor or does chemical fluid-rock reaction play a key role, or both (e.g., progressive increase in acidity upon cooling)? When ore formation was considered a high-temperature process these questions could not rigorously be answered by reaction modeling for the lack of adequate thermodynamic models of solutes in supercritical fluids. However, for the inferred conditions, below 350°C, adequate thermodynamic models are available and this may allow refined assessment of different elements of the model suggested here.

Acknowledgements

This contribution integrates the numerous contributions of enthusiastic graduate students and co-workers, in particular Marianne Landtwing, Leo Klemm, Lorenz Fanger, Tobias Zwyer, Gillian Gruen, Elitsa Stefanova, Philipp Weis, Szandra Fekete, and Michael Schirra. Numerous discussions with experienced colleagues helped sharpening these ideas (that often nucleated from observations and ideas in their papers), namely with John Dilles, Jeff Hedenquist, Richard Sillitoe, and many, many others. Jamie Wilkinson's constructive review is gratefully acknowledged. We thank all mining companies that provided access to their operations!

References


Fertilisation of porphyry magmas by Cu-Au sulfide melt mobilisation in the lower crust

David Holwell, Thomas Knott, Daryl Blanks
University of Leicester, UK

Marco Fiorentini
University of Western Australia, Australia

Iain McDonald
Cardiff University, UK

Cam McCuaig
BHP, Australia

Abstract. The ‘fertility’ of arc magmas to form porphyry Cu-Au deposits in the upper crust is dependant on a number of processes occurring within the source-pathway-sink framework of the evolution of any particular magmatic system. One of the first barriers to fertility is the so-called ‘sulfide trap’ whereby sulfides in lower crustal cumulates will sequester metals such as Cu and Au, thus rendering any subsequent upper crustal melts infertile. Textural evidence from the Ivrea zone in Italy, alongside numerical modelling for lower crustal cumulate complexes, shows that although sulfides may be present in these rocks, they are not necessarily a ‘trap’ as such. Instead, the typical temperatures of these systems allows for incongruent melting and potentially mobilization of Cu-Au sulfide associated with melt networks within these cumulate intrusions. This allows for a mechanism whereby partially molten Cu-Au-rich sulfide can be fractionated from solid Ni-Fe-rich sulfide, which could potentially be mobilized into the upper crust and ultimately supply metals to form porphyry-fertile intrusions.

1 Introduction

Porphyry Cu(-Au-Mo) deposits are amongst the most significant ore deposits on Earth, and are a product of a complex series of processes related to volcanic arc activity (e.g. Wilkinson 2013). These include (1) generation of hydrous basaltic melts from metsomatised mantle wedge above the subducting slab; (2) the accumulation of these basalts in lower crustal amphibole-rich cumulates; (3) the ascent of bouyant, hydrous magmas to upper crustal depths where they pond, differentiate and release magmatic volatile phases leading to (4) porphyry ore formation by precipitation of Cu (and other metal) sulfides from the flow of volatiles triggered by cooling, phase separation, mixing, and/or reaction with wall rocks. For any system to be considered ‘fertile’ it must have experienced, or avoided, a number of key processes along this source-transport-sink pathway.

2 The lower crustal ‘sulfide trap’

The accumulation of basaltic melts at the base of the crust is the earliest staging point in the porphyry system. As such, the processes that occur at this stage represent a fundamental control on the subsequent fertility of any ascending magmas. Long term residence in this zone allows metal- and water-rich melt to accumulate and, depending on magmatic S contents and redox state, sulfide liquids to exsolve and crystallise. Should sulfide saturation occur in these lower crustal magmas, chalcophile metals such as Cu and Au should partition strongly into sulfide melt. As such, sulfides in lower crustal cumulates will sequester much of the metal budget of the magmatic system. Thus, sulfides in lower crustal amphibole-rich cumulates can act as a ‘trap’, and as a first order control on the relative fertility of ascending arc magmas.

Here we outline evidence from lower crustal cumulates that would imply that although these rocks can trap some sulfides, there may also be a mechanism to mobilise sulfides that are preferentially enriched in Cu and Au; thus fundamentally ‘fertilising’ magmas magmas in the precise budget of metals required for subsequently forming fertile upper crustal porphyry intrusions.

3 Lower crustal cumulates in the Ivrea zone, Italian Alps

We utilize samples from the lower crustal mafic complex that forms the lowermost part of the exposed crustal section of the Ivrea zone in the Italian Alps. The Ivrea zone consists of a complete, though partially dismembered section from the upper mantle to upper crustal volcanics exposed following near 90° tilting.

We use samples from the Isola Sill – one of the lowest ultramafic sills in the Ivrea zone that contains disseminated, low grade Ni-Cu sulfides; and the Sella Bassa deposit, which is in the mafic series, stratigraphically higher in the mafic complex, which contains patchy and disseminated Cu-Ni-sulfides.
4 The Jackson et al. (2019) model for mush reservoirs as ‘magma chambers’

Jackson et al. (2019) put forward a model for the development of large mafic complexes that are not ‘magmas chambers’, as such, but instead are made up of series of rapidly cooling sill injections and mush reservoirs. However, through evolution of this setting, the temperature of the ever increasing body of igneous rocks will rise until it intersects the solidus at ~850°C, at which point, melt can mobilise within a permeable melt network along grain boundaries. This upward movement of buoyant melt, or ‘reactive flow’ allows fractionated melt to migrate to the upper parts of the sill complex and form a significant body of melt. Over time this accumulating volume of liquid has the potential to be injected further up in to the crust. Their modelling was based on the lower crustal intrusions of the Ivrea zone, but is applicable to intrusions at any level of the crust.

Early intrusions, like Isola, would cool quickly, thus, any sulfide would be expected to remain trapped as interstitial blebs within the cumulus silicate mineralogy. Later intrusions, further up the magmatic stratigraphy, like Sella Bassa, would be subject to an increase in temperature over time, according to the model. In this zone, initially crystallised cumulates may experience partial remelting when the temperature reaches the solidus. Sulfides would remelt incongruently at this temperature, with the intermediate solid solution (iss; Cu-Fe sulfide) melting, and the monosulfide solid solution (mss) portion (Ni-Fe sulfide) remaining crystalline.

5 Textural evidence of mobile Cu-Au rich sulfides

Textural evidence from the Isola Sill shows an interstitial sulfide assemblage of pyrrhotite>>pentlandite>chalcopyrite within orthopyroxene-clinopyroxene-amphibole-(olivine) cumulates. These record a simple cooling history of an Fe-Ni-Cu sulfide liquid with no remelting.

In contrast, samples from Sella Bassa, higher up the sequence, contain an interstitial assemblage of exclusively pyrrhotite and pentlandite within orthopyroxene-clinopyroxene-amphibole cumulates. Chalcopyrite (along with some minor pyrrhotite +/-pentlandite) is present as veins and stringers formed along grain boundary networks that cross cut the silicate mineralogy (Fig. 1). These Cu-rich veins also contain Au-minerals such as electrum and Ni-Pd-tellurides.

6 Implications for porphyry magma fertility

This work provides clear evidence that Cu-Au-bearing sulfide liquid can be mobilised away from crystalline mss within lower crustal amphibole-bearing cumulates. This demonstrates the ability of lower crustal magmatic processes to not only concentrate metals into sulfide, but, crucially, to fractionate Cu and Au (the most common metals enriched in porphyry deposits) from Ni, Co and the IPGE (which are never found enriched in porphyry systems). As such, the evolution of lower crustal cumulate complexes in the model proposed by Jackson et al. (2019) allows for the presence of potentially mobile Cu-Au sulfide liquid in mush zones during ongoing magmatic activity, which could then be mobilized into upper crustal systems to form porphyry deposits. The operation, or not, of such deep processes may be a primary control on porphyry fertility.

Figure 1. ZEISS Mineralogic mineral map of chalcopyrite and gold rich veins in a sample of amphibole-bearing cumulates from Sella Bassa.

Acknowledgements

This work is funded by NERC grant NE/P017053/1 and NE/P017312/1 “FAMOS: from arc magmas to ores” awarded to the University of Leicester and Cardiff University, respectively; and Australian Research Council grant “Metal Sources and Transport Mechanisms in the Deep Lithosphere” Centre of Excellence for Core to Crust Fluid Systems (CCFS, CE11E0070).

References

Recycling of metal-fertilized lower continental crust: Origin of non-arc, Au-rich porphyry deposits at cratonic edges

Zeng-Qian Hou
Institute of Geology, CAGS, China

Rui Wang
China University of Geosciences, China

Ye Zhou
Gold Detachment No.10 of PAP, China

Abstract. Although studies argue that subduction-modified and fertilized lithosphere controls the formation of porphyry Cu deposits in orogenic belts, it is unclear if and how this fertilization process operates at cratonic edges, where numerous, large, non-arc Au-rich deposits form. Here, we report work on lower-crustal amphibolite and garnet-amphibolite xenoliths, hosted by Cenozoic stocks, that are genetically related to the Beiya Au-rich porphyry-skarn deposits along the western margin of the Yangtze Craton, China. These xenoliths represent cumulates or residuals of Neo-Proterozoic arc magmas that ponded at the base of the arc at the edge of the craton and subsequently underwent high-pressure metamorphism at ca. 740 Ma. The amphibolite xenoliths are enriched in Cu and Au, and a few garnet-amphibolite xenoliths contain higher Au with higher Au/Cu ratios than normal continental crust, suggesting that metal fertilization of the base of an old arc at the edge of the craton occurred in the Neo-Proterozoic via subduction-modification, and has since been preserved. The whole rock geochemical and zircon Hf isotopic data indicate that melting of the Neo-Proterozoic Cu (Au)-fertilized lower-crustal cumulates at 40–30 Ma provided the metal endowment for the Au- rich porphyry system at the cratonic edge.

1 Introduction

Unlike orogenic belts, most cratons have been stable since their formation in the Archean-Proterozoic eon (Griffin et al. 2013). The initial cratonic crust and subcontinental lithospheric mantle (SCLM) are strongly depleted in magmaphile elements, especially Au and Cu (Rudnick and Gao 2003), largely due to the liberation of metamorphic fluids from the deep crust (Cameron 1989) and high-degrees of mantle partial melting (Griffin et al. 2013). These domains have been preserved as durable, rigid, and buoyant rafts. Therefore, the cratons that have not experienced metal fertilization and later activation would be unlikely to host Phanerozoic Cu-Au ore deposits (Groves and Bierlein 2007). However, recent studies have recognized a suite of large, Mesozoic-Cenozoic, Au-rich porphyry Cu deposits (Richards 2009; Griffin et al. 2013; Hou et al. 2015) that have formed at cratonic margins or in the cratonic interior. They are postulated to be genetically related to non-arc potassic magmas derived from the Proterozoic lithosphere (Lu et al. 2013), metamorphosed lower crust (Richards 2009), SCLM (Griffin et al. 2013), and/or crustal fluids from deep reservoirs (Goldfarb et al. 2007), released during later reactivation. All these non-arc Au-rich deposits fall in the category of post-collisional deposits. The occurrence of these Au-rich deposits implies the existence of metal fertilization in cratons during later tectonic episodes (Griffin et al. 2013). However, it is unclear when and how this fertilization process operated, and the factors which ultimately control the formation of Au-rich porphyry copper deposits (Richards 2009).

Here we report the occurrence of Cu-Au-rich lower-crustal amphibolite and garnet-amphibolite xenoliths, hosted by Cenozoic potassic stocks that are genetically related to the Beiya Au-rich porphyry in the western Yangtze Craton, China. We suggest that these xenoliths represent direct samples of the Neo-Proterozoic, fertilized cratonic lower continental crust, which played an important role in the genesis of Au-rich PCDs at cratonic edges.

2 Geological background

The Yangtze Craton, SW China, underwent Neo-Proterozoic lithospheric accretion and Cenozoic tectonic reactivation with Au-Cu mineralization forming at its margin (Fig. 1). It is therefore an ideal place to study Au-rich systems at cratonic edges. The remnants of voluminous 1000–740 Ma arc plutons and volcanic rocks in the western part of the craton (Fig. 1b) suggest that oceanic subduction beneath the craton occurred in the Neo-Proterozoic (Sun et al. 2009). A ~1000-km long, potassic magmatic belt of Eocene-Oligocene intrusive and associated volcanic rocks (40–30 Ma) along the cratonic edge (Fig. 1b) records significant reworking by the Indo-Asia collision which started at ca. 65 Ma (Lu et al. 2013).

The Beiya Au-rich porphyry deposit (304 t Au @ 2.4 g/t Au; 0.6 Mt Cu @0.48% Cu) is the largest among several systems associated with the Eocene-Oligocene collision-related intrusive stocks (~37 Ma, He et al. 2015). The Beiya porphyries are thought to have formed by remelting of thickened mafic lower crust, whereas the Liuhe syenite stocks formed by remelting of the metasomatized SCLM during collision (Lu et al. 2013). Geophysical data reveal
that asthenospheric upwelling appears along the cratonic edge with 42–45 km thick crust, which is thought to have triggered melting of the cratonic lithosphere during collision (Lu et al. 2013).

**Figure 1.** A: Significant orogenic Au deposits (black dots) in the North China craton (NCC, 130–120 Ma; Goldfarb et al. 2007) and Yangtze craton (YC, 38–32 Ma; X. Sun et al. 2009). CAO—Central Asia orogen; TM—Tarim block; CCO—Central China orogen; AHO—Alpine-Himalaya orogen; SGO—Songpan Ganzi orogen; CC—Cathaysia craton. B: Locations of the lower crustal xenoliths (six stars) are shown; xenoliths at Beiya and Liuhe were sampled for this study. The tectonic framework and distribution of Cenozoic porphyry Cu-Au and orogenic Au deposits in the western Yangtze craton are shown.

### 3 Lower-crustal xenoliths and their origin

Abundant xenoliths have been found within Eocene stocks and associated volcanic rocks at six locations exposed along the cratonic edge (Fig. 1b). Amphibolites and garnet-amphibolites are the primary types, the former hosted by Beiya syenites and Beiya monzogranite porphyries (Fig. 2a), and the latter widely occurring in the Liuhe stock (Fig. 2b).

Sulfide phases (<0.3 vol. %) in the garnet-amphibolites are dominated by pyrrhotite with chalcopyrite rims and pyrite. The pyrrhotite occurs as globules, enveloped by garnet grains that lack any fissures and hydrothermal alteration (Fig. 2c). Their globular shape, sharp boundaries, and coexistence of pyrrhotite with chalcopyrite suggest original entrapment as a magmatic sulfide melt (Nadeau et al. 2010). Magnetite occurs inside and outside of amphibole crystals as globules, suggesting dissolution of the sulfide melt by a volatile phase, which was likely oxidized (Nadeau et al. 2010). Pyrite occurs as an interstitial phase within biotite-orthoclase assemblages in the amphibolites and garnet-amphibolites, and is irregular in shape, suggesting a secondary or metamorphic origin. Microprobe analyses of some pyrites show Au enrichment of 170–580 ppm (just above the detection limit of 140 ppm).

The lack of quenched margins (Fig. 2a, b) and the occurrence of metamorphic mineral assemblages in all of these xenoliths indicate that they are unlikely to be autoliths formed during magma crystallization or enclaves formed by injection of mafic melts into the felsic magma chamber. The garnet-amphibolite xenoliths show typical retrograde textures, including: (1) symplectite composed of fine-grained diopside, pargasite, and magnetite, formed by the decompressional breakdown of garnet (Zhao et al. 2003); and (2) fine-grained assemblages of anhedral albite, pargasite and magnetite around coarse diopside grains, likely formed by the breakdown of the Ca Tschermaks’ components in pyroxene (Core et al. 2006). These observations indicate that the xenoliths experienced high-pressure metamorphism and later retrograde metamorphism during exhumation. The clinopyroxene geothermobarometer (Ravna 2000) and garnet-clinopyroxene Fe-Mg geothermometer (Mercier 1980) yield temperature-pressure estimations from 642 °C to 675 °C and 1354 MPa to 1560 MPa for the garnet-amphibolites, which suggests high-pressure eclogitic facies metamorphism at the crustal base (ca. 41–52 km, based on amphibolite density of 3.0 g/cm³). In contrast, the amphibolite xenoliths show massive and gneissic structures and formation at 832 MPa (Al-in-amphibole barometer), corresponding to a metamorphic depth of ~27 km. We therefore argue that the garnet-amphibolite and amphibolite xenoliths were derived from the bottom (ca. 45 km) and upper parts (ca. 27 km) of the lower continental crust, respectively.

Whole-rock analyses indicate that these xenoliths show a close geochemical affinity with the Neo-Proterozoic arc plutons. They have relatively high Y (>15 ppm) and low Sr/Y (<30) and show enrichment in LILE and depletion in HFSE, which are typical characteristics of arc magmas derived from the metasomatized mantle wedge. The inherited zircons from the garnet-amphibolites yield ΔHf values of +0.7 to +14.8,
overlapping with those of the Neo-Proterozoic arc rocks (Zhao and Zhou 2007). Identical zircon Hf isotopic arrays for the xenoliths and arc plutons at ~794 Ma suggest binary mixing between asthenospheric melts and crustal materials during their generation. The least-assimilated xenoliths and arc plutons have high εHf values, similar to primitive arc magmas. These data indicate that both the garnet-amphibolite and amphibolite xenoliths are co-magmatic in origin and that their protoliths are likely lower-crustal cumulates and residue of the Neo-Proterozoic arc magmas, respectively (Fig. 3), which, as juvenile components, led to the crustal growth of the western Yangtze Craton.

4 Au-Cu enrichment/depletion in the xenoliths

The Liuhe xenoliths show variable concentrations of Au, Cu, and S. There is no correlation between Cu-Au contents with the proportions of sulfides. Most garnet-amphibolite xenoliths have lower metal contents (Au<3 ppb; Cu<10 ppm) than normal continental crust (Rudnick and Gao 2003), and only a few show moderate enrichments of Au (6–16 ppb) and Cu (up to 82 ppm). The amphibolite xenoliths have slightly higher Au (5–6 ppb), but remarkably lower Cu (15–18 ppm) contents than calc-alkaline arc magmas (1–2 ppb Au, 50–90 ppm Cu; Lee et al. 2012).

The Au-poor garnet-amphibolites have high modal garnet (>10 vol.%) and diopside (>15 vol.%; Fig. 2d). Accordingly, these xenoliths yield lower contents of mobile elements and LREE than their Au-rich counterparts. This suggests that Au and Cu in the lower-crustal cumulates have been in part extracted by fluids liberated during high-grade metamorphism (Cameron 1989).

By contrast, the Au-rich (6–16 ppb) garnet-amphibolites contain low modal garnet and diopside (<10 vol.%), and have high Au/Cu ratios (up to 7.8 × 10^4), coupled with relatively high contents of Cu (7.6–82.4 ppm) and Ni (143–318 ppm). Such Au enrichment cannot originate by mass exchange between the xenolith and enclosing magma because the Liuhe syenites have very low Au contents (~1 ppb). Metasomatism by volatiles escaping from hydrous lamprophyres is also unlikely to explain this Au enrichment, because the Eocene lamprophyres exposed along the western margin of the Yangtze Craton contain low Au concentrations (1–3 ppb) and lamprophyre melts have a low Au-carrying capacity (Huang et al. 1999). Alternatively, the remnants of globular sulfides shielded by garnet grains in the garnet-amphibolite xenoliths demonstrate Au enrichment in the lower-crustal cumulates before high-grade metamorphism (Fig. 2c). This is consistent with the expectation that small amounts of sulfide (as melt or crystalline phases) can be present, due to the high sulfur contents in arc magmas, which tends to settle out in cumulate zones due to density differences (Richards 2009). As a consequence, the residual cumulates after high grade metamorphism would be depleted in Au (Cu), as demonstrated by the low Cu contents of the Liuhe xenoliths.

We therefore argue that ponding of the Neo-Proterozoic arc magmas with sulfide accumulation at the crustal base had progressively replenished the cratonic lower crust in metal components. The remnants of magmatic sulfides in garnet-amphibolite xenoliths and metasomatic refertilization in amphibolite xenoliths indicate that the fluids, released from the lower-crustal cumulates during later prograde metamorphism, transported Cu (Au) and metasomatized the overlying crust, before or during cratonic reactivation at 730 Ma (Fig. 3). The refertilized juvenile lower crust contains >16 ppb Au and >205 ppm Cu, prior to its dehydration and later remelting, based on the Au and Cu contents of the Liuhe Au-rich xenoliths, and considering remobilization of sulfides during later metamorphism.

5 The formation of Au porphyries by remelting of fertilized Neo-Proterozoic deep crust

Previous studies indicate that the Beiya porphyries are characterized by high Sr/Y and La/Yb ratios coupled with low Y and Yb (He et al. 2015), showing geochemical affinity with adakites (Defant and Drummond 1990). The Beiya porphyries are thought to have been generated by remelting of the Neo-Proterozoic lower-crustal cumulates such as are represented by the xenoliths studied here (He et al. 2015). The breakdown of minor sulfides in the lower-crustal cumulates during later remelting would be expected to produce a S-poor magma (Richards 2009). This is consistent with two facts observed at Beiya: (1) the lack of high-sulfidation alteration; and (2) the small mass ratios of sulfides to magnetite (1:10) in the Au orebodies (He et al. 2015). As low sulfur contents only caused minimal sulfide saturation and consequent Cu (Au) sequestration from the magma (Chiaradia et al. 2012), we therefore presume that the ore-forming magma had a Au/Cu ratio similar to the resultant porphyries at Beiya. The least-altered monzogranite porphyries at Beiya have Au contents of 8–39 ppb and Cu contents of 4–83 ppm (He et al. 2015) with an average Au/Cu ratio of 1.4 × 10^4, which is an order of magnitude higher than that of normal arc magmas (0.4 × 10^5; Gill 1981), but almost identical to that (average = 1.5 × 10^4) of the Liuhe-Beiya xenoliths. Ulrich et al. (2009) found that the Au/Cu ratios of two giant porphyry deposits were identical to the bulk Au/Cu ratios of primary high-temperature ore-forming fluids, which, in turn, likely depends on the ratio in the magma source for a S-poor magmatic-hydrothermal system. If this is the case, then the consistency of Au/Cu ratios in the Beiya porphyries and Liuhe Au-rich xenoliths indicates that remelting of the Au-enriched lower-crustal cumulates could produce the S-poor porphyry Au-Cu system at Beiya.
6 Implications for exploration

Our results demonstrate that arc magmas derived from metasomatized mantle most likely ponded at the crustal base, leading to crustal growth and metal fertilization in the Neo-Proterozoic. The initial Au (Cu) contents and Au/Cu ratios in the fertilized juvenile lower crust likely depend on the amount of accumulated sulfide in the magma ponding at its base (Richards 2009). These ore-forming components (Au, Cu), though locally remobilized during later metamorphism, could be preserved in the lower continental crust, largely due to the secular stability of the craton. The incubation time between crustal base metal enrichment and reactivation can be short in a successive process from subduction to collision, such as in the Gangdese porphyry deposits (Hou et al. 2015; Griffin et al. 2013). Implications of the refertilization process and its relationship to the porphyry Cu-Au system at the cratonic edge. Figure 3.

Acknowledgements

This work was funded by the National Science Foundation of China (NSFC) (41320104004), the National Key Research and Development Project of China (2016YFC0600310), the 973 program of China (2011CB403104), and the International Geoscience Programme IGCP/SIDA-600.

References

Implications of the composite nature of the San Francisco Intrusive complex for the formation of the Rio Blanco-Los Bronces porphyry Cu deposit cluster

Simon J.E. Large, Yannick Buret, Jamie J. Wilkinson
Natural History Museum

Thomas R. Knott
University of Leicester

Ricardo Boric, Pablo Villegas
Anglo American Chile

Abstract. Enhancing our understanding of the processes that lead to the formation of fertile magmas is key to the identification of robust new fertility proxies indicative of porphyry Cu deposits. Once the essential magmatic and hydrothermal processes have been identified, their resulting characteristic geochemical signatures can provide a fast and cost-efficient mean to distinguish between potentially fertile or barren igneous suites. We aim to utilise whole rock and mineral chemistry data from the spatially extensive intrusive suite that hosts the Rio Blanco-Los Bronces deposit cluster to reconstruct the magmatic evolution leading up to the formation of Earth’s largest known porphyry Cu system. The associated intrusive complex was emplaced over more than 10 My of barren and ultimately fertile magmatism, making it an ideal site to develop and test fertility indicators. Temporally resolved whole-rock data reveals the composite nature of the intrusive complex suggested incremental assembly from potentially different source magmas. Next steps include the application integrated accessory mineral petrochronology to reconstruct processes such as emplacement rates and the injection of mafic melts. The influence of these factors on the fertility of the system will be evaluated and potentially useful geochemical signatures in pristine magmatic accessory minerals will be identified.

1 Introduction

Porphyry Cu±Au-Mo) deposits are the world’s main supplier of Cu and major mining companies have increased their efforts in exploring for these large tonnage deposits. However, remaining large deposits are likely to be buried under syn- or post-mineralisation cover, making them difficult and costly to discover; thus, new tools are required to help identify the most prospective areas. Developing new ‘fertility’ indicators for porphyry deposits on the regional scale requires an understanding of the genetic processes leading to their formation. We aim to reconstruct the magmatic evolution of the San Francisco Intrusive Complex culminating in the formation of the world’s largest cluster of porphyry Cu deposits, the Rio Blanco-Los Bronces district. The extensive magmatic activity that resulted in the emplacement of abundant ‘barren’ and ore-related intrusive lithologies (Deckart et al. 2012; Toro et al. 2012) allows the identification of processes that are essential for the formation of porphyry deposits and enables stringent testing of potential fertility indicators. We applied conventional methods, such as whole-rock geochemistry and future work will integrate this data with mineral chemistry coupled with geochronology to provide insights into magmatic processes that are otherwise masked by alteration or the composite history recorded by plutonic rocks. Zircon petrochronology has already been demonstrated as a valuable recorder of magmatic processes (Buret et al. 2016; Tapster et al. 2016; Large et al. 2018) and here we aim to add information from other juvenile accessory phases to further increase our understanding of them. This petrochronological approach has the potential to refine the genetic model for porphyry deposits and could result in the identification of so far undiscovered and robust ‘fertility discriminators’.

2 The geology of the San Francisco Intrusive Complex

The late Miocene Rio Blanco-Los Bronces porphyry cluster consists of several mineralized centres and is the world’s largest known concentration of Cu with >206 Mt contained Cu (Irarrazaval et al. 2010; Sillitoe 2010; Toro et al. 2012). It is situated in Central Chile, east of Santiago, in the Western Main Cordillera of the high Andes. The Western Main Cordillera comprises km-thick volcanic and volcano-sedimentary sequences of the Eocene to Early Miocene Abanico Formation and the Miocene Farellones Formation that are intruded by several plutons and sub-volcanic stocks of Miocene to Pliocene age (Piquer et al. 2015). The Central Chilean arc segment is geotectonically located on the margin of the Southern Volcanic Zone, at the transition between the steeper slab subduction system of southern Chile and the shallower slab subduction regime towards the north (Kay et al. 1999; Mpodozis and Ramos 1990). In addition to the Rio Blanco-Los Bronces cluster, Central Chile also hosts the giant El Teniente and Los Pelambres deposits and is therefore an ideal study site for understanding the processes that result in the generation of fertile arc
The San Francisco Intrusive Complex is the largest such complex in central Chile, stretching ~30 km N-S and ~20 km E-W. It is constituted by numerous different intrusive phases (Piquer et al. 2015) that differ in texture, mineralogy, geochemistry and emplacement age. Published geochronological data suggest that the intrusive activity started at ~17 Ma concurrent with the deposition of the youngest exposed members of the Farellones Formation. This timing coincides with the change from an extensional setting during the deposition of the Abanico Formation to a compressional regime that started in the Early Miocene (Piquer et al. 2015). Intrusive activity continued for some 13 My, culminating in the emplacement of La Copa diatreme at ~4.7 Ma, the youngest igneous feature in the district.

Several porphyry Cu prospects and deposits are hosted by the San Francisco Intrusive Complex. The super-giant Rio Blanco-Los Bronces deposit cluster comprises the Los Bronces and Andina mines and the Los Sulfatos deposit, and is located at the eastern margin of the intrusive complex. The Cu mineralization is considered to be genetically related to abundant tourmaline breccias and porphyry dikes (Irarrazaval et al. 2010). Based on molybdenite Re-Os geochronology these deposits formed towards the end (7 – 4.9 Ma) of the magmatic activity of the intrusive complex, although smaller, sub-economic, porphyry-style hydrothermal centres occur throughout the district and vary in age (e.g. Los Piches, El Plomo).

The large spatial extent of the igneous rocks associated with the San Francisco Intrusive Complex and long time period recorded by the exposed lithologies allow for a detailed reconstruction of the magmatic evolution in Central Chile that culminated in the formation of a world-class porphyry Cu cluster. We build on and add to abundant whole-rock geochemical and isotopic work in the district (e.g. Nyström et al. 2003; Piquer et al. 2017) and will combine this data with new mineral chemistry data of the different lithologies. Whole-rock samples can be affected by hydrothermal alteration that is abundant in the San Francisco Intrusive Complex and this can mask or modify the original geochemical signature. Furthermore, whole rock data record the composite history of plutonic rocks making the identification of specific processes difficult. Therefore, we aim to utilise careful mineral chemistry in order to see through such effects and to investigate the evolution of fertile magmas and the processes related to their generation (e.g. Buret et al. 2016; Loader et al. 2017; Large et al. 2018). This information will be put into a refined temporal context by new U-Pb zircon geochronology on all investigated samples.

### 3 Petrographic observations

The rocks of the San Francisco Intrusive Complex are hosted within the dominantly basaltic to basaltic-andesitic volcanic sequences of the Abanico and Farellones Formations. Individual volcanic units range from homogeneously fine-grained deposits to pyroclastic flow deposits with decimetre-sized clasts. Felsic sequences are rare but can be used as marker lithologies (Fig. 2a), especially within the strongly folded Abanico Formation. The km-thick volcanic sequences are intruded by massive intrusive bodies of variable chemical composition. Identifying contacts of large equigranular bodies requires detailed mapping and earlier studies suggested at least 14 individual intrusive facies (Piquer et al. 2015). Such contacts are sharp and suggest sufficient cooling of older phases before emplacement of the younger intrusions (Figs. 2c,d). Abundant mafic enclaves within the felsic intrusions suggest interaction of mafic and evolved melts during crystallisation (Figs. 2e,f).

Numerous porphyrytic dikes and stocks intrude the intrusive complex with some of them being directly associated with Cu-ore formation (Fig. 2g) and some being apparently barren. Typically, they show no direct relation to their immediate host rocks and are therefore considered to have been sourced from an underlying, unexposed magma reservoir.
Most high-grade copper ores are dominated by hydrothermal tourmaline-quartz-sulphide breccias (Fig. 2h) but classic quartz-sulphide stockwork veining and disseminated sulphide mineralization (Fig. 2g) can also occur. Pre-/syn-Cu intrusions and post-ore dikes have been identified in most prospects and deposits providing an opportunity to constrain the timing of mineralization in each system and their maximum durations. Tourmaline-quartz-sulphide pockets were identified within many of the equigranular host-intrusions (Fig. 2i). These suggest late stage exsolution of B- and metal-rich fluids similar to those that might have formed the giant Cu deposits. However, the intrusive rocks precede main ore formation by up to a few My based on current geochronological information, questioning the direct association.

As strong hydrothermal alteration is characteristic for porphyry Cu deposits, it is not surprising that the San Francisco Intrusive Complex is extensively altered. The greatest potassic to argillic alteration intensities surround the largest deposits, completely modifying whole-rock geochemistry. However, even samples distal to the Rio Blanco-Los Bronces cluster show pervasive if weak propylitic alteration, potentially linked to the abundant smaller hydrothermal centres in the district. This further emphasises the need for detailed mineral chemistry.

Key questions that arise from the petrographic observations relate to the source of the Cu ore-forming fluids, the degree and importance of mafic melt interaction in the magmatic system, and the timing and duration of individual hydrothermal pulses in the area.

4 First geochemical constraints

Samples collected for the study were taken during a field campaign in 2018. They cover the geographical extent of the San Francisco Intrusive Complex and all relevant igneous lithologies from the Rio Blanco-Los Bronces deposit cluster were sampled. Temporally, they cover the entire duration of magmatic activity in the intrusive complex. For comparison, a few samples were also collected from the volcanic sequences in the area.

The igneous rocks in the district range from basaltic to quartz-monzonitic in composition with no systematic temporal trend in degree of differentiation. Major element chemistry also does not reveal a systematic difference between equigranular rocks and porphyritic rocks sampled from the deposits or prospects. The geochemical diversity within the district might be the result of variable magmatic sources over the duration of intrusive activity or variable degrees of fractionation before final emplacement.

The fertility discriminator diagram by Loucks (2014) provides more insight into differences between ore-related and host lithologies. The volcanic and distal/earlier equigranular intrusions fall along or straddle the ‘barren’ trend, whereas the porphyry intrusions and proximal host intrusions display elevated Sr/Y ratios and fall into the ‘fertile’ field. Elevated Sr/Y is commonly inferred to be the result of deep amphibole or garnet fractionation, whereas the ‘barren’ trend is interpreted to
result from fractionation dominated by plagioclase. This would suggest that the porphyries and associated host intrusions were sourced from magmas that underwent a different fractionation history than the more distal and temporally detached intrusions.

Figure 3. Geochemical whole-rock data from investigated igneous rock samples. Rock discrimination diagram after Middlemost (1994). Sr/Y fertility diagram after Loucks (2014).

5 Conclusions

Field observations and geochemical investigation of the San Francisco Intrusive Complex reveal a geochemically diverse magmatic body. This indicates that it was assembled incrementally by injection of chemically different magmas over an extended period with ore formation occurring in during the last stages of recorded magmatism. Understanding the processes, such as magma mixing, fluid exsolution and rates of emplacement acting during the magmatic assembly of the complex and potential changes that resulted in the formation of the porphyry Cu cluster is the main aim of ongoing work. To shed more light on the relationships between the different igneous rock types in the district, mineral chemistry will be used from key phases that can remain unaffected by hydrothermal alteration (e.g. zircon, apatite). These have been shown to allow discrimination between different magma sources and to reveal magmatic processes in underlying, unexposed magma reservoirs.

Acknowledgements

I would like to thank the Anglo American geologists and staff for their help with drill hole and sample selection in the field, in particular Sebastian Ramirez. C. Munóz is acknowledged for providing some of his samples for this work. This work is part of the NERC Grant NE/P017452/1 “From arc magmas to ores (FAMOS)” and scientific input from all colleagues in the consortium is acknowledged.

References


Sillitoe RH (2010) Porphyry copper systems Economic geology 105:3-41


968 Life with Ore Deposits on Earth – 15th SGA Biennial Meeting 2019, Volume 2
Platinum-group elements as a tracer of sulphide saturation in evolving magmas: application to the Río Blanco Cu-porphyry deposit, central Chile

Yamila Cajal, Ian H. Campbell
Research School of Earth Sciences, Australian National University

Abstract. Recent studies show that the platinum-group elements can provide new insights into felsic magma fertility by determining the onset of sulphide saturation. This study aims to test the hypothesis that timing of sulphide saturation, relative to volatile exsolution, controls magma fertility in the Andes of central Chile. To address this aim, samples from the Río Blanco porphyry Cu deposit are being studied. This deposit was formed in the Miocene-early Pliocene magmatic arc of central Chile and it represents the world’s biggest copper reservoir.

The samples include different units from the San Francisco Batholith and porphyritic intrusions associated with the deposit. They were analysed for major elements by XRF, trace elements by LA-ICP-MS, and Re, Au and PGE by a Ni-sulphide fire assay, isotope dilution method. Preliminary results suggest that sulphide saturation in the fractionated series occurred at ca. 2.2-1.8 wt.% MgO, slightly before volatile saturation at ~1.2 wt.% MgO. This is similar to the El Abra porphyry Cu deposit (Cocker et al. 2015). It is suggested that the amount of sulphide that separated from the melt was small, enough to lower the PGE and Au contents, but not enough to have a significant effect on the ultimate Cu fertility of the magma due to its lower partition coefficient.

1 Introduction

Porphyry deposits are the world’s primary source of copper (Richards 2003). They are typically formed in magmatic arcs above subduction zones (Wilkinson 2013). These deposits are usually associated with intermediate to felsic magmas (Sillitoe 2010) that appear to share similar geological characteristics with barren suites. As a consequence, exploration companies spend millions of dollars exploring non-mineralized systems. For this reason, it is highly desirable to improve our understanding of what controls magma fertility in porphyry systems in order to find a method that can distinguish between them.

Recent studies (e.g. Park et al. 2012, 2013, 2015, 2016, 2018; Cocker et al. 2015; Lowczak et al. 2017; Hao et al. 2017, 2019) have shown that the platinum-group elements (PGE) can provide new insights into felsic magma fertility by determining the timing of sulphide saturation relative to volatile saturation. These studies suggest that PGE geochemistry can be used to distinguish between mineralized and barren systems, as well as between Cu-only and Cu-Au porphyries.

Almost half of the world’s copper production comes from the Central Andes (Sillitoe and Perelló 2005), particularly from Chile, which leads the world in copper resources and reserves (Mudd and Jowitt 2018). Until now, only two deposits in this region have been studied exploiting this approach, the El Abra (Cocker et al. 2015) and La Escondida (Hao et al. 2019) Cu-porphyries, both from the middle Eocene to early Oligocene metallogenic belt of Northern Chile. Therefore, it is desirable to expand our understanding of what controls magma fertility in the world’s most prolific copper region.

The aim of this study is to test the hypothesis that timing of sulphide saturation, relative to volatile exsolution, controls magma fertility in the Andes of central Chile. The initial hypothesis is that if sulphide saturation is reached at early stages of magmatic evolution, chalcophile elements, as Cu and Au, will be trapped in sulphides in the magmatic chamber and, therefore, they will not be available to enter the fluid phase when volatile exsolution occurs (Hamlyn et al. 1985, Spooner 1993, Park et al. 2013). Alternatively, if the magma becomes volatile saturated before sulphide saturation, or sulphide saturation does not occur, these elements will be available to enter the fluid phase, be transported by the hydrothermal fluids and, eventually, form an ore deposit. The Río Blanco porphyry copper deposit is being studied to address this aim.

2 Geological setting

The Río Blanco porphyry Cu deposit (Fig. 1) is the largest known concentration of copper in the world, containing 133.9 Mt (Sillitoe 2010, Mudd and Jowitt 2018). The deposit is located in a transition zone between the Chilean flat-slab zone to the north and the Southern Volcanic Zone (Stem et al. 2011; Mpodozis & Cornejo 2012). The flat slab subduction has been generally attributed to the subduction of the Juan Fernandez Ridge during the late Miocene, and linked to the generation of the appropriate compressional conditions for the formation of giant porphyry Cu-Mo deposits (Mpodozis & Cornejo 2012; Piquer et al. 2015, and references therein).

In general terms, the geology of the district comprises volcanic and volcaniclastic rocks of the Abanico and Farellones Formations, with U-Pb (zircon) ages between 22.7 ± 0.4 and 16.8 ± 0.3 Ma (Toro et al. 2012, and references therein). This was followed by the emplacement of a large intrusive complex, dominated by granodiorite plutons, known as the San Francisco Batholith with U-Pb (zircon) ages between 16.4 ± 0.2 and 8.4 ± 0.2 Ma (Toro et al. 2012, and references therein). The main part of the Cu-Mo endowment is linked to the
evolution of this batholith and is hosted in porphyry stocks and breccia bodies formed by magmatic-hydrothermal activity at 8.2 ± 0.5 to 4.31 ± 0.05 Ma (Toro et al. 2012, and references therein). The magmatic activity ended with the emplacement of La Copa Volcanic Complex at 4.9 to 4.1 Ma, which represents a late- to post-mineralization event (Deckart et al. 2005).

3 Samples and methods

Nineteen drill-core samples from the Rio Blanco deposit were collected with the support of CODELCO. The samples were selected to cover a wide range of compositions and to avoid areas with strong hydrothermal alteration. These samples include the different lithologies recognized in the San Francisco Batholith and the porphyritic intrusions.

The samples were initially cut using a diamond saw to remove hydrothermal veins in order to reduce the effect of hydrothermal processes in the geochemical results. About 1 kg of sample was crushed by jaw crusher and then about 200 g of sample was milled using a case-hardened soft iron mill. The samples were analysed for major elements using X-ray fluorescence (XRF) by Intertek Laboratories (Perth, Australia).

Polished thin-sections of selected samples were prepared by the Australian Petrographics Laboratory (NSW, Australia). These were used to better understand the petrography and mineral compositions of the samples, as well as the relationships between magmatic and hydrothermal processes.

Crushed powders of samples were analysed for Re, Au and PGE using the Ni-sulphide fire assay, isotope dilution method described by Park et al. (2012), which allows the determination of PGE at very low concentrations. Additionally, the concentrations of a wide range of trace elements were determined by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of glasses prepared by fusion of rock powders. All these analyses were performed at the Research School of Earth Sciences, Australian National University.

4 Preliminary results and discussion

4.1 Major and trace element geochemistry

Preliminary results show that the samples exhibit a range of degrees of differentiation with MgO contents varying from 2.87 to 0.43 wt.% and SiO₂ contents from 58.96 and 72.02 wt.% consistent with dioritic to granitic compositions. This is as expected considering the geology of the area.

The whole-rock major element geochemistry of the samples indicates that they can be classified as calc-alkaline. They also show the typical trace element patterns of volcanic arc igneous rocks, with a depletion in heavy rare earth elements and high field strength elements compared with light rare earth elements and large-ion lithophile elements, respectively, as well as the Nb negative and Pb positive anomalies.

The rare earth element plot (Fig. 2a) exhibits a listric shape with a depletion in middle rare earth elements that suggests that the magmatic evolution was controlled by amphibole fractionation (Richards and Kerrich, 2007). In addition to this, the absence of a Eu anomaly suggests that magmas were oxidized and hydrous.

The samples also show high Sr/Y (Fig. 2b) and La/Yb, characteristic of the geochemical signature, which has
been interpreted to indicate fusion and/or crystallization of mafic rocks at high pressures (> 10Kb) and/or abundant hornblende crystallization in the upper to middle crust (Richards and Kerrich, 2007).

Figure 2. a. Rare earth element plot and b. Sr/Y ratios plotted against Y (ppm) content for 19 igneous samples of the Rio Blanco Deposit. GDRB: Río Blanco Granodiorite; GDCC: Cascada Granodiorite; DIOR: Diorite; PQM: Quartz Monzonite Porphyry; PFELD: Feldspathic Porphyry; PDL: Don Luis Porphyry.

4.2 PGE geochemistry

PGE are the ideal indicator of sulphide saturation in silicate magmas due to their very high partition coefficients into sulphide melts (Mungall and Brenan 2014) and low solubilities in hydrothermal fluids (Park et al. 2016).

Preliminary results for the PGE (Fig. 3) show that for less differentiated samples, the Pd content increases with the decrease of wt.% MgO until ~2.2-1.8 wt.% MgO, when the Pd content decreases for the samples from the batholith, which can be interpreted to indicate the onset of sulphide saturation. If the ore associated porphyries are assumed to be emplaced at volatile saturation their MgO content, after taking into account their phenocryst content, gives the MgO content of the melt at volatile saturation (Burnham 1979, Cocker et al. 2015), in this case 1.24 to 0.42 wt.% MgO. Volatile saturation is therefore assumed to occur at ~1.24 wt.% MgO, slightly after sulphide saturation.

Figure 3. Pd (ppb) against MgO (wt.%) for 14 igneous samples from the Rio Blanco Deposit. SS: sulphide saturation. The grey line represents the Pd trend for the samples from El Abra-Pajonal Intrusive suite (Cocker et al. 2015). GDRB: Río Blanco Granodiorite; GDCC: Cascada Granodiorite; DIOR: Diorite; PQM: Quartz Monzonite Porphyry; PFELD: Feldspathic Porphyry; PDL: Don Luis Porphyry. MDL: Method Detection Limit. Data from the older GDRB are not reported.

However, the data from the porphyries samples are scattered as also observed by Hao et al. (2019) in La Escondida ore-related porphyries, which has been attributed to the formation of hydrothermal PGE nuggets. For this reason, samples will be run in duplicate to test this hypothesis.

5 Conclusion

The preliminary results suggest that sulphide saturation occurred ca. 2.2-1.8 wt.% MgO (Fig. 3), slightly before volatile saturation at ~1.2 wt.% MgO. This is similar to El Abra porphyry Cu deposit (Cocker et al. 2015), where it has been suggested that the amount of sulphide separated from the melt was small, enough to lower the PGE and Au contents, but not enough to have a significant effect on Cu due to its lower partition coefficient. This resulted in a Cu-dominated porphyry rather than a Cu–Au deposit.

However, due to the narrow compositional range (2.87 to 0.43 wt.% MgO) of the samples analyzed from the batholith and the porphyries, it is necessary to expand this study to include a wider range of compositions to better understand the timing of sulphide saturation and magmatic evolution in the system. For this reason, samples from the older (Farellones Formation) and younger (La Copa Volcanic Complex) volcanic units identified in the deposit will be studied.
6 Further studies

Further studies will include PGE analysis in duplicates and hydrothermal veins in order to evaluate the possible effect of PGE nuggets and hydrothermal alteration in the samples, respectively. A new batch of samples from the batholith and the porphyries will be analyzed for major elements, trace elements and PGE, as well as a group of samples from the Farellones Formation and La Copa Volcanic Complex. In addition, zircons will be separated to determine the emplacement age of the magmas involved by U-Pb dating using LA-ICP-MS, which can help to understand better the magmatic evolution of the area. Additionally, the $fO_2$ of the melt, which controls sulphur solubility, will be determined by analysing Ce$^{4+}$/Ce$^{3+}$ ratios in zircons. Oxygen isotopes will be analysed by Sensitive High-Resolution Ion Microprobe (SHRIMP) to gain some insights into the source of the parent magma.

Acknowledgements

This work was funded by the Australian Research Council (ARC) grant to Ian Campbell and Andrew Berry (DP170103140). The authors would like to acknowledge the Andina Division of CODELCO for supporting this research, especially Claudio Martinez and his team. Yamila Cajal would like to thank CONICYT PFCHA/DOCTORADO BECAS CHILE/2017 – 72180607 for supporting her studies at ANU.

References


The nature of fluid exsolution and migration in porphyry systems – evidence from the Yerington district, Nevada

Lawrence C. Carter, Ben J. Williamson
Camborne School of Mines, Cornwall, UK

Robin N. Armstrong
Natural History Museum, Cromwell Road, London, UK

Simon R. Tapster
NIGL, BGS, Keyworth, UK

Abstract. Porphyry copper deposits provide most of the world’s copper and are an important source of gold and other metals. Although many aspects of these deposits are well understood, there remains uncertainty regarding the source and transport mechanisms of mineralising fluids. Due to tectonic tilting, the classic Yerington District, Nevada, offers the rare opportunity to study a well-exposed section through the Yerington Batholith and a number of porphyry centers to a palaeo-depth of circa 8 km, from the volcanic to plutonic environments. From detailed textural studies, we present evidence that, rather than exsolving from granite magmas in the upper region of the associated Luhr Hill granite pluton, as suggested in previous studies (e.g. Dilles 1987; Schöpa et al. 2017), mineralising fluids were derived from aplite dykes which themselves emanated from deeper (unobserved), and probably more evolved internal regions of the Luhr Hill granite. We propose that these fluids were upwardly transported and focused through the aplite dykes via inter-crystal spaces, in a ‘mush’ network, in sufficient quantities for porphyry ore formation.

1 Context

Porphyry copper deposits provide around 75% of the world’s copper and are an important source of gold and other metals (Sillitoe 2010). One aspect of porphyry deposits that is poorly understood is whether the mineralising fluids from which they form are derived from:

(i) high-level, Cu-rich, porphyry stocks;
(ii) feeder chambers at mid-upper crustal levels;
(iii) a lower crustal reservoir; or
(iv) a combination of these in a transcrustal mush zone (e.g. Cashman et al. 2017). Despite magmatic-hydrothermal mineralisation often being spatially, temporally and texturally linked to high-level porphyry stocks, it is unlikely that enough fluid could be derived from such a limited volume of magma (Sillitoe 2010). From mass-balance calculations and high-precision CA-ID-TIMS U-Pb zircon studies (Buret et al. 2016; Tapster et al. 2016), it is probable that mineralising fluids emanated from a more extensive, longer-lived, deeper, yet rarely observed magmatic source, possibly at 5 to 15 km depth. How and when such fluids were transported from these depths is poorly understood.
2 The Yerington district, Nevada

Due to tectonic tilting, the classic Yerington District, Nevada (Fig. 1), offers a well exposed, ca. 8 km deep, section through the Yerington Batholith, including volcanic rocks, plutons and a number of porphyry deposits (Dilles 1987). This provides a rare opportunity to study temporal relationships in the deeper magmatic parts of the system, important to porphyry formation, and the magmatic-hydrothermal transition.

The Mid-Jurassic Yerington Batholith is composed of three major plutonic units which are, in order of decreasing age and volume, and increasing emplacement depth and silica content: 1) the McLeod Hill quartz monzodiorite; 2) Bear quartz monzonite; 3) Luhr Hill granite (Fig. 1). Swarms of granite-composition porphyry dykes are thought to have emanated from the upper and central portions of the Luhr Hill granite (Dilles 1987). Their emplacement, and that of the apophyses of the Luhr Hill granite through which most are concentrated (Fig. 1), is likely to have been structurally controlled.

Closely associated with the dykes are the District’s four known porphyry deposits: Ann Mason, Yerington, McArthur and Bear (listed in order of decreasing size; Bryan 2014; Henderson et al. 2014; Kulla et al. 2017).

The aim of the current study is to determine whether porphyry-forming fluids in the Yerington District were derived from either: 1) the Luhr Hill granite; or 2) transported from a deeper source via the dykes.

3 Fluid exsolution and mineralisation

3.1 Granite cupola

Existing conceptual models for the Yerington District (e.g. Dilles 1987; Schöpa et al. 2017), and porphyry formation in general (e.g. Seedorff et al. 2005; Corbett 2009), commonly suggest that cupola zones, or dykes emanating from cupolas, are the source of mineralising fluids. In contrast, from our field observations, there is no textural evidence (e.g. miarolitic cavities; Candela 1997) for fluid exsolution in the cupola of the Luhr Hill granite or large porphyry dykes. Quartz-feldspar orbicules within the granite cupola show well defined graphic texture at their margins (Fig. 2), which is generally thought to form in highly viscous, flux-poor, highly undercooled melts (Candela 1997; London and Morgan 2012). We suggest that their presence thus indicates that the Luhr Hill granite magmas, close to the roof of the pluton, were strongly undercooled, probably due to depressurization as a result of regional uplift, upward emplacement, fracturing and/or dyke propagation, and were fluid undersaturated. They are therefore unlikely to have been the source of the mineralising fluids.

3.2 Aplite dykes

Aplite dykes in the Yerington District are volumetrically minor yet occur pervasively from below to within the Ann Mason and Yerington deposits. They cross cut the upper parts of the Luhr Hill granite and therefore their source is likely to be greater than ~8 km. In previous work (e.g. Dilles 1987) these aplites were interpreted as late- or post-mineralisation. From our field observations, however, including mingling relations with larger porphyritic dykes, that they are often mineralised and host mineralised miarolitic cavities (Fig. 3), and that they are cross-cut by later mineralised veins, the aplite dykes were penecontemporaneous with, yet distinct from, porphyritic dyke intrusions, and were syn-mineralisation. In addition, we have observed textures that appear to indicate that the aplite dyke magmas were coeval with a separate hydrothermal fluid phase (Fig. 4).

Figure 2. Field photograph of quartz-feldspar orbicules in the Luhr Hill granite cupola. Inset is a photomicrograph in crossed nicols showing graphic texture at the margins of the orbicule.

Figure 3. Photograph of drill core from the Ann Mason porphyry deposit showing an aplite dyke within Luhr Hill granite. The aplite dyke has quartz unidirectional solidification textures (USTs) growing inwards from its margins, hypogene chalcopyrite (Ccp) within its centre and molybdenite (Mo) along its margins. The USTs within the aplite dykes likely indicate rapid pressure fluctuations (Kirwin 2005) during dyke emplacement.
Cathodoluminescence (CL) imaging of quartz from the Luhr Hill granite, porphyry and aplite dykes, mineralised miarolitic cavities as well as A-, B- and D-type veins has revealed the presence of a number of generations ranging from clearly zoned varieties with an invariably bright CL signal, to later infilling or ‘healing’ quartz characterized by little to no CL response. Of note is that quartz with the same textural and CL character is observed within both miarolitic cavities and the groundmass of the aplite dykes (false coloured orange and purple in Fig. 5c). As the quartz in the miarolitic cavities contains inclusions of chalcopyrite (Fig. 5b), we also interpret the hypogene copper mineralisation (chalcopyrite-bornite) to be associated with the relatively late ‘healing’ quartz phase (false coloured purple in Fig. 5c).

4 MUSH transport mechanisms and the magmatic-hydrothermal transition

From our detailed scanning electron microscopy (SEM) and CL imaging of the aplite dykes, they can be seen to contain a wormy, highly interconnected generation of quartz throughout their groundmass, false coloured purple, as well as discrete quartz grains, false coloured orange (Fig. 5c). The wormy texture can be continuously traced in 2D across entire thin sections. Akin to descriptions of interconnected miarolitic cavities by Candela and Blevin (1995), the fact that this quartz phase can be traced notable distances in 2D indicates that, without a doubt, it has very high orders of connectivity in 3D. We interpret this wormy texture as marking an interconnected flow path for fluids through inter-crystal spaces in a mush framework of magmatic minerals, where we use the term mush to refer to a continuous crystal framework (Cashman et al. 2017). This is significant as it demonstrates how mineralising fluids could have continuously migrated upwards through the aplite dykes post their emplacement until hydrothermal quartz precipitated into and sealed the inter-crystal spaces. Consequently, through their crystallisation history, the volumetrically small but pervasive aplite dykes could have acted as conduits for the upward...
transport of large volumes of hydrothermal fluids, potentially in sufficient volumes for porphyry ore formation and associated alteration.

We have also observed the interconnected quartz texture within the aplite groundmass directly ‘feeding’ into miarolitic cavities (e.g. Fig. 5). This appears to be indicated not only by their spatial relationships, but also by identical CL responses between interconnected quartz in the groundmass of the aplite dykes and mineralised miarolitic cavities. Given that miarolitic cavities are undoubted evidence for magmatic fluid exsolution (Candela 1997), we present this as evidence for the magmatic-hydrothermal transition being recorded in the aplite dykes.

5 Concluding conceptual model

We conclude that, within the Yerington District, the roof zone of the Luhr Hill granite and its apophyses was a carapace rather than a mineralising cupola. We suggest that the spatial distribution of the apophyses and subsequent dyke emplacement were structurally controlled and that the sharp, cross-cutting relations throughout the apophyses indicate that the aplite dykes were probably sourced from an unexposed, inner portion of the Luhr Hill granite pluton. Mineralising fluids were transported upwards and focused through the aplite dykes via a network of inter-crystal spaces within a partially crystallised magmatic-hydrothermal ‘mush’. This ‘mush’ formed late in the crystallisation history of the aplite dykes and was maintained as a result of the continuous upward flow of fluids from depth. Increasing fluid pressures within these dykes resulted in brittle failure of the wall rocks and subsequent formation of A- and, in turn, B-type veins, with an associated pressure drop. As the veins were sealed, pressures consequently increased again in a cyclic pattern, as evidenced from the presence of USTs within the aplite dykes (Fig. 3).

Acknowledgements

The lead author is supported by a NERC GW4+ Doctoral Training Partnership studentship from the Natural Environment Research Council [NE/L002434/1] and is thankful for support from NIGL and additional funding from the Society of Economic Geologists Foundation’s Hugh McKinstry Fund. Further thanks go to Quaterra Resources and Hudbay Resources (previously Mason Resources) for access to drill core and field support. This work is supported by the NERC Highlight Topic award “FAMOS” [NE/P017452/1].

References

“Chlorimetry” of porphyry copper forming magmas, why does it matter?

Cyril Chelle-Michou
Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Switzerland

Abstract. Chlorine is an essential element for the transport of ore metals making porphyry copper deposits. However, unlike Cu and S, Cl is not preserved in the rock record and is a largely overlooked element. In fact, it is commonly assumed that there is enough Cl in the system to transport all the available Cu as well as other metals (Fe, Zn, Pb, etc). Recent experimental, numerical modelling and mass balance studies have highlighted that Cl can be a limiting factor as well as a decisive element to make a giant porphyry copper deposit. As new tools are being made available to retrieve the magmatic Cl concentration of porphyry copper related magma, it is becoming possible to test the importance of Cl in controlling the size of porphyry copper deposits. Such “chlorimeters” rely on Cl-bearing minerals such as apatite or hornblende and could easily be implemented in exploration programs to help decision making and advance our understanding of magmatic-hydrothermal systems.

1 Introduction

Chlorine plays a fundamental role in the formation of magmatic-hydrothermal ore deposits such as porphyry copper systems, Sn deposits, IOCG deposits. By complexing with Cu, Zn, Pb, Sn, Fe, Ag (and potentially Mo and Au), chlorine ensures the transport of economic metals from their source to the site of mineralization where they may form economic deposit (e.g. Kouzmanov and Pokrovski 2012). Chlorine is also a commonly used element to study of magma degassing processes at volcanoes (e.g. Villemant et al. 2008; Aiuppa et al. 2009; Humphreys et al. 2009). In porphyry copper deposits, the chlorine required to form the deposit is dominantly sourced by the magma. Ultimately, magmatic chlorine in arcs is derived from the sea-water altered subducting oceanic plate (e.g. Kent et al. 2002).

Geochemical studies of porphyry copper forming magmatic systems have mostly focused on the critical role of H2O, Cu and S, while only seldomly exploring the role of chlorine. In fact, it has often been assumed that unlike H2O, Cu and S, the abundance of Cl is not a limiting factor for the formation of porphyry copper deposits.

Yet, recent experimental data, mass balance constraints, and numerical modelling highlight the critical role of Cl in the formation of porphyry copper deposit. Here, I summarize those new data and models, and explore the ways magmatic “chlorimetry” could be implemented in academic studies and exploration programs to help the search for the richest ore bodies.

2 The overlooked role of magmatic chlorine in the formation of porphyry Cu deposit

2.1 Evidence from new experimental data and numerical modelling

Although the influence of fluid salinity on the fluid/melt partition coefficient of Cu was already documented in the 1980’s (e.g. Candela and Holland 1984), it is not until the study of Tattitch et al. (2017), that the partitioning behavior of chlorine has been calibrated for the entire range of fluid salinity encountered in porphyry copper systems. This study quantifies the predominance of several Cl complexes in the partitioning behavior of Cu, with minimal additional impact from the presence H2S in the magmatic fluid.

Available experiments highlight that pressure, melt composition and the total concentration of Cl in the system all impact on the partitioning behavior of Cl between fluid and melt (e.g. Shinozaki et al. 1989; Signorelli and Carroll 2000; Botcharnikov et al. 2015). Yet, many of these studies used melt compositions distinct from typical subduction zone magmas, hampering their quantitative application to porphyry-related magmatism.

New experiments on calc-alkaline andesite to rhyolite by Tattitch et al. (submitted) have made possible to calibrate an empirical fluid/melt partitioning function accounting for pressure, melt composition and Cl concentration in the system. Further, Tattitch et al. (submitted) implemented this relationship into a Monte Carlo numerical model accounting for the chemical feedbacks imposed by constantly changing melt H2O (pressure), Cl and major element concentrations during magma degassing. Their study reveals the primacy of magmatic chlorine concentration at the point of fluid saturation in promoting efficient copper extraction from intermediate to silicic magmas (Fig. 1). Indeed, while initial Cl concentration of 5000 ppm is able to extract about 100% of the Cu initially available in the melt, initial Cl concentration of 500 ppm could only extract 50% of the available copper (Fig. 1). This effect is even more pronounced if sulfides are able to crystallize and scavenge Cu during. Therefore, for any given magma volume, the amount of Cl available in the system can strongly modulate the Cu endowment of the subsequently forming porphyry copper system.
2.2 Evidence from mass balance constraints

A number of studies have been looking at the volume of magma that would be required to form a given porphyry copper deposit (e.g. Cline and Bodnar 1991, Steinberger et al. 2013, Chelle-Michou et al. 2017). These studies invariably used constraints from the mass of metals (Cu, Mo, Au), sulphur and/or quartz that have been deposited in the deposit. Yet, none of these questioned the amount of Cl necessary to transport these metals.

One of the main challenges in approaching mass balance calculation from the angle of Cl, relies on our ability to estimate the minimum mass of Cl required to form a given deposit. The bulk of the fluid-transported Cl is not preserved in the rock record (with the exception of volumetrically insignificant fluid inclusions). Consequently, estimating the mass of Cl needed to form a deposit requires indirect approaches and some assumptions.

In a recent study, Chelle-Michou and Chiaradia (2017) used core logging and grade-tonnage modelling information to estimate the total amount of hydrothermally sourced Fe at the Corocohuayco Cu(-Au-Fe) porphyry-skarn deposit, Peru. Unlike Cu, Fe is a major cation in magmatic fluids (Kouzmanov and Pokrovski 2012). Assuming that the relative proportions of Fe, Na and K in the magmatic fluid at Corocohuayco closely resemble those of the world average intermediate-density fluid inclusions, they could estimate that the formation of Corocohuayco required on the order of 366 Mt of Cl (Fig. 2). Further, the initial melt Cl concentration of the ore-forming intrusions could be estimated using apatite chemistry in conjunction with the partitioning model of Li and Hermann (2017). It resulted in an estimated Cl concentration of 2000–3000 ppm.

This exercise revealed that a minimum of 60–169 km³ of magma was required to source the 366 Mt of Cl (Fig. 2). A similar approach concluded that the 3 Mt of Cu and 20 Mt of S deposited at Corocohuayco were probably sourced by a magmatic system of 33–131 km³ and 43–365 km³, respectively (Fig. 2). The similarity of these three minimum magma volume estimates suggests that the amount of Cl in the magma is at least as critical as the amount of S and Cu to form an economic porphyry copper deposit.

3 Magmatic “chlorimetry” in the search for porphyry copper deposits

The theoretical conjectures and empirical evidence presented above both highlight that magmatic chlorine may be one of the most important chemical parameters for the formation of porphyry copper deposits. Global compilation of volcanic arc rock composition (Chiaradia 2014) and sulphur speciation in the deep crust (Matjuschkin et al. 2016) suggest that sulphide saturation and accompanying Cu sequestration is unavoidable in the arc crust. It follows that Cu-rich intermediate to felsic calc-alkaline magmas typical to those forming porphyry
deposits are unlikely to exist in most arcs, providing limited leverage of the Cu concentration (10–60 ppm, inversely correlating with SiO₂). Similarly, sulphur concentration in those magma typically range from 100–1000 ppm (Wallace and Edmonds 2011), providing more than enough S in most cases to precipitate the observed amount of sulphides and sulphates at porphyry systems. In turn, the Cl concentration in intermediate to felsic arc magmas ranges from 500 ppm to ~1 wt% with no correlation to melt SiO₂ (Webster et al. 2018). Such a high range of values virtually independent of melt composition, offers an equally large range of possibilities to extract the available copper from the melt.

Thus, estimating magmatic Cl concentration from the rock record ("chlorimetry") may be a useful new method for more efficient mineral exploration. Despite its huge potential, this conjecture still requires to be tested on a large number of mineralized and barren magmatic systems in order to confirm and refine its use in mineral exploration.

Successful “chlorimetry” requires analyzing Cl-bearing magmatic minerals together with appropriate thermodynamic models describing the partitioning of Cl between these phases and the melt. Recent advances in the thermodynamic description of apatite (Li and Hermann (2017) and amphibole (Iveson et al. 2017) provide the necessary tools for accurate quantification of magmatic Cl concentrations. However, magmatic amphibole is commonly intensely altered at most porphyry deposits, making its use as a chlorimeter impractical. In turn, while apatite can suffer some (potentially indicative) hydrothermal alteration (Bouzari et al. 2016), fresh magmatic apatite can be found at most porphyry deposits. Its ability to survive erosion and to be preserved in sediments makes it the ideal tool for regional “chlorimetric” survey.

Acknowledgements

This synthesis resulted from numerous discussions with Brian Tattitch, Jon Blundy, Massimo Chiaradia and Mauro Bongiovanni, may they all be acknowledged.

References


Chiaradia M (2014) Copper enrichment in arc magmas controlled by overriding plate thickness. Nature Geosci 7:43–46. doi: 10.1038/ngeo2028


Steinberger I, Hinks D, Driesner T, Heinrich CA (2013) Source plutons driving porphyry copper ore formation: combining geomagnetic data, thermal constraints, and chemical mass balance to quantify the magma chamber beneath the Bingham Canyon deposit. Econ Geol 108:605–624. doi: 10.2113/econgeo.108.4.605


Tattitch BC, Chelle-Michou C, Blundy JD, Loucks RR (submitted) Chemical feedbacks during magma degassing control chlorine partitioning and metal extraction in volcanic arcs.


Fertility assessment in porphyry copper exploration – an industry perspective

Christian Ihlenfeld
Anglo American plc, London, United Kingdom

Abstract. Fertility assessment plays an increasingly important role in porphyry Cu exploration programs to support effective area selection and target identification from the province- to the prospect-scale. Lithogeochemical proxies of porphyry Cu fertility have been used relatively widely by industry and have been shown to be reasonably effective in differentiating barren from potentially mineralized systems. With the ambition to develop new fertility proxies that allow us to discriminate more effectively between well-endowed and poorly endowed systems, research and industry have focused in recent years on the chemistry of various accessory minerals, including zircon and apatite. However, our ability to harness the potential wealth of fertility-related information recorded by these minerals is still limited and developing. Industry and academic research need to collaborate to address this important and challenging task.

1 The importance of fertility assessment in exploration

Understanding the fertility (i.e., potential endowment) of mineral systems is of fundamental strategic relevance to mineral exploration. Within the general framework of mineral system analysis (e.g., McCuaig and Hronsky 2014), an assessment of system fertility supports effective area selection and target identification during an exploration program from the province- to the prospect-scale. If fertility assessment is effectively implemented, less money and time will be required to identify and prioritize the most prospective targets within a district, facilitating quicker and better decisions on drill target selection, and thereby increasing the chances of a successful discovery within existing exploration budgets.

Effective implementation of fertility assessment in the exploration process requires two critical aspects:

(a) An understanding of the fundamental controls governing mineral system fertility, and of the extent to which these controls have varied in space and time.

(b) Effective, measurable and mappable proxies that are predictive of system fertility at the respective scale.

The subject of this talk is the latter aspect and focuses on the utility of the currently available geochemical proxies of porphyry Cu fertility. The talk will present and review the results of in-house case studies and published work to highlight the strengths and limitations of these proxies for exploration targeting. Based on this review, outstanding questions and key areas for future research and development will be identified.

2 Available proxies of porphyry copper fertility – strengths and limitations

2.1 Lithogeochemical proxies

Lithogeochemical proxies of porphyry Cu fertility, such as those developed by Loucks (2014), have been used relatively widely by industry and have been shown to be reasonably effective in differentiating barren from potentially mineralized systems. One of the key advantages of these proxies is that the proxy information can be generated routinely, fast and at relatively low cost through commercial laboratories. The lithogeochemical proxies can be used from the regional down to the district scale to identify arc segments, individual igneous complexes within them, and stages in the evolution of long-lived magmatic centers that match the chemical features of copper-ore-forming arc magmas. Detailed lithogeochemical work by the author in the Los Bronces (Chile) and Quellaveco (Peru) districts, for instance, identified and mapped out in both districts the geochemical evolution and development of porphyry Cu fertility of the host batholith and related porphyry intrusions in space and time (over a 15 Myr period), culminating in both cases in the formation of major world-class porphyry Cu deposits.

However, a known limitation of the lithogeochemical proxies of porphyry Cu fertility is that they generally do not provide a clear indication of the quality/endowment of the system and may generate a relatively high rate of false positives. This is illustrated, for instance, by the results of the stochastic modelling by Chiaradia and Caricchi (2017) of the deep magmatic controls on porphyry Cu deposit endowment. While the modelling corroborates the empirically observed association of porphyry Cu deposits with a specific interval of Sr/Y ratios (~100 ± 50) in the magmatic rocks, it also shows that 2/3 of the model simulations within this Sr/Y interval produce systems with <10 Mt Cu (including barren systems). By contrast, only 9%, 4% and 0.2% of simulations within this Sr/Y interval produce giant to super-giant systems containing 30-50 Mt Cu, 70-90 Mt Cu and >90 Mt Cu, respectively.

The likely reason for the inability to effectively discriminate between variably endowed porphyry systems is that the lithogeochemical proxies of porphyry Cu fertility reflect to a large extent only a single (albeit very important) parameter/process (i.e., the development of water-rich magmas during long-term residence and differentiation in lower crustal “hot zones”; Annen et al. 2006), whereas the endowment of porphyry Cu deposits is controlled by a combination of critical factors.
Therefore, lithogeochemical fertility proxies like those developed by Loucks (2014), constrain a necessary, but not sufficient, condition of a system to develop a major porphyry Cu deposit.

### 2.2 Mineral chemistry proxies

With the ambition to develop additional or more comprehensive proxies of porphyry Cu fertility that allow us to effectively and reliably discriminate between well-endowed, poorly endowed and barren systems, research and industry have focused in recent years on the chemistry of accessory and alteration minerals, including zircon, apatite, titanite, magnetite, rutile and chlorite.

Zircon and apatite have received particular attention as they potentially record intrinsic magma characteristics that are widely considered important in the formation of porphyry Cu deposits, such as oxidation state and elevated water content in the case of zircon, and S and Cl contents in the case of apatite. In addition, zircon and apatite persist during weathering and transport in the surface environment, which potentially allows their use as fertility proxies in mechanically dispersed surface sediments (e.g., drainage sediments, till). Other favorable properties of zircon include that it is largely resistant to hydrothermal alteration, can be precisely dated and provides information on its crystallization temperature and the relative degree of magmatic fractionation. Furthermore, zircon morphology and growth zoning as revealed by cathodoluminescence imaging may potentially provide important information on changing conditions during zircon crystallization that may help to distinguish between fertile and barren suites (e.g., Lu et al. 2016; Corfu et al. 2003). Analysis of specific growth zones may also provide evidence of episodic recharge of mafic magmas (Buret et al. 2016), which is considered by some a potential trigger of porphyry formation and source of excess S and metals (e.g., Zajacz and Halter 2009). Like zircon, igneous apatite is also frequently zoned, with S/Cl-rich cores and S/Cl-poor rims observed in some fertile systems that are interpreted to reflect fluid exsolution and degassing (e.g., Bouzari et al. 2017). However, in contrast to zircon, apatite is sensitive to alteration overprint (e.g., Bouzari et al. 2016) and may be present as both igneous and hydrothermal apatite in porphyry systems. The composition of hydrothermal apatite has been shown to reflect the nature of the mineralizing fluid and may potentially record useful fertility information (Loader 2017). Characteristic compositional and luminescence features of altered apatite may be used to recognize the existence and type of hydrothermal alteration in dispersed surface sediments (Bouzari et al. 2016).

However, despite this potential wealth of fertility-related information recorded by zircon and apatite, our ability to harness this information is still limited and developing. For instance, extracting reliable quantitative or even semi-quantitative information on the oxidation state of the magma from the chemistry of zircons has remained elusive so far despite some potentially promising recent progress (Loucks et al., submitted). Furthermore, the effects of co-crystallizing phases on the compositions of zircon and apatite and their potential implications for the assessment of porphyry Cu fertility remain to be fully understood (e.g., Loader et al. 2017).

Anglo American has been conducting several pilot studies in recent years to trial the utility of zircon and apatite mineral chemistry as porphyry fertility indicators. The studies have been conducted in various geological settings, using well-constrained rock and stream sediment samples to get a first-hand understanding of the type and quality of fertility-related information that can be obtained, to develop appropriate workflows and to identify key knowledge gaps and outstanding challenges. Overall, the results of these pilot studies corroborate the potential usefulness of zircon and apatite as porphyry fertility indicators, but also highlight that the ability to effectively and reliably discriminate between well-endowed, poorly-endowed and barren systems remains a challenge, in particular when comparing results between districts. Recognition of fertile signatures in drainage sediments is feasible, but depending on the geological setting and background lithologies effective pre-screening of the zircon and apatite separates prior to LA-ICP-MS and EMP analysis may be required to make the approach time- and cost-effective.

### 3 Concluding remarks

Fertility assessment plays an increasingly important role in porphyry Cu exploration programs to support effective area selection and target identification from the province-down to the prospect-scale. However, despite this importance the currently available lithogeochemical and mineral chemical proxies of porphyry Cu fertility have limitations and generally only discriminate broadly between barren and fertile systems, but do not allow to effectively and reliably discriminate between well- and poorly endowed systems. This is partly due to our incomplete understanding of the fundamental controls that govern the endowment of porphyry Cu systems, but also due to our limited ability to harness the wealth of fertility-related information recorded by the geochemical compositions of rocks and minerals. To address the shortcomings in both aspects, it is necessary to collect a much larger number of integrated datasets for whole rock and multiple mineral indicators in carefully selected, well-characterized samples from porphyry Cu systems and barren analogues that cover the entire endowment spectrum. Industry and academic research need to collaborate on this challenging task.

### Acknowledgements

I would like to thank the session organizers for the invitation to give this presentation and Anglo American for their permission to accept this invitation and to share some of our in-house results and ideas on the topic of porphyry Cu fertility.
References


Zircon-hosted apatite inclusions at La Granja Cu-Mo Porphyry, Peru: Implications for the use of apatite as a probe of magma petrogenesis

Emily Brugge1,2, Jamie J. Wilkinson1,2, Yannick Buret2, Andrew J. Miles3
1Department of Earth Science and Engineering, Imperial College London, UK
2London Centre for Ore Deposits and Exploration, Department of Earth Sciences, Natural History Museum, London, UK
3Department of Geology, University of Leicester, Leicester, UK

Abstract. Apatite is widely used as a petrogenetic indicator mineral. However due to the rapid diffusion of some elements, the degree to which apatite retains original magmatic compositions in porphyry environments is unclear. To investigate this we have analysed fine-grained (< 10 µm) apatite inclusions in zircon using modified electron microprobe (EMP) and laser ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS) methods. The inclusions (Apinscl) are inferred to preserve primary apatite compositions, which can be compared with the composition of apatite from the groundmass of the porphyritic rocks (Apmtrx). We find that Apinscl contain higher concentrations of Cl, S, Sr and lower concentrations of Mg and Mn than Apmtrx. We infer that the groundmass apatite has re-equilibrated with a later fluid phase. These observations have important implications for how apatites in porphyry systems are used to infer crystallisation conditions. We conclude that the majority of apatite crystals in such systems will undergo re-equilibration and therefore do not record primary crystallisation conditions. Instead, apatite compositions reflect the character of porphyry ore-forming fluids and therefore may have utility as an indicator of ore-forming potential. Apatite inclusions in zircons, although less abundant and more challenging to analyse are more representative of magmatic crystallisation conditions.

1 Introduction

Apatite has regularly been used to help constrain the petrogenesis of igneous rocks (Webster and Piccoli 2015), and more recently to discriminate between ore-hosting and unmineralised intrusions (Duan and Jiang 2018). The growing popularity of apatite is due to the large number of trace elements that can be analysed using methods such as LA-ICP-MS. The chemical composition of apatite can be used as a record of its crystallisation environment and has the potential to be used as an exploration tool for both in situ and detrital grains. In a porphyry environment, the halogen and S contents of apatite can be associated with hydrothermal and ore-forming components, and elements such as REE, Sr, Y etc. reflect magmatic processes including co-crystallising accessory phases. However, metasomatised apatite is common in hydrothermally-altered portions of porphyry systems and even where grains appear unaltered, high diffusion rates in apatite (e.g. F-OH-Cl: 8.1x10^-8 m^2/s; Mn: 5.4x10^-7 m^2/s; Cherniak 2010) mean that primary magmatic features, such as zoning, are not well preserved. Apatite hosted in zircon may provide a more robust record of the original composition as the diffusion rates in zircon are considerably lower (Cherniak 2010).

In this study, apatite inclusions in zircon (Apinscl) from the La Granja Cu-Mo porphyry, Peru were analysed. The compositions were then compared to apatite grains within the groundmass (Apmtrx). Previous studies have found apatite inclusions in zircon to mirror the composition of the groundmass apatite in the rock (Jennings et al. 2011; Bruand et al. 2016). Therefore, at La Granja any difference in composition between Apinscl and Apmtrx may be due to re-equilibration of the latter. Based on our findings, we question the extent to which the chemistry of Apmtrx sampled from intrusive rocks belonging to a porphyry system can be used to interpret the magmatic crystallisation conditions. However, our evidence suggests that apatite inclusions in zircon can provide a faithful record of magma petrogenesis.

2 Geological Setting

La Granja Cu-Mo porphyry deposit (-6.35203, -79.127159; Fig. 1) is located in northern Peru within the Western Cordillera. The Miocene deposit is hosted within the Eocene volcanic belt and contains total resources of 4329 MT of ore with an average grade of 0.51% Cu (Rio Tinto annual report 2018).

La Granja comprises two main porphyry complexes, Paja Blanca and Mirador, which lie approximately 1 km apart. Both porphyry complexes are composed of a similar sequence of nested porphyry intrusions and range from ~ 14 – 17.6 Ma (Table 1). Of the lithologies sampled for this study, for each porphyry complex the intermineral dacite porphyry is the oldest, followed by the dacite porphyry and then a late quartz porphyry. The system has been subjected to intense hydrothermal alteration (sericitic and argillic overprinting potassic-propylitic) that is focused in the centre of the deposit (Schwartz 1982).
3 Sample Petrology

3.1 Rock descriptions

Samples of the porphyritic lithologies were collected from drillcore from both Paja Blanca and Mirador. Compositionally the three rock types are very similar. The intermineral dacite porphyry has a crowded texture containing feldspar phenocrysts (50%, < 4 mm), rare quartz eyes (< 5%, 2 mm) with biotite and amphibole within a fine-grained quartz-feldspar-biotite groundmass. This unit does not contain any significant Cu mineralisation. The dacite porphyry is interpreted to be one of the main mineralising intrusions. Its mineralogy and texture is very similar to the intermineral dacite porphyry but it contains abundant disseminated Cu-sulphides that are also occasionally present within the quartz eyes. The late quartz porphyry is texturally distinct from the earlier lithologies and contains abundant quartz eyes (≥ 10%, 2-5 mm), feldspar, biotite and amphibole (< 5%) phenocrysts in a glassy matrix (~50%). The alteration of the samples ranges from propylitic to chlorite-sericite. Pseudomorphs of primary mafic minerals are dominated by chlorite and the alteration of feldspar phenocrysts is a prevalent feature.

3.2 Apatite textures

The textural context of Ap incl and Apmtrx are distinct (Fig. 2). Apatite is one of the most common inclusions in zircon crystals, and are present as small (<10 µm width), prismatic to acicular crystals that cut across the zircon growth zones. Most are located towards the centre of zircon hosts.

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Age (n) [MSWD]</th>
<th>Ap incl (EMPA/LA-ICP-MS)</th>
<th>Ap mtrx (EMPA/LA-ICP-MS)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Paja Blanca</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Late quartz</td>
<td>15.09 ± 0.28 (25) [1.3]</td>
<td>(1/2) (46/25)</td>
<td></td>
</tr>
<tr>
<td>porphyry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dacite porphyry</td>
<td>15.96 ±0.27 (38) [1.5]</td>
<td>(8/5) (31/10)</td>
<td></td>
</tr>
<tr>
<td>Intermineral dacite porphyry</td>
<td>16.81 ± 0.22 (30) [1.4]</td>
<td>(0/2) (24/7)</td>
<td></td>
</tr>
<tr>
<td><strong>Mirador</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Late quartz</td>
<td>14.24 ± 0.26 (24) [1.4]</td>
<td>(3/0) (29/4)</td>
<td></td>
</tr>
<tr>
<td>porphyry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dacite porphyry</td>
<td>15.06 ± 0.26 (41) [1.9]</td>
<td>(2/4) (33/14)</td>
<td></td>
</tr>
<tr>
<td>Intermineral dacite porphyry</td>
<td>17.58 ± 0.27 (35) [1.4]</td>
<td>(7/1) (0/0)</td>
<td></td>
</tr>
</tbody>
</table>

Ap mtrx crystals comprise < 5% of the rock. They are generally euohedral to subhedral in shape and occur as micro-phenocrysts in assemblages predominantly made up of quartz, feldspar and minor biotite. In BSE images the Ap mtrx grains appear relatively unaltered with an even surface brightness; some grains do contain small inclusions of monazite.

4 Analytical methods

Mounted zircon separates (for Ap incl; Fig. 2a) and thin sections (for Ap mtrx; Fig. 2b) were made from each sample. Apatite was imaged using scanning electron microscopy (SEM) and then analysed by electron microprobe (EMP) and laser ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS). U-Pb zircon ages obtained for each unit together with the number of analytical spot data acquired using each of the methods are presented in Table 1. Ap incl data from inherited (xenocrystic) zircons were not used in this study.

Due to the small size of the Ap incl, specially modified EMP and LA-ICP-MS methods were adopted. The accuracy and precision of the results were monitored by repeat analysis of Durango, a natural apatite standard (Young et al. 1969). EMP analyses were carried out in the Imaging and Analysis Centre and LA-ICP-MS analyses in...
the LODE Laboratory at the Natural History Museum, London.

4.1 EMPA method

Major elements were analysed using a Cameca-SX100 electron microprobe with a 20 kV accelerating voltage and 20 nA beam current. A spot size of 1 µm was used. This set up is non-ideal for F analysis in apatites and resulted in artificially raised values in some cases, likely produced as the result of the orientation of a F-rich apatite (Stormer et al. 1993; Fig. 3) but was necessary because of the very small size of the Apincl crystals.

4.2 LA-ICP-MS method

LA-ICP-MS analyses were collected using a New Wave ESI 193 µm excimer laser coupled to an Agilent 7700 quadrupole ICP-MS. The analyses were collected using a spot size of 5 µm, and a fluence of 3.5 Jcm⁻² and a pulse frequency of 10 Hz were used. NIST610 was used as the external standard and Ca was used for internal standardisation.

5 Results

5.1 Major elements: Apincl vs. Apmtrx

The Cl and F concentrations in apatite are inversely correlated as is expected for elements substituting into the same structural site. All apatites are fluorapatite and have an average mole fraction chlorapatite of 0.05. Fluorine contents range from 1.56 wt. % to above the stoichiometric limit. Overall, Apincl display higher average CI and S concentrations (0.85 wt. %, 1.00 wt. % respectively) than Apmtrx (0.26 wt. %, 0.15 wt. %; Fig. 3).

Figure 3. Plot of F against CI for different apatite types (data acquired by EMPA). Crosses indicate Apmtrx and squares indicate Apincl. Lithologies are denoted by colour: intermineral dacite porphyry (purple), dacite porphyry (red), late quartz porphyry (pink). The stoichiometric limit for F substitution in apatite is shown.

5.2 Trace elements: Apincl vs. Apmtrx

REE patterns of Apincl and Apmtrx are broadly similar (Fig. 4) with LREE enrichment and negative Eu anomalies. However, Apincl are characterised by more homogenous patterns and are more LREE-enriched and HREE-depleted than Apmtrx.

Figure 4. Chondrite-normalised REE patterns for apatites from the dacite porphyry. The Apincl (red) are slightly depleted in HREE and enriched in LREE relative to Apmtrx (grey).

The percentage change in elements between the two textural varieties of apatite is illustrated in figure 5. Apatites from the late quartz porphyry tend to display smaller compositional variability in comparison with the other samples.

Figure 5. Percentage change in element concentration between Apincl and Apmtrx. Lithologies are denoted by colour: intermineral dacite porphyry (purple), dacite porphyry (red), late quartz porphyry (pink).

6 Discussion

Previous studies have observed similar compositions for Apincl and Apmtrx in unaltered plutonic rocks (Jennings et al. 2011; Bruand et al. 2016). In this study, the elements that show the greatest variation are those known to have high diffusivity rates in apatite (Cherniak 2010) and are mobile in metasomatized apatite (e.g. CI, LREE etc. Fig. 3; Fig. 4; Webster and Piccoli 2015). Therefore we propose that Apmtrx have equilibrated to a fluid phase.

Based on apatite concentrations from the dacite porphyry, Apincl are assumed to represent an original magmatic endmember composition (Fig.6). Apatites
analysed within veins (Ap_{vein}) are also plotted and are assumed to represent a purely hydrothermal endmember. The compositions of the Ap_{mtrx} correspond to the vein apatites and the graph shows a trend in the apatite composition reflecting the magmatic and magmatic-hydrothermal portions of the porphyry system.

In addition, Ap_{mtrx} and Ap_{incl} analyses from the late quartz porphyry display the smallest differences in composition, with a lot of overlap in the data (Fig. 5). If Ap_{mtrx} chemistry is a result of re-equilibration, this observation can be explained by the late emplacement of the quartz porphyry and its exposure to limited volumes of hydrothermal fluids as indicated by the lack of associated alteration and copper mineralisation.

![Figure 6. Plot of Mn (ppm) against Sr (ppm) from LA-ICP-MS analyses of Ap_{incl} (squares) and Ap_{mtrx} (crosses) from the dacite porphyry. Vein apatite composition, for grains found within the same sample (BSE image inset), are plotted as triangles.](image)

7 Conclusions

At La Granja, apatite in porphyritic rocks found as inclusions in zircon have different compositions to apatite in the groundmass. It is proposed that the difference is a result of the groundmass apatite (Ap_{mtrx}) having re-equilibrated with a fluid. The results of this work have implications for the application of apatite as an indicator mineral; the composition of apparently fresh apatite in porphyry systems may represent later fluid events that may be associated with mineralisation.

The composition of apatite hosted in zircon (Ap_{incl}) is thought to preserve the original magmatic composition more faithfully than Ap_{mtrx} due to the protective properties of the zircon host. Future work will build on this idea, Ap_{incl} from porphyry rocks at La Granja will be compared to Ap_{incl} from older, barren Eocene igneous rocks from the area in order to compare characteristics between porphyry forming, and non-porphyry forming melts.

Acknowledgements

This PhD project is funded by a NERC Industrial Case studentship award (NE/N007883/1) to JJW, with additional funding from Rio Tinto. We thank Paul Agnew at Rio Tinto for his support of this research project and the Rio Tinto team at La Granja, Peru for their help in the collection of the samples used in this study.

References


Cherniak DJ (2010) Diffusion in accessory minerals: zircon, titanite, apatite, monazite and xenotime. Reviews in Mineralogy and Geochemistry 77:627-869

Dua DF, Jiang SY (2018) Using apatite to discriminate synchronous ore-associated and barren granitoid rocks: a case study from the Edong metallogenic district, South China. Lithos 369-380


Using PGE geochemistry to assess magma fertility in the Polo Sur and Penacho Blanco porphyry copper deposits, Centinela District, Northern Chile

Carlos I. Carrasco-Godoy and Ian H. Campbell
The Australian National University

Abstract. The Centinela District is host to several mineralized porphyries, including both Cu-only and Cu-Au deposits. This study focuses on the known Polo Sur and Penacho Blanco porphyry Cu±Mo deposits as cases of study to assess their Cu-Au fertility.

PGE are sensitive indicators of sulphide saturation in silicate melts due to their strong partitioning into sulphide melts. They also have relatively low mobility in hydrothermal fluids, minimizing any effects of addition during hydrothermal alteration. If a parent magma reaches sulphide saturation early in its history, an immiscible sulfide melt will extract chalcophile metals trapping them at depth, potentially preventing them from entering the volatile ore-forming phase. In contrast, if sulphide saturation occurs close to the time of volatile saturation, or does not occur, then metals will be available to enter the fluid phase to form a deposit.

Thirty igneous rock samples from both deposits were analysed for major and trace elements. A subset of these samples were analysed to determine their PGE concentrations. Preliminary results suggest that sulphide saturation may occur before the MgO content of magmas at Penacho Blanco fell below 3.5 wt.% but the timing of sulphide saturation, if it occurred at all, at Polo Sur is unclear.

1 Introduction

Copper is one of the most widely used metals in our society and it is essential in electronics, vehicles, telecommunications, electrical power generation and distribution systems, industrial and domestic piping, chemicals, currency and general infrastructure (Mudd and Jowitt 2018). The main source of this metal is porphyry copper deposits which provide nearly three-quarters of the world’s copper and a fifth of its gold (Mudd and Jowitt 2018). The main source of this metal is porphyry copper deposits which provide nearly three-quarters of the world’s copper and a fifth of its gold (Mudd and Jowitt 2018). The main source of this metal is porphyry copper deposits which provide nearly three-quarters of the world’s copper and a fifth of its gold (Mudd and Jowitt 2018).

Porphyry ore deposits are related to igneous rocks, usually of dioritic to granitic composition, that form in magmatic belts above subduction zones (Richards 2003; Seedorff et al. 2005; Sillitoe 2010; Audétat and Simon 2012; Wilkinson 2013). The magmas produced in this setting are usually of basaltic composition, hydrated and oxidized, and ascend until they reach the base of the crust where they stagnate due to the contrast of density (Richards 2003). Here, they evolve to more felsic compositions that are able to ascend to upper crustal levels where a decrease in temperature and pressure can lead to the exsolution of a volatile phase (Wilkinson 2013, and references therein). These fluids can transport metals and have the potential to develop ore systems, known as porphyry copper deposits. However, not all porphyry systems contain economic concentrations of metals, and ‘barren’ systems share many features with fertile ones. Although there is an understanding of the general processes that can lead to a mineralized system, the factors that control the fertility of porphyry systems remain unclear (Wilkinson 2013, and references therein).

The aim of this project is to test the hypothesis that the timing of sulphide saturation, relative to volatile saturation, is an important factor controlling the type (Cu or Cu-Au) and fertility of porphyry systems from the Centinela District, Northern Chile. If a parent magma reaches sulphide saturation before volatile saturation, an immiscible sulfide melt will form, which will extract chalcophile metals, such as Cu and Au, and may trap them at depth so that they are unable to enter the volatile ore-forming phase (Fig. 1A), potentially resulting in a barren system. In contrast, if volatile saturation occurs before sulphide saturation, if the fraction of immiscible sulfide to form is small, if the time difference between these events is short, or if does not happen, most of the metals will remain in the melt and be available to enter the fluid phase and form an economic Cu or Cu-Au deposit (Fig. 1B). To address this aim, two porphyries from the Centinela District were studied, Penacho Blanco and Polo Sur.

Recent advances in platinum group element (PGE) analysis, developed at the Research School of Earth Sciences (RSES) at the Australian National University (ANU), are allowing analysis of PGE at ultra-low concentrations (Park et al. 2012a). Therefore, it is now possible to study rocks with low abundance of these elements, such as felsic suites, including the rock types associated with porphyry copper deposits. The PGE have been demonstrated to be sensitive indicators of sulfide saturation due to their high partition coefficients into sulfide melts (Mungall and Brenan, 2014). Furthermore, they are substantially less mobile in hydrothermal fluids than Cu and Au (Park et al., 2016) so are less likely to be impacted by post-magmatic hydrothermal addition.

Recent studies used PGE geochemistry to establish the timing of sulfide saturation in the El Abra porphyry Cu deposit in Northern Chile (Cocker et al. 2015) and in the
Cu-Au deposits of the Northparkeres region, New South Wales, Australia (Hao et al. 2017). The latter work also included barren suites from the same region allowing the PGE geochemistry of barren rocks to be contrasted with the mineralized bodies. The results suggest that sulfide saturation occurred at earlier stages of magmatic differentiation for the non-mineralized suites than in the Cu-Au porphyries, where sulfide saturation occurred slightly before volatile saturation. Moreover, the results from the El Abra porphyry copper system showed that sulfide saturation occurred earlier than at Northparkeres, which is consistent with the former being a Cu-only (gold removed early by limited sulfide saturation) and the latter being a Cu-Au deposit.

2 Geological Background

The Centinela District, located in northern Chile, is part of the middle Eocene to early Oligocene metallogenetic belt which contains a number of renowned deposits like Chuquicamata and La Escondida (Sillitoe and Perelló 2005). The Centinela District forms a NE-trending block of approximately 40 km length and 25 km width, limited by the Coastal Cordillera to the west and the Domeyko Cordillera to the east. It is associated with the northern tip of the Sierra de Varas Fault, part of the Domeyko Fault System which is related to most of the mineralization in this belt (Perelló et al. 2010; Mpodozis and Cornejo 2012).

The district is host to at least seven identified mineralized porphyries, including both Cu-only and Cu-Au deposits, and has accounted for nearly 24.8 Mt of refined copper by 2017 (Antofagasta Minerals plc, 2017). Encuentro (41 Ma) and Esperanza (42 Ma) are currently being mined, together with exotic copper deposits at Tesoro and Mirador (Fig. 2). These features make the district a perfect natural laboratory to test whether the timing of sulfide saturation relative to volatile saturation affects the nature of the mineralization (i.e. Cu or Cu+Au).

The Penacho Blanco (formerly Centinela) and Polo Sur deposits account for the 25% of the resources known in the district, with 1.25 Mt contained Cu in the former and 5.14 Mt in the latter (Perelló et al. 2010; Antofagasta Minerals plc 2017). These are the oldest deposits in the district with dates between 45-44 and 42-41 Ma, respectively, and are classified as Cu-Mo porphyries (Perelló et al. 2010; Mpodozis and Cornejo 2012).

Penacho Blanco comprises subvertical cylindrical bodies of granodioritic composition hosted in volcanic rocks and a pre-mineralization diorite. Its alteration pattern is concentric with a central potassic zone overprinted by sericitic alteration. The main hypogene mineralization is dominated by chalcopyrite with an important and well-developed blanket of secondary sulfides that include chalcocite and covellite. The oxidation zone is not well developed and marginal (Perelló et al. 2010).

The Polo Sur porphyries are irregular to cylindrical bodies of dacitic composition emplaced in Paleocene to early Eocene volcanic rocks. Its alteration zonation is concentric with a potassic core overprinted by sericitic
alteration that grades to propylitic alteration laterally and it is capped by an advanced argillic lithocap. The sulfide mineralization is mainly chalcopyrite with minor bornite and, in contrast to Penacho Blanco, the oxidation zone is well developed (Perelló et al. 2010).

3 Samples and Methods

A representative group of samples from the deposits were selected according to two main criteria: i) unmineralized samples with a low intensity of alteration were preferred; ii) to encompass the full compositional range of the igneous rocks. Fifteen samples from Penacho Blanco and thirteen from Polo Sur ranging from diorites to dacite porphyries were studied. Three samples of rhyodacite porphyry from the TYC (Telégrafo and Caracoles, Fig. 2) area, which correspond to the youngest porphries (39 Ma) in the district, were included to extend the temporal range.

Samples were cleaned of visible veinlets and ground in an in-house hardened case soft iron mill until grit-free. Major elements were determined at Intertek Genalysis in Perth, Australia, by Li-borate fusion and analysis by XRF. Trace elements were analyzed by LA-ICP-MS in fused glass beads using a Lambda Physic Complex 110 excimer laser coupled with an ANU-designed HelEx ablation cell and an Agilent 7700x ICP-MS.

Twenty-three samples were selected based on composition to span the range from the most mafic member (highest MgO content) to the most felsic (lowest MgO). These were analyzed for PGE using the isotopic dilution, Ni-sulfide fire assay method described by Park et al. (2012). Concentrations of monoisotopic Rh and Au were calculated by the method described by Meisel et al. (2003) and Park et al. (2012b), using the ratio between $^{103}$Rh and $^{106}$Pd and $^{197}$Au and $^{194}$Pt, respectively, assuming that the loss of each element was similar during the analytical procedure. Eighteen duplicate samples were analyzed to evaluate the possible impact of PGE heterogeneity in the samples.

4 Results and discussions

The results from major and trace elements indicate that the magmas from Polo Sur and Penacho Blanco are typical calc-alkaline series with a subduction zone signature of Nb depletion and Pb enrichment.

The rare earth element patterns, normalized to chondrite are spoon-shaped, with an enrichment of LREE and depleted in MREE. The europium anomaly varies from slightly positive to slightly negative. The rocks from both deposits present a sub-adakite to adakite-like signature with high values of Sr/Y and La/Yb, especially in the more felsic samples. This signature has been proposed to result from a high water content of the magma (>2%) that suppresses plagioclase crystallization in early differentiation stages and promotes fractional crystallization dominated by hornblende (Richards and Kerrich 2007, and references therein).

Preliminary results show that the MgO content varies between 0.6 to 3.5 wt. % with one high value at 5.5 wt.% and that Pt and Pd vary from 0.01 to 1.85 and 0.04 to 3.27 ppb, respectively. The results from duplicates yield values that lie close to the corresponding original values (Fig. 3).

Pd is the most appropriate element to identify the onset of sulfide saturation because it accumulates in the melt up to sulfide saturation and then drops abruptly following saturation (Park et al. 2013). There is no obvious trend in the Polo Sur data. Thus, it is not possible to identify a sulfide saturation signature in this deposit (Fig. 3A). There is a weak trend of decreasing Pd with decreasing MgO for the Penacho Blanco samples, however, it may be possible to assume that sulfide saturation happened before 3.5 wt.% MgO (Fig. 3B). The trend and values are similar to those observed in the Cu-only El Abra porphyry deposit (Fig. 3B; Cocker et al. 2015).

Although the samples span dioritic to rhyodacitic compositions, it was not possible to establish evidence for a clear onset of sulfide saturation for these deposits. However, the geochemistry still reflects the nature of the processes involved in the formation of porphyry copper
deposits. According to the chalcophile element fertility diagram (Fig. 4) of Park et al. (2018) they are classified as mainly porphyry Cu-Only deposits. A group of Polo Sur samples fall in the Cu-Au area which may be related to small amounts of gold (0.06 g/t) reported in sulfides (Antofagasta Minerals plc 2017).

Finally, the study of the PGE geochemistry of felsic rocks gives us a proxy to better understand how sulfides behave in magmatic systems related to porphyry copper deposits which frequently are overprinted by hydrothermal alteration.

**Figure 4.** Chalcophile element discriminator from Park et al. (2018). Most of the samples fall into the Cu-Only field. Open circles indicate duplicate analyses.

**Acknowledgements**

This work was funded by the ARC Discovery Project DP17010340 to Ian Campbell and Andrew Berry. CCG acknowledges Antofagasta Minerals for their support collecting samples, specially Pepe Perello, Constantino Mpodozis, Pedro Apablaza and Leonardo Torres. Special thanks to Paula Cornejo and Jaime Osorio for their support and discussions at the beginning of this project. This program was funded by CONICYT PFCHA/MAGISTER BECAS CHILE/2017 – 73180502.

**References**


Titanite petrology and chemistry from the Strontian Igneous Complex, Scotland

Tom Matthews¹,²*, Jamie Wilkinson ¹,² and Matthew Loader¹,²
¹Department of Earth Sciences and Engineering, Imperial College London, UK
²LODE, Department of Earth Sciences, Natural History Museum, UK

Abstract. Whole rock Sr/Y and mineral indicators are commonly employed to assess porphyry Cu fertility. Despite the favourable characteristics of titanite, its utility as an indicator of porphyry Cu fertility has not been evaluated. Magmas of the Strontian Igneous Complex exhibit a fertile Sr/Y signature but are not associated with a known porphyry. Titanite petrology and trace element chemistry from the Strontian Igneous Complex suggests that titanite may track petrogenetic processes that influence porphyry Cu fertility. Furthermore, titanite crystallisation may affect the utility of other mineral indicators in assessing porphyry Cu fertility.

1 Introduction

The ability of accessory minerals to sequester large quantities of trace elements from a melt is crucial to understanding melt evolution. Accessory minerals can be used for geochronology and can also indicate intensive parameters such as temperature and fO₂. In a world where ore deposits are becoming increasingly scarce, utilisation of accessory phases to better understand the genesis of magmatic-related ore deposits is of particular relevance. Magmas associated with porphyry Cu deposits (PCD’s) are typically hydrous, oxidised and exhibit anomalously high Sr/Y. However, the factors that control porphyry fertility are not well constrained.

Titanite (CaTiSiO₅) can incorporate a variety of trace elements (e.g. REE, HFSE and LILE), demonstrating excellent preservation of primary magmatic textures that can be identified using backscattered electrons (BSE). Titanite has been employed as a geochronometer (Frost et al. 2000), as a thermometer (Hayden et al. 2008) and has been suggested to track magma mixing (Piccoli et al. 2000). Despite this, the utility of titanite as a fertility indicator has not yet been explored.

The Strontian Igneous Complex (SIC) displays a ‘fertile’ Sr/Y signature with no known associated PCD. Hence, the SIC either signifies an eroded PCD, or a fertile magma that failed to form a PCD. The SIC also represents a rare opportunity to study the genesis of a fertile igneous rock that has experienced relatively minor alteration. Textural and trace element data of titanite grains from the SIC are presented hereafter.

2 Strontian Igneous Complex

The Strontian Igneous Complex (SIC) is a ~25km long calc-alkaline pluton that was emplaced into Moine metasediments of the Northern Highlands Terrane, during the late Caledonian orogeny (Atherton & Ghani 2002; Bruand et al. 2014; Fig. 1). The SIC is one of several plutons of the Argyll and Northern Highlands suite, that exhibit anomalous Sr and Ba whole rock concentrations, which have previously been attributed to assimilation of carbonate rich sediments (Fowler et al. 2008).

The SIC exhibits normal zonation comprising zones of: (outer to inner) quartz diorite, quartz monzonite and biotite granite. The SIC is crosscut by diorite dykes, that are in turn crosscut by felsite dykes (Birt 2019). Mafic enclaves are common within the SIC, on the cm to >100 metre scale. U-Pb dating of zircon and titanite from the quartz monzonite yield ages of 425 ± 3Ma and 423 ± 3Ma respectively (Rogers & Dunning 1991).

3 Methods

Samples were collected from the main intrusive units of the SIC, and their locations are shown by Fig. 1. These
were subsequently prepared into thin sections, prior to analysis at the Natural History Museum, London. 10 thin sections were selected for analysis (01, 03, 07, 09, 10, 13, 15, 16, 19, 21) based on the size and abundance of titanite.

Titanites were imaged and analysed using a Zeiss EVO SEM, with a beam current of 3 nA and an accelerating voltage of 20kV. Backscatter electron (BSE) imaging was employed to reveal titanite zonation and major element data was collected by energy dispersive spectroscopy (EDS). EDS was also employed to identify mineral inclusions in titanite grains. Trace element analysis was conducted using an ESI New Wave Research 193nm excimer laser coupled to an Agilent 7700cs quadrupole ICP-MS. Ca, as determined by quantitative SEM analysis, was employed as the internal standard and NIST-610, GSD-1G and BCR-2G glasses were used as primary, secondary and tertiary external standards respectively.

The laser was operated with a 10 Hz frequency, a fluence of 3.5 J cm\(^{-2}\) and a spot size of 30 \(\mu m\).

4 Results

4.1 General characteristics

Titanite is present in all lithologies except the felsite, which has therefore been excluded from this study. However, within the biotite granite titanite grains are only present in sample 13, which is close to the contact with the quartz monzonite. Titanite exhibits modal abundances of 1-4%, with crystals ranging from 0.1-1.5mm in length. BSE images reveal that zoning in titanite is ubiquitous, and individual grains display one or several of the following types: sector, normal, oscillatory and patchy (Fig. 2).

Figure 2. SEM-BSE images of titanites from the SIC. (a) Euhedral titanite showing normal and sector zoning. (b) Subhedral titanite showing patchy zoning and partial dissolution. The core contains bornite, apatite and Fe-Ti oxide inclusions. Apatites are included in both core and rim. (c) Interstitial sector zoned titanite containing pyrite, apatite, chlorite and hornblende inclusions. (d) Interstitial reverse zoned titanite containing pyrite, chalcopyrite, ilmenite and apatite inclusions.
4.2 Lithological variation

A range of crystal habits and phase relationships are observed within the same rock, and between lithologies. In the quartz monzonite and biotite granite, titanite is commonly euhedral, occurring as inclusions within mafic minerals e.g. hornblende and biotite (Fig. 2a). In the quartz diorite, diorite and mafic enclaves, titanite is typically anhedral and included in feldspars (Fig. 2b-d). Apatite inclusions are present in most grains, whilst zircon inclusions are less common. Devitrified melt inclusions are also common, comprising quartz + feldspar.

Sulphides (pyrite, chalcopyrite and bornite) are included within grains from the quartz diorite, diorite and mafic enclaves, but are absent from the quartz monzonite and biotite granite. Zones that are rich in unmixed Fe-Ti oxide inclusions are present in all lithologies and are often associated with patchy zoning, partial dissolution or sulphide inclusions. These Fe-Ti oxide inclusion zones are found exclusively in grain cores in all lithologies, except the biotite granite, where they are also observed in rims.

4.3 Titanite chemistry

Trace element concentrations of titanite grains from all lithologies, show core to rim variations (Fig. 3). All grains exhibit marked reductions in the concentrations of HREE and LREE, with a broadly consistent ratio of ~1:1. Core to rim variation in Sr/Y is dominated by Y, which is highly variable (250 – 2500 ppm) in comparison to Sr (60 – 90 ppm). Whilst Sr typically shows minimal variation from core to rim, Y is strongly depleted.

5 Discussion

Sulphide and Fe-Ti oxide inclusions are interpreted to be of magmatic origin, due to their presence only in particular zones. The presence of Fe-Ti oxide inclusion zones has previously been suggested to indicate magma mixing events. Piccoli et al. (2000) suggested that the introduction of hotter, more primitive magmas with a lower fO₂ could stabilise ilmenite over titanite and result in the partial resorption of titanite. If Fe-Ti oxide inclusion zones represent magma mixing events, then their omnipresence would suggest that magma mixing was widespread in the SIC. This is supported by the common occurrence of mingling textures between felsic magmas and mafic enclaves observed in the field. The confinement of these Fe-Ti oxide inclusion zones to grain cores (excluding the biotite granite) suggests that magma mixing typically occurred early during titanite crystallisation.

Where sulphide inclusions are found associated with Fe-Ti oxide inclusion zones, then sulphide saturation may be triggered by magma mixing. Nevertheless, the occurrence of sulphide inclusions within titanite indicates that titanite crystallised during magmatic sulphide saturation.

Titanite rims (relative to cores) are strongly depleted in REE and Y, representing systematic depletion in the residual melt. This depletion likely results from the crystallisation of REE-compatible phases such as titanite itself, or hornblende. Hence, any phases that crystallise following titanite saturation may also be strongly depleted in these components. This has important implications where REE and Y concentrations are utilised in mineral fertility indicators (e.g. zircon).

Our data suggests that titanite can be utilised to assess the importance of magma mixing and sulphide saturation in affecting porphyry Cu fertility. Furthermore, the saturation of titanite has the ability to strongly influence mineral indicators of porphyry fertility.

Figure 3. Core to rim trace element chemistry of titanite grains. Each colour represents core to rim variation in an individual titanite grain. (a) Total Heavy REE vs Total Light REE (b) Sr vs Y.

Acknowledgements

This study forms part of the lead author’s PhD project, that is in part funded by Rio Tinto Exploration. Miranda Birt is thanked for the provision of samples. Yannick Buret (LA-ICP-MS), Tobias Salge (SEM) and John Spratt (SEM) are thanked for their assistance during the analyses.

References


Magma fertility related to porphyry copper mineralization potential in Sangilo, Baguio Mineral District, Philippines

Jillian Aira Gabo-Ratio, Karl D. Jabagat
University of the Philippines
Naoto Kugizaki, Kotaro Yonezu
Kyushu University, Japan
Graciano P. Yumul, Jr.
Itogon Suyoc Resources Inc. - Apex Mining Company Inc., Philippines

Abstract. The Sangilo epithermal deposit is located in the Baguio Mineral District (BMD) in northern Luzon, Philippines. Epithermal mineralization in Sangilo is hosted by the Early Miocene dark-colored hornblende quartz diorite (HQD), Middle Miocene quartz diorite and Pliocene porphyritic andesite dikes. Recent exploration activities in the area reveal manifestations of an older porphyry copper mineralization hosted by the hornblende quartz diorite. The mineral chemistry of magmatic plagioclase and amphibole crystals in the Sangilo host rocks were thus investigated in order to relate magmatic conditions with porphyry copper mineralization potential. The physico-chemical calculations from amphibole mineral chemistry show that the andesite has the highest calculated ranges of pressure, temperature and H2O% in melt. These andesite dikes appear to be mantle-derived melts which triggered mineralization in the BMD during the Pliocene-Pleistocene. The hornblende quartz diorite on the other hand, which also reflected high water content and oxygen fugacity, might correspond to an earlier episode of mineralization (Early-Middle Miocene) which is responsible for the observed porphyry copper mineralization signature in the area.

1 Introduction

The increasing difficulty in discovering hydrothermal deposits led to the formulation of various exploration tools apart from conventional geophysical and geochemical methods. One of the challenges being addressed in recent works is assessing the fertility of a system by looking at the mineral chemistry of igneous source rocks as formational triggers. Fossil specimens of magmatic systems represented by igneous intrusive complexes offer a window into understanding the evolution of magmatic processes. These various processes are not only spatially and temporally, but also genetically critical to the onset of associated porphyry copper and epithermal gold mineralization (Sillitoe, 2010; Walker et al., 2013). Physico-chemical conditions (e.g. pressure, temperature, oxygen fugacity, H2O percentage in melt) prevailing in the magmas during crystallization significantly govern the metallogenesis of hydrothermal systems. These conditions were inferred to vary on mineralized and barren magmatic bodies (Mason, 1978; Cao et al., 2018).

This study focuses on the Baguio Mineral District, which is a world-class district in terms of porphyry copper and epithermal mineralization. We evaluate the plutonic host rocks in Sangilo, a known epithermal gold deposit but with manifestations of porphyry copper mineralization recently observed in the underground mine workings. This study therefore looks into the magmatic and physico-chemical conditions and porphyry copper mineralization potential in Sangilo by investigating the mineral chemistry of plagioclase and amphibole crystals of the hornblende quartz diorite, tonalite and andesite host rocks.

2 Geologic Outline

2.1 Regional Tectonic Setting

Luzon island belongs to the Philippine Mobile Belt, which is an amalgamation of magmatic arcs, ophiolitic complexes, metamorphic terranes, sedimentary basins and continental fragments (Yumul et al. 2008). The island is bounded by oppositely dipping subduction zones: the east dipping Manila Trench to the west and the west dipping East Luzon Trough-Philippine Trench to the east (Figure 1). Excess stress generated by the oblique subduction along the Philippine Trench resulted in the formation of the left-lateral strike-slip Philippine Fault Zone (PFZ) transecting the island in a northwest-southeast trend (Aurelio 2000). Major and minor splayes of the PFZ played a crucial role in the evolution of hydrothermal systems in north Luzon and the formation of metalliferous deposits (Bellon and Yumul 2000; Yumul et al. 2008).

2.2 Sangilo epithermal deposit

The Sangilo deposit is located in the Baguio Mineral District (BMD), which forms a 25-km-long and 7-km-wide north-trending belt located in the central portion of Luzon island. The BMD is host to world-class porphyry copper, epithermal gold and skarn deposits that are mostly Pliocene in age (Waters et al. 2011). The basement of the district consists of ophiolitic and metamorphic complexes overlain by Late Cretaceous to Quaternary volcanic arcs (Aurelio 2000; Hollings et al. 2011). The BMD also hosts the Sangilo epithermal deposit in Itogon, Benguet that contain quartz-carbonate veins.
linked to the N-W to E-W trending veins of Acupan to its west. Epithermal mineralization in Sangilo is hosted by three rock units: the Early Miocene dark-colored hornblende quartz diorite (HQD) of the Central Cordillera Diorite Complex, Middle Miocene quartz diorites of the Itogon Quartz Diorite and minor Pliocene porphyritic andesite dikes (Figure 1). Mineralized structural fabrics in Sangilo have three major orientations: NE, NNE and due west. These structures are related to the zone of dilation produced by the northerly splays of the Philippine Fault zone. These vein-filled structures cut the igneous host rocks suggesting that the epithermal veins are not genetically linked with them. In addition, recent underground mapping revealed the presence of stockwork veinlets and disseminated chalcopyrite and bornite, which was also reported in the adjacent Acupan porphyry-type mineralization by Waters et al. (2011). This porphyry-type mineralization is only observed in the hornblende quartz diorite

![Geologic setting of the Sangilo epithermal deposit. The figure on the left shows Luzon Island and its tectonic features. The red star shows the location of the study area. The right figure shows the geologic map of the Sangilo epithermal deposit, including the major faults and veins that host the epithermal mineralization.](image)

Figure 1. Geologic setting of the Sangilo epithermal deposit. The figure on the left shows Luzon Island and its tectonic features. The red star shows the location of the study area. The right figure shows the geologic map of the Sangilo epithermal deposit, including the major faults and veins that host the epithermal mineralization.

3 Petrography and Mineral Chemistry

The hornblende quartz diorite (HQD), which hosts most of the epithermal veins, is medium to coarse grained, holocrystalline, composed mainly of euhedral to subhedral plagioclase feldspar, hornblende and anhedral quartz together with accessory magnetite, apatite and zircon. Minor chlorite and epidote alteration is also evident. The relatively younger quartz diorite unit contains less hornblende and a higher percentage of quartz compared to the HQD. Plagioclase feldspars in the quartz diorite exhibits distinct zoning compared to the unzoned plagioclase in the hornblende quartz diorite. Porphyritic andesite dikes which post-dates both the aforementioned host units are composed of euhedral to subhedral plagioclase feldspars and subhedral amphiboles as phenocrysts set in a groundmass of plagioclase microlaths. Accessory magnetite minerals are also present in this unit. Minor sericite and calcite alteration is apparent.

Selected polished sections were analyzed by a JEOL-JXA 8230 electron probe microanalyzer at the National Institute of Geological Sciences, University of the Philippines. Amphiboles in the HQD are ferrohornblende in composition whereas amphiboles in the quartz diorite vary from magnesiohornblende to actinolite. Amphiboles from the basaltic andesite were classified as pargasite, which is a higher temperature and pressure variety of amphibole. Plagioclase in both the HQD and tonalite is dominated by zoned andesine with minor labradorite while plagioclase from the basaltic andesite is anorthite in composition.

4 Discussion

Physico-chemical calculations from amphibole mineral chemistry calculated from Ridolfi et al. (2010) shows that compared with the quartz diorite, the HQD has relatively higher calculated ranges of pressure (HQD: 100-142 MPa; quartz diorite: 88-96 Mpa; oest: 11-14 Mpa) (Figure 2A), temperature (HQD: 771-865°C; tonalite: 760-812°C; oest: 22°C) and H2O% in melt (HQD: 5.1-6.4 wt.%; quartz diorite: 4.2-5.4 wt.%; oest: 0.4 wt%) (Figure 2B).

The andesite, which is the youngest unit, has the highest values of pressure (300-350 MPa), temperature (957-968°C) and has a relatively high H2O% in melt (4.6-5.2 wt%).

The crystallization depth was also calculated by the method of Ridolfi et al. (2010) using a crustal density value of 2890 kg/m³. The calculated depths coincide with the calculated pressures and temperatures (Table 1). The hornblende diorite revealed depths of crystallization of 3.8-4.9 km. The quartz diorite reflected shallower crystallization depths ranging from 1.9-3.1 km. Amphiboles in the andesite reflected the deepest depths of crystallization ranging from 10.8-12.5 km. Oxygen fugacity computations showed high fO2, with the HQD and andesite plotting above the NNO slope and the quartz diorite straddling the NNO+2 slope (oest: 0.4 logfO2) (Figure 2C).

Varying magmatic sources were identified for the host rocks using the diagram of Jiang and An (1984) utilizing TiO2 and Al2O3 wt% in amphiboles (Figure 2D). The basaltic andesites were sourced from mantle-derived melts that underwent minimum crustal contamination. The hornblende diorite plotted in the mixed crust and mantle derived melt suggesting a hybrid origin. Lastly, the quartz diorites both plotted in the hybrid and crust source suggesting higher degrees of crustal contamination compared to the HQD.

Recent studies like Wilkinson (2013) and Richards (2011) emphasized the role of factors such as high magmatic water content, relatively high oxidation states and high sulfur content in enhancing the fertility of arc magmas in generating hydrothermal ore deposits.

Based on the calculated physico-chemical conditions, the Middle Miocene quartz diorite is considered as barren. The barren nature of the intrusive can be explained by its crust-derived affinity suggesting minimum interaction with mafic melts during its formation which could have supplied ample amount of sulfur and water. This explanation is supported by the relatively lower magmatic water content reflected in the amphibole.
chemistry.

The basaltic andesite dikes in Sangilo correspond to mafic-derived melts which interacted with silicic crustal melts during the Plio-Pleistocene resulting in the ubiquitous mineralization in the Baguio Mineral District. Addition of a more primitive melt increased sulfur content in the resulting hybrid magma. Aside from increasing the contained sulfur, formation of amphibole at depth suggests that the basaltic andesite has high initial water content which could also enhance fertile conditions in the resulting magma.

Lastly, the Early Miocene HQD is considered to be responsible for the older porphyry copper signature present in the area. Aside from field evidence, the mix crust-mantle signature of the HQD suggests interaction with primitive melt which is favorable for hydrothermal mineralization. This assumption is supported by high magmatic water content and oxygen fugacity calculated for the host rock.

![Figure 2. The pressure (A), temperature (B) and oxygen fugacity (C) of amphiboles based on diagrams by Ridolfi et al. (2010). (D) Source composition diagram of Jiang and An (1984)](image-url)

5 Summary and Conclusions

This study investigated the mineral chemistry of the three intrusive rock units in Sangilo to look at the physico-chemical conditions during magmatism and assess their potential for porphyry copper mineralization. The mineral chemistry data indicates that the basaltic andesites has the highest calculated ranges of pressure, temperature and relatively high initial H₂O wt% in melt. These mantle-derived melts triggered mineralization in the BMD during the Pliocene-Pleistocene. The hornblende quartz diorite which also reflected high water content and oxygen fugacity, might correspond to an earlier episode of mineralization (Early-Middle Miocene) responsible for the observed porphyry copper mineralization signature in the area. These findings provide new insights into the link between physico-chemical conditions and fertility of intrusive bodies in the Baguio Mineral District.

Acknowledgements

The authors acknowledge the Itogon-Suyoc Resources Incorporated (ISRI), the Rushurgent Working Group Laboratory of the National Institute of Geological Sciences, University of the Philippines and the Economic Geology Laboratory of the Department of Earth Resources Engineering, Kyushu University for the logistical support and laboratory analyses. This study is partially funded by the University of the Philippines Office of the Vice President for Academic Affairs Balik-PhD Grant to the first author and by the Japan Society for the Promotion of Science Asia Africa Science Platform to the fourth author.

References


Role of breccias in porphyry copper formation

Richard H. Sillitoe
Independent consultant, London, England

Abstract. Three volumetrically important, cross-cutting breccia types can occur in association with porphyry copper ± molybdenum ± gold deposits: magmatic-hydrothermal, phreatomagmatic (diatreme), and phreatic, each reliant on a specific aqueous fluid-induced process and characteristic of a particular position in and evolutionary stage of deposit development. With few exceptions, these various hydrothermal breccias were generated during and after, rather than before, porphyry copper and overlying high-sulfidation epithermal gold ± silver deposit formation. They are located near the apices of and above their causative porphyry intrusions. Consequently, even where breccia bodies contain juvenile igneous material, they could not have controlled ascent of the magmas that gave rise to the main mineralized intrusions. The syn-mineral magmatic-hydrothermal breccias are blind, having failed to approach the paleosurface, so could not have been connected in any way to subaerial volcanism during porphyry copper formation. Indeed, available evidence requires that porphyry copper deposits are normally generated beneath non-brecciated roof rocks, which are generally much older than the deposits themselves. Any direct connection between porphyry copper systems and volcanic paleosurfaces is usually via phreatomagmatic diatremes and generally a late- to post-mineral event; however, in rare cases, porphyry copper stocks intruded early, pre-mineral diatremes.

1 Introduction

Hydrothermal breccias – fragmental rocks whose genesis involved hot aqueous fluids – are common and prominent features of porphyry copper ± molybdenum ± gold deposits worldwide. They typically constitute <10 volume % of the porphyry copper ore but, exceptionally, can approach 50% (e.g., Río Blanco-Los Bronces, Chile; Toro et al. 2012); however, breccias may be entirely absent (e.g., Chuquicamata, Chile; Rivera et al. 2012). Some breccias are economically important because they constitute the highest-grade parts of porphyry copper or overlying epithermal precious-metal deposits and, where suitably located, can be extracted early in mine lives to accelerate capital payback. The characteristics and relative timing of the principal breccia types in porphyry copper systems and the roles that they can and cannot play in deposit formation are the subjects of this brief review.

2 Breccia types

Three end-member breccia types can be volumetrically important in porphyry copper systems (Sillitoe 1985): magmatic-hydrothermal breccias, in close association with porphyry intrusions; phreatomagmatic (diatreme) breccias, rooted in intrusions but spanning the full vertical extents of the porphyry systems, including their lithocaps; and phreatic breccias, largely confined to the lithocap environment (Fig. 1).

1.5 km

Phreatomagmatic breccia

Magmatic-hydrothermal breccia

Phreatic breccia

Lithocap

Early + inter-mineral porphyries

Figure 1. Cartoon to illustrate typical positions and relative timing of magmatic-hydrothermal, phreatomagmatic (diatreme), and phreatic breccias in porphyry copper systems

2.1 Magmatic-hydrothermal breccias

Magmatic-hydrothermal breccias, the products of over-pressured aqueous fluids following their exsolution from magma, are generally emplaced as irregular to pipe-like bodies during porphyry copper formation; they are closely associated with the upper flanks and tops of porphyry intrusions (Fig. 1), in common with which they display potassic alteration at depth and sericitic (± tourmaline) and, uncommonly, advanced argillic alteration at shallower levels (e.g., Río Blanco-Los Bronces; Irazuza et al. 2010; Toro et al. 2012). The breccia bodies, typically tens to hundreds of meters across and, locally, >1,000 m in vertical extent, can have gradational or abrupt host-rock contacts, the latter marked in places by vertically extensive zones of sheeting. The breccia bodies are blind, i.e. they typically do not extend far above the associated porphyry intrusions; however, some of the larger breccia volumes at Cananea in Mexico, Río Blanco-Los Bronces, and elsewhere can continue for hundreds of meters above their causative intrusions (Bishnell 1988; Toro et al. 2012).
clast space in the deeper parts of magmatic-hydrothermal breccia bodies, giving rise to what are termed igneous breccias (Gustafson and Hunt 1975).

### 2.2 Phreatomagmatic breccias

Phreatomagmatic breccias, products of explosive energy release during interaction between magma and hot aqueous solutions, commonly including ground water, fill kilometer-scale, upward-flared diatreme vents that can be vertically extensive (2–3 km; Fig. 1). Remnants of the magma bodies responsible for phreatomagmatism are observed to underlie and intrude the diatreme breccias as dikes (e.g., El Teniente, Chile; Howell and Molloy 1960) and shallow plugs, which may have attained the paleosurface as volcanic domes (e.g., Guinaoang, Philippines; Sillitoe and Angeles 1985; Fig. 1). Most diatremes breached the paleosurface to form maar volcanoes (Fig. 1) as confirmed by the presence within them of subsided blocks of base surge and lacustrine sedimentary deposits and chunks of carbonized wood. Accretionary lapilli are characteristic of these subaerial base surge deposits, but can also form within the diatreme vents themselves.

The breccias are predominantly heterolithic, matrix supported, and highly milled (Fig. 2b) and, by definition, contain juvenile igneous material: broken crystals (tuff) admixed with the rock-flour matrix and/or wispy, plastically deformed clasts of either dense or vesicular magma. Diatreme breccias generally display low-temperature clay alteration and disseminated grains of pyrite although, at the shallow lithocap level (Fig. 1), some diatremes were subjected to advanced argillic alteration and may host structurally controlled or disseminated, high-sulfidation epithermal precious-metal mineralization, particularly along their margins (e.g., Yanacocha, Peru; Longo et al. 2010).

### 2.3 Phreatic breccias

Phreatic breccias form in the shallower parts of porphyry copper systems, typically within their lithocaps (Fig. 1) – permeable, lithologically determined rock volumes with fracture-controlled feeder zones – when fluid pressures in deeper reservoirs were transmitted to shallow accumulations of vapor, especially where these contained CO₂. Commonly, the vapor pockets seem to have been confined beneath self-sealed zones of silicification. Intrusions at depth may perturb the shallow hydrologic regime to greater degrees, inducing more energetic vapor separation (flashing) and potentially more deeply penetrating brecciation. Phreatic eruptions can be accompanied by rock fragmentation to depths of at least 1,000 m below the paleosurface (Ohba et al. 2007). The term phreatic in the context of porphyry copper systems is used to signify any aqueous liquid, irrespective of whether it is of meteoric, largely magmatic, or, as commonly the case, mixed origin.

The breccias occupy dike-like to irregular bodies that may either be restricted to the subsurface or attain the paleosurface to form hydrothermal eruption craters.
rimmed by breccias and finer-grained ejecta (Hedenquist and Henley 1985; Fig. 1). The clast- to matrix-supported breccias are typically heterolithic, commonly rich in silicified clasts derived from the breached seals, and cemented by chalcedony (Fig. 2c), which can host gold and/or silver mineralization. End-stage cavities may be lined by quartz, barite, and/or other minerals.

### 3 Breccia timing

Magmatic-hydrothermal breccias are typically related to inter-mineral porphyry phases (Fig. 1) rather than to the first porphyry intrusions to be emplaced (e.g., Sillitoe and Gappe 1984; Bushnell 1988; Anderson et al. 2009; Vry et al. 2010; Perelló et al. 2012). Phreatic breccias are normally also inter-mineral in the context of the enclosing lithocap and normally later than potassic alteration in underlying porphyry copper deposits. Hence, these two breccia types commonly contain clasts of altered, veined, and/or mineralized rocks generated during earlier stages of porphyry copper system development. Clast-confined quartz veinlets in magmatic-hydrothermal breccia and vuggy residual quartz clasts in phreatic breccias are emblematic.

Diatremes, present in ~20–30% of deposits worldwide, are normally also late features, post-dating porphyry copper formation. Consequently, centrally located diatremes can be porphyry copper destructive and are everywhere sub-ore grade or barren; however, as noted above, their shallow, lithocap-hosted parts may be subject to at least the final stages of high-sulfidation epithermal precious-metal mineralization (e.g., Dizon, Philippines, Caspiche, Chile, Tujuh Bukit, Indonesia, and Wafi-Golpu, Papua New Guinea; Sillitoe and Gappe 1984; Sillitoe et al. 2013; Harrison et al. 2018; Rinne et al. 2018). Nonetheless, a minority of diatremes pre-date porphyry intrusion and mineralization (e.g., Tujuh Bukit and Grasberg, Indonesia, and Boyongan, Philippines; MacDonald and Arnold 1994; Braxton et al. 2018; Harrison et al. 2018), although they may not in every case be genetically related given that >3 Myr separate the diatreme and copper-gold mineralization at Tujuh Bukit (Harrison et al. 2018).

### 4 Implications for copper deposit formation

It is clear that the majority of hydrothermal breccias associated with porphyry copper deposits formed after at least the earliest porphyry intrusions had been emplaced and, in the case of most phreatomagmatic and phreatic breccias, after all but the latest intrusions were already in place, hydrothermally altered, and mineralized. Therefore, any juvenile igneous material in most porphyry copper-associated breccias was likewise later than the early porphyry intrusions. Thus, these inter- and late-mineral breccias could not have acted as conduits for ascent of the magmas that fed the porphyry intrusions most closely related to the early, highest-grade porphyry copper mineralization.

Many porphyry copper deposits were formed beneath or, less commonly, in the basal parts of volcanic edifices, including stratovolcanoes and dome complexes (Sillitoe 1973). However, magmatic-hydrothermal breccias, the most closely related type to porphyry copper deposit formation, cannot have been connected to overlying volcanic features because they terminate subsurface, mainly beneath or in the lower parts of lithocaps (Fig. 1). This conclusion is widely corroborated by the results of core drilling, which further show that the apices of porphyry intrusions, where preserved in shallowly eroded systems, commonly beneath lithocaps, display abrupt contacts with non-brecciated, older (typically much older) host rocks (e.g., Rečsk, Hungary, Red Mountain, Arizona, Far Southeast, Philippines, Pampa Escondida and Valeriano, Chile, and Wafi-Golpu; Baksz et al. 1980; Quinlan 1981; Hedenquist et al. 1998; Sillitoe 1999; Hervé et al. 2012; Sillitoe et al. 2016; Rinne et al. 2018; Fig. 1).

Therefore, in the majority of porphyry copper deposits, emplacement of early, ore-related porphyry intrusions was likely facilitated not by breccia bodies but by structural and rheological anisotropies, particularly the dilatant portions of deeply penetrating faults and their associated damage zones (Tosdal and Richards 2001). The only exceptions could be the few deposits that were preceded by and emplaced into diatremes (Grasberg, Tujuh Bukit, and Boyongan; see above), which may have helped guide magma ascent. Nonetheless, even though these early diatremes may have attained the paleosurface in the form of maar volcanoes, an active, through-going connection to the paleosurface was not retained during subsequent porphyry copper formation. Furthermore, when the more numerous late-mineral diatremes formed and vented, porphyry copper deposit formation was declining or had already ended. The small-volume ignimbrite eruptions that concluded porphyry copper formation at Río Blanco-Los Broncos and Bajo de la Alumbrera, Argentina were similarly terminal events (Toro et al. 2012; Buret et al. 2017).

### 5 Conclusions

Porphyry copper deposits are commonly associated with one or more varieties of hydrothermal breccia, most of which were emplaced during the hydrothermal alteration and mineralization events, including their waning stages. Therefore, most breccias did not act as either conduits for pre-mineral magma ascent or provide pre- or syn-mineral connections to any suprajacent volcanic activity. Nearly all breccias that could potentially have attained the paleosurface are late and post-dated porphyry copper formation, although they may have overlapped with high-sulfidation epithermal precious-metal mineralization hosted by lithocaps. The field evidence further shows that porphyry stocks and dikes were overlain at the time of copper ± molybdenum ± gold mineralization by intact host rocks.

Therefore, intrusions that underwent main-stage porphyry copper development lacked significant through-going connections to the overlying volcanic environment, a situation that may well be a prerequisite for effective ore deposition. A direct volcanic connection, via diatremes,
developed during the waning stages of a minority of porphyry copper systems, and precursor diatremes are also recognized but of extremely minor occurrence.

These conclusions further suggest that porphyry copper deposits are generated during volcanic dormancy, beneath parasitic vents on volcano flanks (e.g., Bajo de la Alumbrera; Proffett 2003), or following final construction of the edifices, with the last two alternatives undoubtedly favoring their preservation.

Acknowledgments

Thanks are due to porphyry copper-related breccias worldwide for revealing some of their secrets and to Jeff Hedenquist and Pepe Perelló for helpful manuscript reviews.

References


Howell FH, Molloy JS (1960) Geology of the Braden orebody, Chile, South America. Econ Geol 55:863-905


Sillitoe RH (1985) Ore-related breccias in volcanoplutonic arcs. Econ Geol 80:1467-1514


Sillitoe RH, Burgoa C, Hopper DR (2016) Porphyry copper discovery beneath the Valeriano lithocap, Chile. Soc Econ Geol Newsl 106:1, 15-20


The hypogene evolution of the Spence porphyry copper system, northern Chile

Edward G. Bunker  
University of Bristol, UK

Simon R. Tapster  
NERC Isotope Geosciences Laboratory, British Geological Survey, UK

Frances J. Cooper, Jon D. Blundy  
University of Bristol, UK

Abstract. The timing and duration of magmatism and ore formation in Porphyry Copper Deposit (PCD) systems offer valuable insight into the geological processes leading to ore formation which may aid in future exploration efforts and can provide constraints upon the potential metal endowment of a deposit. The Spence PCD in Northern Chile is centered upon granodioritic porphyry stocks of Palaeocene age. Whilst Spence formed at ~57 Ma, spatio-temporal constraints on the evolution of magmatism are poorly defined and the deposit’s geological model lacks the detail required for to investigate the evolution of the deposit at high resolution. We redefine the sequence of igneous units at the deposit based on key textural characteristics, these lithologies are then mapped using a novel and non-intrusive mapping strategy which utilises drill-core. We apply high precision CA-ID-TIMS U-Pb geochronology to the deposit using the lithologies defined in this study to reveal a complex magmatic history with at least four independent pulses of mineralising hydrothermal fluid. Our data illustrate that magmatism and hydrothermal activity initiated in the SSW of the deposit and gradually migrated NNE following the trend of the pre-existing Antofagasta-Calama Lineament.

1 Introduction

Ore deposit models underpin our understanding of the geological processes leading to ore formation and provide a theoretical basis which may be used in minerals systems exploration strategies and to generate exploration criteria which may be applied in the field. More locally, ore deposit models are used in day-to-day decision making at mines which influence pit design, ore processing and efficiency gains.

Spence was discovered in Region II of northern Chile in 1995-96 during an exploration drilling campaign by Rio Algom Ltd. (Sillitoe 2000). The deposit was a blind discovery beneath Miocene age gravels of the Atacama Formation (Guzman-Cruces 2001) which limited the level of detail that could be observed in drill-core and through remote sensing at that early stage. We conduct a detailed study of the intrusive sequence at the Spence PCD through textural study, geological mapping and high precision CA-ID-TIMS U-Pb zircon geochronology leading us to propose a revised geological model for the hypogene evolution of the deposit based upon observable textural criteria and cross-cutting relationships.

We reveal the absolute time-frame of this complex geological system demonstrating that each zone of the deposit developed independently from one another and that magmatism was more protracted toward the south. Several mineralising hydrothermal events are identified that occurred diachronously across the deposit. Magmatic and hydrothermal activity are shown to migrate from the SSW to NNE across the deposit following pre-existing crustal structures.

2 Geological setting

The Spence PCD is located in the Paleocene-early Eocene metallogenic belt of northern Chile (Sillitoe and Perelló 2005). The deposit consists of three mineralised igneous centers and a zone of sub-economic dykes which are termed the South, Central South, Central North and North Zones and which are aligned along an NNE trending axis.

Rowland (2001) determined that Spence was comprised of three intrusive phases which are differentiated by cross-cutting relationships and timing relative to mineralisation. These are a syn-mineralisation granodiorite termed Quartz Feldspar Porphyry 1 (QFP1), a post mineralisation granodiorite termed Quartz Feldspar Porphyry 2 (QFP2) and a monzodiorite dyke termed Feldspar Porphyry (FP) which represented the latest igneous event. Preliminary studies constrained the emplacement age of Spence by 40Ar-39Ar biotite geochronology to 57.00 ± 0.69 Ma (Rowland & Clark, 2001).

3 Redefining the igneous sequence at Spence based upon igneous texture

The igneous stratigraphy of Spence was set out by Rowland (2001) who argued that the deposit was comprised of three igneous units QFP1, QFP2 and FP. Whilst subsequent work has acknowledged that the geology of Spence is more complex than this simplified geological model suggests (Sillitoe 2011) Rowland’s
Magmatic hydrothermal systems: from Porphyry to Epithermal

1003

Figure 1. Representative modal compositions for the igneous lithologies recognized at Spence in this study, determined by point counting. The results indicate a gradual decrease in crystallinity of the syn-mineral intrusives with relative age, apart from the hornblende porphyry. Post mineral intrusives generally have elevated pyrite contents which is reflected in the modal opaque composition.

Figure 2. Relative chronology of igneous units and hydrothermal veins in the four zones of the Spence PCD. Veins are classified after the terminology of Gustavson and Hunt (1975): A – A-vein, EB – Early B vein, B – B-vein, D – D-vein, HS – High Sulphidation vein. Lithological abbreviations are as follows: CG – Crowded Granodiorite, QFBP – Quartz Feldspar Biotite Porphyry, QFP2 – Mairolitic porphyry and rock flour, FP – Feldspar Porphyry, HP – Hornblende Porphyry, NZP North Zone Porphyry.

4 Developing a geological map through interpolated drill-core study

4.1 Mapping rationale and methods

Whilst the geological model proposed by Rowland (2001) facilitates the day-to-day operation of the mine, it does not reflect the spatial and textural complexity of the deposit’s igneous lithologies as determined in this study. In order to better illustrate the geology of the deposit, and to investigate its geological and spatial complexity in greater detail, the deposit required re-mapping.

At the time of discovery, Spence was concealed beneath 15-120 m of Miocene gravels, subsequent access to surface exposure of the geology of Spence has been limited due to logistical and safety considerations relating to mining operations ongoing at the site. To overcome this, we utilized the extensive library of drill-core which covers the deposit at a high spatial resolution in order to interpolate the geology of the deposit at a depth of our choosing.

We studied 10 m intercepts from 252 drill-cores that were distributed across the deposit. The igneous lithologies were logged according to the textural criteria defined in section 3; geological contacts were recorded as well as the location of tectonic breccias which were interpreted as faults. An irregular drill-core spacing was used with high sample density in geologically complex areas, and less densely spaced in simpler regions.

4.2 Observations

The Jurassic age Cerritos Bayos Formation was differentiated into a calcareous and silicic member based principally upon its colour; the contact between these sub-units defined the axis of a north plunging anticline that had not been previously recognized. The fold axis parallels the axis of the deposit and constrains the intrusive zones of the deposit in the South and Central South Zones (Fig 3). The deposit is further bounded by faults trending SSW-NNE, NW-SE and N-S.

The crowded granodiorite (CG) occurs in the South and Central South zones where it is cut by the quartz feldspar biotite porphyry (QFBP), the contact between these two units is often faulted, but where it is observed the contact is diffuse over several meters. In the South and Central South zones, QFBP is cut by the post-mineralisation mairolitic porphyry which grades from a competent porphyry unit to a breccia with igneous matrix or a rock flour with occasional igneous clasts. The magmatic breccia is most extensive in the South Zone and is overprinted by a later phase of hydrothermal breccia which is cemented by a fine-grained sericite, tourmaline and molybdenite matrix. Feldspar Porphyry contacts in drill-core and hand-sample scale cross-cutting relationships (Fig. 2). There were no clear relative relationships between igneous units within different zones of the deposit, therefore the relative progression of events occurring in different zones of the deposit could not be determined in the field.
(FP) cuts the hydrothermal breccia in the South Zone as an NNE trending dyke that represents the youngest intrusive event in this zone of the deposit.

The North Zone Porphyry (NZP) is observed in the Central South, where it cuts the post-mineralisation mairolitic porphyry and rock flour, however despite cutting these units, the NZP exhibits B-vein and disseminated mineralisation. The NZP represents the only lithology identified in the Central North and North Zones.

Figure 3. A sub-surface geological map of the Spence PCD at 1400m above sea level (~350 m below surface) which was obtained through the study of >250 10 m intervals of drill-core intersecting the same datum. Sample locations for U-Pb CA-ID-TIMS dating are indicated on the map as colour-coded shapes.

5 CA-ID-TIMS U-Pb zircon geochronology

In order to place absolute constraints upon the newly defined igneous stratigraphy and relative chronology, we applied high-precision Chemical Abrasion Isotopic Dilution Thermal Ionisation Mass Spectrometry (CA-ID-TIMS) U-Pb zircon geochronology to a representative suite of samples from Spence (Fig. 4). The samples were distributed across the deposit and were selected to cover the full igneous history of the deposit as determined through relative chronology; the sample locations are shown in Figure 3.

Deposit formation commenced in the South Zone when the crowded granodiorite intruded at 57.286 ± 0.025 Ma. Magmatism subsequently migrated gradually toward the north through time, with the final pulse occurring in the North Zone at 56.616 ± 0.032 Ma, indicating that magmatism was ongoing for at least 670 ± 41 kyr. The duration of magmatism varies between zones, with the South Zone displaying the longest interval of magmatism of 412 ± 78 kyr, the Central South Zone indicating a duration of 224 ± 39 kyr and single pulse durations constrained in the Central North and North Zones.

6 Discussion

6.1 The magmatic and hydrothermal evolution of the Spence PCD

We present a new igneous stratigraphy for Spence which is differentiated texturally, spatially and temporally. Our stratigraphy defines a complex progression of igneous events with each zone having a unique igneous history. The syn-mineralisation intrusive suite is separated in to at least four distinct pulses which have distinct vein associations, the relative progression of vein types determined from cross-cutting relationships in hand sample indicate that there were at least four distinct pulses of magmatic hydrothermal fluid. Within the main phase of mineralisation the age of syn-mineral intrusives is roughly proportional to the phenocryst/groundmass ratio of the sample.

Magmatism onset in each zone of the deposit defines a steady migration from SSW to NNE following the 4 km long axis of the deposit. The SSW-NNE structural fabric of the deposit is reflected in the orientation of early faults and the axis of the pre-emplacement fold along which the deposit is emplaced.

We identify texturally similar units that were emplaced diachronously across different zones of the deposit, illustrating a shortfall in the correlation of rocks by texture alone. The potential for texturally similar but temporally distinct intrusive events to occur within a short period of time in the same magma system is not well understood, but this may become an increasingly common phenomenon as the available precision of dating techniques improves.

6.2 Structural evolution of the Spence PCD

Prior to the emplacement of Spence, the Jurassic age Cerritos Bayos Fm. was folded in to a N-plunging anticline, that may have influenced the
location and orientation of the deposit. NNE-trending faults bound the South and Central South Zones of the deposit; elongate porphyry dykes coincide with these faults indicating that they were active at the time of deposit emplacement. These faults are aligned with a major trans-crustal fracture that runs through the region termed the Antofagasta-Calama Lineament which may have influenced the location of PCD formation during the Palaeocene (Arriagada et al. 2003; Cameron et al. 2004; Palacios et al. 2007).

7 Implications

A revised geological model for the hypogene evolution of the Spence PCD is presented that indicates that each zone of the deposit has a unique formational history which is independent from respective zones of the deposit. Magmatism began at Spence 57.286 ± 0.025 Ma and lasted for at least 670 ± 41 kyr however over this time the magmatic activity migrated gradually NNE, influenced by the regional structural fabric of the Antofagasta-Calama Lineament.

Acknowledgements

This work was funded by BHP. We are grateful to Jean des Rivières for permitting this work and for offering guidance alongside Cam McCuaig, Aldo Vasquez, Jaime Cortes and Jill Terry. We thank Reinaldo Guzmán and his team at Spence who gave us great geological insight and access to the drill-core used in this study. We are grateful to Lia Ituarte for providing logistical and communicative support throughout the project.

References


Palacios, C. et al. 2007. The role of the Antofagasta-Calama Lineament in ore deposit deformation in the Andes of northern Chile. Mineralium Deposita 42(3):301–308

Rowland, M.G. 2001. Geology of the Spence porphyry copper deposit, Northern Chile.


Sillitoe, R.H. 2011. Comments on the Cerro Colorado and Spence hypogene models, northern Chile.

Ore genesis of the Devonian superimposed Yulekenhalasu porphyry Cu-Mo deposit in CAOB: Insights from paragenesis and fluid inclusions

Chao Wu, Huayong Chen
Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China

Abstract. The Yulekenhalasu porphyry Cu–Mo deposit is located in the Devonian Halasu copper belt, part of the East Junggar block in northwest China. At Yulekenhalasu, Cu and Mo mineralization commonly occurs as disseminations or veinlets in both porphyry-type alteration zones and late high-grade Cu sulfide-bearing veins. Seven hydrothermal alteration stages were identified at the deposit, including sodic-calcic alteration (Stage I), potassic alteration (Stage II), propylitic alteration (Stage III), phyllic alteration (Stage IV), late Cu sulfide-bearing veins (Stage V), argillic alteration (Stage VI), and supergene alteration (Stage VII). Fluid inclusion assemblage (FIA) microthermometry coupled with cathodoluminescence (CL) imaging reveals that mineralizing fluid for Stage II–IV had intermediate to high temperatures and variable salinities. The Stage V late Cu sulfide-bearing veins were associated with intermediate temperatures and dilute hydrothermal fluid, in contrast to low-temperature and dilute fluid in Stage VI. Stage II and III veins were overprinted by hydrothermal fluid associated with Stage V and VI via reopening of early hydrothermal veins. Discrete multi-stage alteration features in Yulekenhalasu can represent a typical example of the Paleozoic porphyry copper deposit (PCD) systems formed in the Central Asian Orogenic Belt (CAOB).

1 Introduction

The CAOB, one of the world’s largest subduction-accretionary orogens (Carroll et al. 1990; Sengör et al. 1993; Mossakovsky et al. 1994), hosts several giant PCDs including Oyu Tolgoi, Samarka and Aktogai-Aiderly, consequently it is considered one of most crucial porphyry Cu belts in the world (Perelló et al. 2001; Yakubchuk 2004; Mao et al. 2014; Seltmann et al. 2014). Corresponding to recognized magmatic-hydrothermal-tectonic overprinting events (Zhang et al. 2015; Xue et al. 2016), many PCDs in the CAOB initially formed in an island arc setting underwent the Late Paleozoic collision and subsequent post-collision and intra-plate extension, and raise critical challenges and opportunities for mineral exploration (Yakubchuk 2004). The Yulekenhalasu deposit, one of the earliest discovered PCDs in the Chinese Altay – East Junggar (CAEJ) orogenic belt, is characterized by typical porphyry-type mineralization overprinted by late-stage hydrothermal events. Previous studies suggest that Upper Devonian porphyry mineralization was probably formed by island arc-related flat subduction, followed by Late Carboniferous intra-plate tectonic overprinting (Wu et al. 2015; Xue et al. 2016). However, the detailed processes involved in the evolution of the hydrothermal fluid in various tectonic settings, including from the subduction to post-subduction stages, and their contributions to the metal endowment are still inadequately understood.

FIA represents the finest temporal resolution as to the timing of initial closure of the inclusion vacuoles (Goldstein and Reynolds 1994), while CL microscopy can distinguish compositional variations in quartz crystals resulted from the growth, fracturing-healing, and recrystallization (Rusk and Reed 2002). Rather than lumping together of multiple events, methods such as FIA and CL allow us to consider each growth zone and each event of fracture healing as separate events in geological history at Yulekenhalasu deposit.

Aiming to address the current lack of understanding the detailed paragenetic history of this vital deposit in NW China, this study presents microthermometric data, including new FIA coupled with CL imaging on hydrothermal quartz sampled from different alteration zones at the Yulekenhalasu deposit, the combination of which contributes not only to a better understanding of the complex hydrothermal evolution of the Yulekenhalasu deposit, but also to the more generalized metallogenic model for similar multi-stage mineralization in the CAOB porphyry Cu deposits.

2 Deposit geology

The area surrounding the Yulekenhalasu deposit is host to remnants of a succession of marine volcanic or volcaniclastic rocks, dominated by the Middle Devonian Beitashan Formation that contains mafic to intermediate lavas and corresponding tuffs, breccias and sandstones, and the Early Carboniferous Jiangbasitao Formation that consists primarily of carbonaceous black shale, slate, conglomerate, tuffaceous sandstone and intermediate tuff intercalated with minor andesite (Zhang et al. 2009). Of the three principal fault orientations recognized in the district (Fig. 1), including NNW-, NE- and WE-trending fault systems, the NNW-trending fault system has a similar strike direction to the principal ore bodies at Yulekenhalasu, and appear closely associated with the regional Fuyun fault which dips sharply to the northeast.
Intrusive rocks of Middle Devonian to Carboniferous age comprise the pre-mineralization (porphyritic syenite, ca. 390 Ma), syn-mineralization (quartz diorite and diorite porphyry, ca. 382–372 Ma) and post-mineralization (quartz porphyry and alkali granite porphyry, ca. 350–320 Ma) episodes of intrusive activity in the district. The emplacement of these porphyries are generally controlled by the NW-trending fault system, and are cross-cut by WE-trending faults (Fig. 1). The porphyritic syenite (ca. 391 Ma) occurs as NW-trending stocks and contains coarse-grained K-feldspar phenocrysts within a groundmass of fine-grained quartz and K-feldspar. The quartz diorite (ca. 379 Ma), which crops out as a large stock along the south margin of the district, locally intruded the Beitasshan Formation (Fig. 1) and comprises plagioclase, quartz, and biotite, with minor alkali feldspar, titanite, apatite, magnetite, and zircon. The diorite porphyry (ca. 377 Ma) is separated from the overlying Jiangbasitao Formation by an NW-trending fault (Fig. 1) and generally contains a weak to moderately porphyritic texture, consisting of plagioclase, quartz, K-feldspar, minor biotite and hornblende. Post-mineralization quartz porphyry is exposed as dykes in the Jiangbasitao Formation and is characterized by a porphyritic texture with quartz and minor plagioclase as phenocrysts, and a groundmass of quartz, plagioclase, and biotite (Yang et al. 2014). The alkali granite porphyry (ca. 327 Ma) is dominated by coarse-grained K-feldspar and minor biotite phenocrysts within a groundmass of fine-grained K-feldspar, quartz, and biotite (Wu et al. 2015).

Two mineralized zones (west and east) have been recognized in the Yulekenhalasu ore district (Fig. 1). The eastern zone occurs within the diorite porphyry and is host to the main copper reserve; it extends for approximately 800 m in length and 20 m to 120 m in width (Fig. 1). The western zone occurring in basalt and porphyritic syenite is distributed in the NW part of the ore district, and extends for about 300 m in length, with a width of 10–80 m, consisting of three smaller scale copper mineralized bodies. Sulfide minerals at the Yulekenhalasu deposit consist primarily of chalcopyrite, pyrite, and molybdenite, with lesser amounts of bornite, galena, sphalerite, and pyrrhotite. Gangue minerals are dominated by quartz, feldspar, magnetite, biotite, gypsum, sericite, chlorite, epidote and calcite. Ores occur in various textural forms including disseminated grains, veinlets, stockwork veins, metasomatic relict grains, and cataclastic textures, as described in more detail below.

3 Superimposition and evolution of hydrothermal fluids at the Yulekenhalasu deposit

Seven hydrothermal alteration stages were identified at the Yulekenhalasu deposit, including Stage I sodic-calcic alteration, Stage II potassic alteration, Stage III propylitic alteration, Stage IV phyllic alteration, Stage V late Cu sulfide-bearing veins, Stage VI argillic alteration, and Stage VII supergene alteration. Of the above alteration stages, the potassic and late Cu sulfide-bearing veins were the principle ore-forming stages. The paragenetic study of the Yulekenhalasu deposit indicates that potassic alteration was superimposed by later phyllic alteration and further overprinted by Stage V late Cu sulfide-bearing veins and Stage VI argillic assemblages. Similar overprinting textures of magmatic-hydrothermal features have been widely recognized in deposits containing multiple mineralizing events, including the Bingham Canyon porphyry Cu–Mo–Au, Questa porphyry Mo, Acupan porphyry-epithermal Au–Ag, and Dabaoshan porphyry Mo deposits. Cooke and Bloom (1990) suggested that intermittent rupture events could produce late hydrothermal veins encrusting or crosscutting early veins before sealing, eventually leading to repeated seal/rupture cycles, wherein late fractures and reopened veins also act as pathways for late-stage fluid circulation, resulting in complex overlapping of fluids from different stages (Cooke and Bloom 1990).

The combination of microthermometric data and CL imaging in this study supports the premise of there being multi-stage hydrothermal superimposition events onto pre-existing mineral assemblages at the Yulekenhalasu deposit. For example, firstly, the presence of CL-bright quartz cores with CL-dark overgrowths in Stage II quartz veins implies the superimposition of Stage IV phyllic alteration onto early-formed Stage II potassic alteration. Subsequently, in Stage II veins, the presence of cobweb-like networks of CL-dark quartz (Stage V) cutting CL-bright quartz grains of Stage II, indicates overprint of Stage V hydrothermal fluid on the precursor Stage II quartz. Finally, continuous stringers of CL-dark quartz that hosts low-temperature FIs are observed to cut across cobweb-like CL-dark quartz containing Generation II FIs, combined with above observations, thus suggesting that the early homogeneous quartz veins forming in Stage II were initially overprinted by phyllic alteration (Stage IV), subsequently reopened in response to Stage V CO2-bearing fluid represented by cobweb-like CL-dark quartz, and eventually modified by injection of a Stage VI fluid, producing new CL-dark quartz of continuous stringers in Stage II veins.

Based on textural studies of multi-generation quartz veins in porphyry Cu systems (e.g., Grasberg, Butte,
In the porphyry-type alteration stage, the fluid associated with Stage II potassic alteration is characterized by higher temperatures and salinities than for Stage III propylitic alteration, which is most likely due to the distance from the heat source. The occurrence of Type C fluid inclusions suggests that the salinity for potassic alteration could reach up to 30 wt.% NaCl equiv., although the measured data mostly have lower salinities. Also, the recognition of boiling at about 400 °C in the potassic stage implies the lowest trapping depth of ~0.55 km under lithostatic pressure and ~2.3 km under hydrostatic pressure. Therefore, it is inferred that hydrothermal fluid originated from magma may ascend along preexisting fractures, syn-mineralization faults or permeable contacts provided by pre-existing intrusions, and then reach the boundary between lithostatic and hydrostatic pressure. The hydrothermal fluid may have mixed with meteoric water to yield lower salinity Stage IV phyllic alteration. The hydrothermal fluid for Stage V is markedly CO2-rich and characterized by low salinity, and temperatures of around 300 °C, while Stage VI argillic-related fluid is characterized by temperatures of approximately 160 °C with a wide range of salinity. Although late Cu sulfide-bearing veins of Stage V overprinted on potassic assemblages thus are termed to postdate Stage II, the relative timing between Stage IV and Stage V remained undecided, with no unambiguous evidence uncovered.

Acknowledgements

We sincerely thank Zhenjiang Liu form No. 4 Brigade of the Xinjiang Geology, Mineral Exploration and Development Bureau for the field support in the Halasu PCD belt. This research is financially supported by Type-B Chinese academy of sciences strategic pilot science and technology special (XDB18030206)

References


Abstract. Timing of sulfide precipitation in porphyry Cu deposits has been assumed to correlate with quartz vein formation and K-silicate alteration at high temperatures. Cathodoluminescence imaging challenged this traditional model by revealing the textural link between sulfides and a dull-luminescent quartz generation post-dating the main stockwork vein quartz. At Batu Hijau, inconspicuous sulfide veinlets (“paint-veins”) associated with pervasive chlorite-sericite alteration are genetically related with dull-luminescent quartz and introduce all Cu-Fe sulfides into the system after a period of quartz dissolution. Fluid inclusions characterize the mineralizing fluid as a magmatic low-salinity liquid-like phase at temperatures of 350° to 300°C. Consequently, quartz vein formation is decoupled from the precipitation of bornite and chalcopyrite, which occurs in an overprinting event at lower temperatures at Batu Hijau, a prototypic porphyry Cu deposit. This finding adds to the growing evidence that sulfide precipitation occurring at low- to moderate temperatures is a common process in porphyry copper formation.

1 Geological framework of the Batu Hijau porphyry Cu-Au deposit

The world-class porphyry Cu-Au deposit Batu Hijau is located in the SW corner of Sumbawa, an island in the tectonically active Sunda-Banda intra-oceanic arc system, Indonesia. Mineralization is centered on a porphyritic tonalite complex that intruded into a thick sequence of volcanoclastic sediments (Garwin 2000). Alteration pattern and vein-types follow the common model for porphyry copper deposits (Sillitoe 2010), with a central zone of biotite alteration associated to quartz stockwork veins hosting most of the copper-iron sulfides (Mitchell et al. 1998; Clode et al. 1999; Arif and Baker 2004). Quartz veins are classified into A-, AB-, and B-veins, becoming thicker, straight-walled and more continuous in this chronological order (Fig. 1A and B). Thin sulfide-veinlets with green chlorite-sericite alteration selvages (“paint-veins”; Fournier 1967) crosscut earlier quartz vein generations. During this stage, primary and secondary biotite is replaced by chlorite and sericite, producing the characteristic pale-green color of the mineralized rocks (Fig. 1B). Pyrite veinlets (D-veins) accompanied by feldspar-destructive sericite-clay alteration are the last veining-stage, crosscutting all other vein-types.

The general positive correlation of ore grade with quartz vein density as well as the spatial overlap of the highly mineralized zone and biotite alteration close to the porphyry center (Mitchell et al. 1998), sulfides are thought to have precipitated during quartz stockwork formation at high temperatures (Garwin 2000; Arif and Baker 2004; Proffett 2009).

Cathodoluminescence (CL) imaging reveals the complex internal structure of quartz veins marked by several superimposed quartz generations and dissolution events (Fig. 1C). Chalcopyrite and bornite hosted by quartz veins are always related to a network of cracks filled with dull-luminescent quartz or to minor euhedral dull-luminescent quartz grains within paint-veins, illustrating a genetic link of sulfide precipitation and paint-vein formation. Consequently, physical and chemical
conditions of ore formation at Batu Hijau might differ significantly from the common model.

2 Insights from fluid inclusions

2.1 Fluid inclusion types and distribution

Four main types of fluid inclusions (FIs) can be distinguished at Batu Hijau based on phase proportions at room temperature: intermediate density (ID) FIs, low-density low-salinity vapor (V) FIs, high-density high salinity brine (B) FIs, and high-density low- to medium-salinity aqueous (A) FIs. Due to the large number of FIs, the unambiguous identification of primary or pseudosecondary FIs is difficult and therefore most inclusions are considered to be of secondary origin.

In quartz veins from the deepest, non-mineralized parts of the deposit the predominant type of FIs are of intermediate density, < 5 to 40 µm big and consisting of liquid and gas in equal proportions. With decreasing depth, the abundance of ID FIs decreases rapidly while B and V FIs become the dominant FI-type within mineralized quartz veins. Polyphase B inclusions contain a small gas bubble (10 – 30 vol.%) and a halite daughter crystal. Many more solids can be present in individual inclusions, including sylvite, hematite, chalcopyrite, anhydrite, and calcite. In V FIs the gas bubble occupies the majority of the inclusion volume (70 – 95 vol.%) and a small triangular chalcopyrite is commonly present. Coexisting B and V FIs on healed fracture planes demonstrate immiscibility of hydrothermal fluids during and after quartz vein formation. All three FI-types (V, ID, and B FIs) are hosted by and are genetically related to bright-luminescent quartz generations in the stockwork veins within the biotite-altered center of Batu Hijau. The dull-luminescent quartz generation enclosing all sulfides post-dates those quartz generations and exclusively hosts A FIs. This inclusion-type consists of a small gas bubble (around 20 vol.%) and liquid. Most A FIs follow the microfracture network healed by dull-luminescent quartz along which the sulfides occur. Rarely, unambiguously primary FIs can be found within euahedral quartz of paint-veins growing into open spaces. On the other hand, pseudosecondary A FI-trails truncated by sulfides along a specific growth zone are commonly present and suggest entrapment immediately before or during sulfide precipitation (Fig. 2).

2.2 Microthermometric characterization

Heating and freezing experiments were conducted on selected fluid inclusion assemblages (FIAs), defined as trails or groups of FIs with similar phase proportions at room temperature (Goldstein and Reynolds 1994).

ID FIs show very homogenous salinities of 3.5 to 4 wt.% NaCl eq. with decreasing homogenization temperatures (TH) from 430° in A- to 350°C in B-veins. The deep barren core of Batu Hijau is assumed to have been formed at paleodepths of around 3 km (Garwin 2000) and the respective pressure corrections indicate entrapment temperatures between 500° and 400°C for A- and B-veins, respectively (Fig. 3).
Poly-phase B FIs homogenized by either bubble disappearance or halite dissolution (FIAs on the halite saturation curve in Fig. 3) at temperatures between 280° and 480°C. The TH and salinities of B FIs within AB-veins are higher than in B-veins. Most B FIs from boiling trails homogenize within a narrow range from 370 to 390°C and have salinities between 35 and 40 wt.% NaCl eq. Microthermometry results of V FIs are difficult to obtain due to the small amount of liquid present and hence phase-transitions are easy to miss. However, the TH of V FIs should be similar to those of B FIs along boiling trails, and their salinities were calculated using the SoWat software (Driesner 2007, Driesner and Heinrich 2007) to be around 0.1 wt.% NaCl eq.

The A FIAs coeval with formation of paint-veins show homogenization temperatures mainly in the range of 310 to 350°C with a few exceptions at lower and higher temperatures. In few cases high salinities of up to 25 wt.% NaCl eq. were observed from A FIAs within cores of dull-luminescent euhedral quartz crystals. The majority of pseudosecondary and secondary FIs, however, have lower salinities between 0.5 to 10 wt.% NaCl eq.

Most A FIs from D-veins homogenize at temperatures below 300°C, and their salinities overlap with the lower range of A FIs from paint-veins.

2.3 Chemical composition of fluids

LA-ICP-MS analysis of individual FIs were conducted at ETH Zürich and the results for selected elements are shown in figure 4. In general, analyzed elements can be divided into three different groups based on their behavior during phase separation. For elements like K, Cs, and Rb, ratios relative to Na stay constant within all FI types and hence throughout the lifespan of the hydrothermal system at Batu Hijau. In contrast all detected base metals partitioned into the brine phase, while Li, B, Ag, and As preferred the vapor phase relative to Na during phase separation. Most strikingly however, is the fact that element/Na ratios in ID and A FIs perfectly overlap for most of the elements analyzed.

Copper concentrations within B FIs are very high (up to 10 wt.%) and decrease with decreasing TH to values as low as 1000 µg/g, whereas Fe concentrations are rather constant at around 10 wt.% over the whole temperature range. The A FIs related to the paint-vein stage and the mineralization have much lower Cu and Fe concentrations, typically between 100 and 1000 µg/g.

3 Porphyry mineralization from a low-salinity fluid at moderate temperatures

Due to the textural position of sulfide grains within or attached to the dull-luminescent quartz generation, mineralization at Batu Hijau postdates locally the formation of quartz stockwork veins, which are characterized by much brighter luminescent quartz (Q1 and Q2). In addition, the general absence of B FIs within the dull-luminescent quartz argues against sulfide precipitation from a highly saline fluid, although B FIs contain the highest Cu concentrations of up to several wt.%. Decreasing Cu concentrations of B FIs with lower TH was interpreted to document sulfide precipitation at Bingham Canyon (Landtwing et al. 2010) and is also observed at Batu Hijau (Fig. 4). However, unchanging Fe concentrations demonstrate that the Cu depletion cannot be the result of chalcopyrite ± bornite precipitation but might be attributed to other effects, such as decreasing partitioning coefficients between liquid and vapor with decreasing temperatures (Zajacz et al. 2017). Occasionally detectable sulfur concentrations in B FIs (not shown here) also stay constant and do not decrease with temperature.

The occurrence of A FIs within dull-luminescent quartz as pseudo- and secondary trails imply that they represent the fluid present either during or immediately before sulfide precipitation. Consequently, Cu and Fe concentrations of A FIs represent either the remaining...
sulfide precipitation. Even if the analyzed average Cu concentration of around 730 μg/g is regarded as the maximum of Cu dissolved in the low-salinity fluid, a medium-sized magma chamber of 47.5 km³ would be able to produce the required amount of fluid for transporting the copper at Batu Hijau (assuming 100% precipitation efficiency and initial magmatic water contents of 5 wt.%). Main trigger for sulfide precipitation was cooling over a temperature interval from 350° to 310°C as indicated by Ti of A FIs. The Ti-in-quartz (Huang and Audétat 2012) and the chlorite thermometer (Jowett 1991), indicate a comparable range of temperatures (370° to 330°C and 350° to 290°C, respectively) for the formation of paint-veins and their characteristic alteration.

Based on the chemical similarities between ID and A FIs, the mineralizing fluid represents an ascending and cooling magmatic fluid, which becomes denser (from 0.55 to 0.75 g/cm³). Without any drastic depressurization event, like the change from lithostatic to hydrostatic regime (Fournier 1999) that caused phase separation of previous fluid pulses, the ascending fluid stays within the single-phase field following a path of decreasing pressure and temperature parallel to the two-phase boundary. Mixing with variable amounts of vapor and brine explains the range of salinities in A FIs (Fig. 3). However, the bulk composition of the mineralizing fluid changed only slightly. Constant fluid chemistry from initial magmatic fluids, entrapped as ID FIs in A-veins of the deep barren core, to the mineralizing fluid represented by A FIs demonstrate that no significant processes within the magma chamber or the hydrothermal system, like phase separation or intensive mixing with meteoric fluids, were important for the porphyry Cu-Au mineralization at Batu Hijau.

4 Conclusion and outlook

Detailed petrographic observations, microthermometry, and LA-ICP-MS analyses of FIs entrapped during or slightly before sulfide precipitation support ore formation at moderate temperatures (350° to 310°C) from a low-salinity high-density fluid during the paint-vein stage characterized by chlorite-sericite alteration. Similar conditions for sulfide precipitation have been reported from several other porphyry copper deposits, such as Santa Rita (Reynolds and Beane 1985), Far Southeast (Hedenquist et al. 1998), El Teniente (Klemm et al. 2007), and Nuevo Chaquiro (Bartos et al. 2017). This study emphasizes that paint-veins and apparently disseminated Cu-Fe-sulfides texturally postdating quartz vein formation carry the greatest part of Cu and probably Au, even in a deposit that was traditionally considered a typical example of high-temperature bornite-rich Cu-Au mineralization.

Acknowledgements

We would like to thank the geology staff at Batu Hijau, who hosted and guided us during our visits. Special thanks go to Oscar Laurent for helping with the LA-ICP-MS analyses and Tobias Zwyer for collecting some of the samples used in this project. This research was funded by the Swiss National Science Foundation (project 200020_166151).

References

Driesner T (2007) The system H₂O-NaCl. II. Correlation for molar volume, enthalpy, and isobaric heat capacity from 0 to 1000 degrees C, 1 to 5000 bar, and 0 to 1 XNaCl. Geochim Cosmochim Acta 71:4902-4919
Driesner T, and Heinrich CA (2007) The system H₂O-NaCl. I. Correlation formulae for phase relations in temperature-pressure-composition from 0 to 1000°C, 0 to 5000 bar, and 0 to 1 XNaCl. Geochim Cosmochim Acta 71:4880-4901
Fournier RO (1999) Hydrothermal processes related to the movement of fluid from plastic to brittle rock in the magmatic-epithermal environment. Econ Geol 94:1193-1211
Jowett EC (1991) Fitting iron and magnesium into the hydrothermal chlorite geothermometer. GAC/MAC/SEG Joint annual meeting, 16, Toronoto, Canada
Magnetite alteration and formation of porphyry Cu (Au) deposits

Huaying Liang, Wenting Huang, Weidong Sun, Long Ren
Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China

Abstract. Porphyry Cu-Au(±Mo) deposits are usually associated with highly oxidized felsic magmas and the sulfur in the magmas is present as sulfate. The high oxidation state not only triggers the destruction of sulfide from the source of magma and formation of magmas with high concentrations of chalcophile element and sulfur, but also leads to enrichment of chalcophile element and sulfur in evolved magmas, given that the sulfur remains as sulfate in the magmas. The sulfur presents mainly as sulfide in porphyry Cu-Au(±Mo) deposits. Magnetite is found in almost all porphyry Cu-Au(±Mo) deposits. It is suggested that a redox reaction of Fe$^{2+}$ to Fe$^{3+}$ and S$^{6+}$ to S$^{2-}$, leading the formation of magnetite provides enough S$^{2-}$ for sulfide precipitation and plays a key role in the formation of porphyry Cu-Au deposits. It is concluded that porphyry ore prospect targeting should be focused on areas with low magnetic susceptibility in regions with high magnetic susceptibility.

1 Sulfur species in porphyry Cu-Au(±Mo) magmas

Giant porphyry Cu-Au(±Mo) deposits contain not only high concentrations of metals such as Cu and Au, but also a very large sulfur budget, usually over 1 billion tons (Chambefort et al. 2008). The high oxidation triggers the destruction of sulfide from the sources of magma and the formation of magmas with high concentrations of chalcophile element and sulfur. Almost all giant porphyry Cu-Au(±Mo) deposits have genetic link to oxidized magmas (Sillitoe 1997; Mungall et al. 2002; Liang et al. 2009; Sun et al. 2013), usually with oxygen fugacity ($\log f_{O_2}$) >FMQ+2 (Sun et al. 2013). Sulfur remains as sulfate in magmas with FMQ>2 (Fig. 1) (Jugo et al. 2005) Anhydrite inclusions in quartz phenocrysts found in the Yulong giant porphyry Cu-Au deposit indicate also that sulfur is the dominant species in oxidized magmas. This keeps magmas sulfide undersaturated during ascending and evolution, which favors enrichment of chalcophile elements and sulfur and provides enough metal and sulfur for the formation of giant porphyry Cu-Au(±Mo) deposits.

2 Sulfur species in porphyry Cu-Au(±Mo) deposits

Ore minerals of porphyry deposits are composed primary of sulfides, such as chalcopyrite, bornite, pyrite, molybdenite, galena, sphalerite, etc. and therefore, the S$^{2-}$ is the dominant species in the porphyry main mineralization stage (Fig. 1c). Daughter mineral assemblages of chalcopyrite and ± anhydrite were found in fluid inclusions from the early stage and main stage mineralization in the Yulong porphyry Cu-Au deposit (Fig. 2a, 2b) (Liang et al. 2009), respectively, suggesting that the S$^{6+}$ and S$^{2-}$ coexist in the early stages of mineralization (Fig. 1b) and S$^{2-}$ is the dominant species in the main stage mineralization (Fig. 1c). It is therefore, that the sulfur remains dominantly as S$^{6+}$ in magma stage, S$^{6+}$ and S$^{2-}$...
in the early mineralization state, and dominantly as S\(^2\) in the main mineralization stage (Fig. 1). The presence of S\(^{2+}\) and S\(^2\) could be due to sulfate reduction or the disproportionation of SO\(_2\) during fluid cooling. The S\(^2\) dominated in main mineralization stage should triggered mainly by sulfate reduction rather than disproportionation of sulfate. The final large scale precipitation of sulfide is controlled by sulfate reduction. What kinds of processes trigger the redox reaction?

3 Magnetite alteration and redox reaction of sulfate to sulfide in porphyry Cu-Au ore forming systems

Sulfur species in magmatic-hydrothermal system are controlled by redox potential (Fig. 1). The redox potential is usually buffered by redox-sensitive elements such as C, H, S and Fe (Evans 2006), through reaction involving mafic minerals (Carmichael 1991) and oxides (Sun et al. 2004). Fe is the most effective and abundant redox agent in magmas. The most abundant mafic silicate minerals in porphries are amphibole and biotite. Biotite usually contains minor amount of Fe\(^{3+}\), while amphibole has Fe\(^{3+}/(Fe^{3+}+Fe^{2+})\) ratios less than 30%. Fe\(^{3+}\) in magnetite accounts for more than 66% percent of the total Fe. Once mafic silicate minerals are replaced by magnetite, a large amount of Fe\(^{2+}\) must be oxidized to Fe\(^{3+}\). The Fe\(^{2+}\) could act as important reducing agent that reduces the S\(^{6+}\) to S\(^2\) in the porphyry ore forming system during magnetite alteration (Sun et al. 2004) as shown by the following equation:

\[
12[FeO] + H_2SO_4 = 4Fe_3O_4 + H_2S \quad (1)
\]

Figure 3. photo showing amphibole replaced by mt, bio. And ksp (a, b) and Mt by Py (c, d). Amph: amphibole, Mt.: magnetite, Ksp: K-feldspar, Bio: biotite, Py: pyrite

Magnetite usually occurs in the potassic alteration zone and shows a close association with K-feldspar (Fig. 3a, b). This association could be illustrated by the following reaction:

\[
8KFe_3AlSi_3O_{10}(OH)_2 + 2H_2SO_4 = 8KAlSi_3O_8 + 8Fe_3O_4 + 8H_2O + 2H_2S \quad (2)
\]

Fe\(^{2+}\) could be transported by low-density aqueous vapor at high pressures in magmatic-hydrothermal ore forming system (Simon et al. 2004). The oxidation of Fe\(^{2+}\) transported by magmatic fluid could form magnetite as shown by the following equation (Field et al 2005):

\[
12FeCl_2 + 12H_2O + H_2SO_4 = 4Fe_3O_4 + 24HCl + H_2S \quad (3)
\]

The above three reactions indicate that the formation of magnetite could transfer S\(^{6+}\) to S\(^2\), which supplies enough reduced sulfur to the porphyry ore forming system, favoring the precipitation of sulfide minerals in porphyry ore forming system.

Magnetite alteration is commonly found in the early alteration stages of porphyry ore deposits (Sillitoe, 1997; Liang et al. 2009). Magnetite in porphyry Cu-Au deposits was inferred to form either prior to potassic alteration, or during the main stage potassic alteration (Arancibia and Clark 1996). Given sulfate is the dominant species in oxidized porphry magmas, magnetite alteration prior to main stage mineralization, which could transform sulfate in magmas to reduced sulfur in mineralization stage, plays a key role in the formation of porphyry Cu-Au deposits.

4 Implication for porphyry ore exploration

Magnetite is abundant in porphyry Cu-Au deposits and it is therefore that ore bearing porphyries are characterized by high magnetic susceptibility. Intense sodic-calcic or potassic alteration would increase the abundance of magnetite. Hydrolytic alteration would destroy magnetite. This is due to the reaction of magnetite with H\(_2\)S to form pyrite in the acidic condition (Fig. 3 c, d). The relatively strong mineralization zone should have low magnetite susceptibility. Porphyry ore prospecting target should focus on areas with low magnetic susceptibility in a region with high magnetic susceptibility.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (Grants 41772065) and the National Key R&D Program of China (Grant 2016YFC0600407).

References


Carmichael ISE (1991) The redox stage of basic and silicis magmas: a reflection of their source regions?. Contributions to Mineralogy and Petrology 103:129-141


Field CW, Zhang L, Dilles JH, Rye RO, Reed MH (2005) Sulfur and oxygen isotopic record in sulfate and sulfide minerals of early, deep, pre-Main Stage porphyry Cu-Mo and late Main Stage base-metal mineral deposits, Butte district, Montana. Chemical Geology 215 (1-4):61-93

Liang HY, Sun WD, Su WC, Zartman RE (2009) Porphyry copper-
gold mineralization at Yulong, China, promoted by decreasing redox potential during magnetite alteration. Economic Geology 104 (9):587-596


Chlorite alteration in porphyry Cu systems: New insights from mineralogy and mineral chemistry

Bing Xiao, Huayong Chen, Yuzhou Feng,
Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China

Pete Hollings
Geology Department, Lakehead University, Canada

Yu Zhang
School of Geosciences and Info-Physics, Central South University, China

Abstract. Chlorite is one of the most widely developed hydrothermal alteration minerals in porphyry deposits, and provides an important tool to investigate the nature of fluid-rock reactions and mass transfer during hydrothermal fluid advection. Samples of chlorite from alteration systems around three large porphyry Cu deposits, i.e., Tuwu (NW China), Atlas (Philippines) and Xiaokelehe (NE China), were used to investigate element transfer between chlorite and pyroxene, amphibole and biotite during alteration.

Hydrothermal titanite occurred together with chlorite in all samples. Titanite formed during chlorite alteration of biotite has higher Al₂O₃ and F contents compared with that formed during hornblende and pyroxene chloritization. There is a clear elemental transition zone which occurs between biotite and chlorite, whereas there are no transitions between hornblende or pyroxene with chlorite. FeO₇ and MgO contents of chlorite are more likely controlled by the crystal structure of the precursor minerals (not only the compositions), whereas TiO₂ and Al₂O₃ are probably controlled by the similar formation temperature of chlorite without obvious influence of precursor minerals. Thus, TiO₂ and Al₂O₃ contents of chlorite could be more suitable to be used as mineral geochemical vectoring tool in exploration of porphyry deposits.

1 Introduction

Chlorite mainly forms through replacement of ferromagnesian minerals (such as biotite, hornblende and pyroxene) as a result of hydrothermal fluids (Walker 1993). The detailed process and mechanism of element transport and enrichment during chlorite alteration is relatively poorly understood (Hart et al. 2016), and the impacts of chemical concentrations of precursor minerals on chlorite have received attention (Wilkinson et al. 2015; Xiao et al. 2018). We focus on chlorite alteration of biotite, hornblende and pyroxene in porphyry deposits, and investigate how the chemistry and texture of precursor minerals affect chlorite compositions based on detailed mineralogical observation and geochemical analysis.

2 Sampling

Granodiorite porphyry samples from Xiaokelehe, quartz diorite porphyry samples from Atlas, and basalt samples from the Tuwu Cu deposit, were collected. Representative samples were examined with EMPA to aid mineral identification and determine compositions. Samples containing chlorite were all selected from major alteration zones of porphyry deposits. They include chlorite alteration of 1) biotite in the Xiaokelehe granodiorite; 2) biotite in the Atlas quartz diorite; 3) hornblende in the Atlas quartz diorite and 4) pyroxene in the Tuwu basalt.

3 Chlorite alteration processes in porphyry deposits

Two approaches have been proposed for using the chemical composition of chlorite to determine the formation temperature: (1) the use of empirical calibrations based on the tetrahedral aluminium (AlIV) occupancy as a function of measured temperature in geothermal systems (Cathelineau 1988), and (2) thermodynamic calculation of equilibrium conditions for chlorites (Walshe 1986). For the thermodynamic method the chlorites must coexist with quartz, which is not consistent within this study. We calculated the chlorite formation temperatures using the chlorite thermometer of Cathelineau (1988) which yielded temperatures of 249 - 278 °C (average of 264 °C) for Xiaokelehe chlorite; 212 - 282 °C (average of 264 °C) for Atlas Type A chlorite; 265 - 304 °C (average of 282 °C) for Atlas Type B chlorite; 254 - 295 °C (average of 273 °C) for Tuwu chlorite. The temperature ranges for all the chlorite studied are broadly the same.

In Xiaokelehe and Atlas samples, chlorite replaced biotite along the cleavage and is associated with the formation of abundant titanite grains. In all samples the K₂O, Na₂O, TiO₂, SiO₂, F and Cl concentrations decrease, while MgO, FeO₇, Al₂O₃ and MnO concentrations increase from biotite to chlorite, over a gradual transition zone. Both titanite and chlorite contain no or limited Na, K and Cl, suggesting that the process of biotite chloritization results in Na, K, and Cl entering the hydrothermal fluid rather than chlorite or titanite. In the
compositional profiles through hornblende and pyroxene to chlorite, there are sharp contacts between hornblende/pyroxene and chlorite. Atlas hornblende contains Na$_2$O = 1.18 – 1.64 wt.% and K$_2$O = 0.21 – 0.47 wt.%, and Tuwu pyroxene contain Na$_2$O = 0.33 – 0.42 wt.%, whereas Na$_2$O and K$_2$O contents of chlorite formed from Atlas hornblende and Tuwu pyroxene are either close to or below the detection limits of EPMA. This suggests that chloritization releases Na and K of Atlas hornblende, and Na of Tuwu pyroxene to enter into the hydrothermal fluid. Biotite and chlorite are both phyllosilicate minerals, whereas pyroxene is a single-chain silicate and hornblende is a double chain silicate. The similarity between the structure of chlorite and biotite means that chlorite is more likely to inherit part of biotite structure during alteration which would explain the gradual transition between biotite and chlorite, compared to the abrupt transition between hornblende/pyroxene and chlorite.

Figure 1. TiO$_2$, MgO, FeO$_7$, and MgO contents of chlorite, biotite, hornblende and pyroxene.

4 Genesis of hydrothermal titanite in chlorite alteration
Titanite is a dominant Ti-bearing phase and widespread accessory mineral in igneous rocks, metamorphic rocks, and hydrothermal mineral deposits, such as porphyry and skarn deposits (Xie et al. 2018). In this study, titanite coexists with chlorite formed by the alteration of biotite,
hornblende and pyroxene in all samples from the three porphyry systems. In Xiaokelehe and Atlas samples with biotite chloritization, needle-like titanite grains occur along cleavage of biotite, whereas it occurs as irregular crystals associated with Atlas hornblende and Tuwu pyroxene chloritization, which may be possibly related to different crystal structure of precursor minerals. Titanite grains in this study all exhibit good negative linear relationships between $\text{Al}_2\text{O}_3 + \text{FeO}_T$ and $\text{TiO}_2$, and positive relationships between $\text{Al}_2\text{O}_3 + \text{FeO}_T$ and $F$, indicating that $\text{Al}$ and $\text{Fe}$ substitute into the Ti octahedral site with an additional Al-involved reaction ($[\text{Al}, \text{Fe}]^{3+} + (\text{F}, \text{OH})^- \leftrightarrow \text{Ti}^{4+} + \text{O}^{2-}$; Xie et al. 2018). In addition, nearly all titanite grains plot within the hydrothermal titanite field consistent with their occurrence with hydrothermal chlorite.

The occurrence of titanite associated with chlorite alteration suggests the transfer of abundant Ca and Ti from the hydrothermal fluid or precursor minerals. The Xiaokelehe biotite, Atlas biotite and hornblende, and Tuwu pyroxene have high TiO$_2$ contents (2.95 – 3.86 wt.%, 3.32 – 4.81 wt.%, 0.85 – 1.43 wt.% and 0.68 – 1.14 wt.%, respectively), whereas Xiaokelehe and Atlas biotite only has minor Ca. This suggests that the Ti was likely derived from the precursor minerals, whereas Ca was derived from hydrothermal fluids and/or precursor minerals (such as hornblende and pyroxene). Our results also suggest that Ti could be transported into hydrothermal solutions of porphyry Cu deposits, although it is typically considered to be an immobile element in hydrothermal environments (Jiang et al. 2005). Titanite formed during chloritization at Xiaokelehe and Atlas contains higher $\text{Al}_2\text{O}_3$ and $F$ contents than titanite formed in Atlas hornblende and Tuwu pyroxene, whereas, Xiaokelehe and Atlas biotite has higher $\text{Al}_2\text{O}_3$ and $F$ contents than Atlas hornblende and Tuwu pyroxene. These results suggest that $\text{Al}_2\text{O}_3$ and $F$ contents of titanite may be controlled by the chemistry of the precursor minerals.

5 Impacts of precursor mineral on chlorite compositions

The hydrothermal fluids that generated chlorite alteration at Xiaokelehe, Atlas, and Tuwu are all related to porphyry systems and were likely broadly similar, consistent with the similar formation temperatures. TiO$_2$ and Al$_2$O$_3$ contents of all the chlorite studies are generally similar (Figs. 1a, c), regardless of the variable TiO$_2$ and Al$_2$O$_3$ contents of precursor minerals (Figs. 1b, d). Xiao et al. (2018) found that TiO$_2$ and Al$_2$O$_3$ contents of chlorite correlate positively with formation temperature of chlorite. This would suggest that TiO$_2$ and Al$_2$O$_3$ contents of chlorite may be mainly controlled by formation temperatures rather than the concentration of the precursor minerals. However, FeO$_T$ and MgO contents of chlorite are influenced by precursor minerals (Figs. 1e-h). For example, FeO$_T$ contents of chlorite increase with its decreasing trend in precursor minerals (Figs. 1e, f); MgO contents are variable in precursor minerals but uniformly high in chlorite altered from biotite (Figs. 1g, h). Obviously, these concentrations are not controlled simply by their abundances in precursor minerals. Instead, these unexpected variations could be caused by different crystal structure of precursor minerals. Compared to pyroxene and hornblende, during chlorite alteration process of biotite, the octahedral-site $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ will be moved out from biotite and more Mg$^{2+}$-Fe$^{2+}$ occupied the octahedral sites in chlorite structure, which can further decrease the FeO$_T$ content of chlorite but the MgO can always be increased due to substitution of Mg and Fe in chlorite (Foster 1962). In summary, FeO and MgO contents of chlorite are clearly affected by precursor minerals (including both composition and texture) compared to TiO$_2$ and Al$_2$O$_3$ which are possibly mainly controlled by temperature or other factors.

Acknowledgements

This study was funded by the Chinese National Science Fund for Chinese National Science Foundation (41702068), Distinguished Young Scholars (41725009) and Chinese academy of sciences strategic pilot science and technology special (XDB18030206).

References

Foster MD (1962) Interpretation of the composition and a classification of the chlorites. Geological Survey Professional Paper
Porphyry Cu(Mo) deposits of the Urals: insights from molybdenite trace element geochemistry

Olga Y. Plotinskaya, Vera D. Abramova
Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow, Russia

Dmitry Bondar
University of Bayreuth, Germany

Reimar Seltmann, John Spratt
Natural History Museum, Department of Earth Sciences, CERCAMS, London, UK

Abstract. The first data on EMPA and LA-ICPMS study of molybdenite from four porphyry deposits of the South and Middle Urals (Tomino, Mikheevskoe and Benkala porphyry Cu and Talitsa porphyry Mo deposits) are presented. It is shown that most trace elements form mineral inclusions within molybdenite in all the deposits studied; only Re and W are most likely to be incorporated into the molybdenite lattice. Porphyry Cu deposits (Tomino and Mikheevskoe) formed within oceanic arc settings are featured by high contents of Re (mostly over 400 ppm) and low contents of W (<10 ppm) in molybdenite; porphyry Cu deposits from Andean-type geotectonic environment (Benkala) are featured by lower Re content (hundreds ppm) and high contents of W (tens ppm) in molybdenite. Molybdenite from porphyry deposits from collisional setting (Talitsa) has low content of Re and elevated W contents (tens ppm). It is demonstrated that trace element geochemistry of molybdenite is a useful tool to define the source of metal components and the geotectonic environment for porphyry Cu(Mo) deposits.

1 Introduction

Porphyry Cu (±Mo,Au) deposits of the Urals (Fig. 1) can be subdivided into the following groups according to their link to subduction zones of different ages (Plotinskaya et al. 2017):

(1) Deposits of the East-Uralian volcanic terrane related to Silurian intra-oceanic arc: porphyry Cu deposits of the Birgilda-Tomino ore cluster and several subeconomic occurrences.

(2) Deposits within the Magnitogorsk volcanic megaterrane linked to the Magnitogorsk intra-oceanic arc which was active from Early Devonian (Emsian) and collided with the East European plate in the Late Devonian (Famennian). These are Middle Devonian Salavat and Voznesenskoe porphyry Cu deposits, and Late Devonian Yubileinoe porphyry Au deposit and Verkhneuralskoe porphyry Mo occurrence.

(3) Deposits located in the Trans-Urals megaterrane and linked to the Late-Devonian to Carboniferous subduction events. This is the Late Devonian to Early Carboniferous Mikheevskoe porphyry Cu deposit linked to an intra-oceanic arc. Tevelev et al. (2006) however supposed a subduction under the accretion prism on the eastern margin of the East-Uralian microcontinent. This group includes also Early Carboniferous deposits formed due to eastward Andean-type subduction under the Kazakh continent (Benkala porphyry Cu deposit and several occurrences).

(4) Continent-continent collision of the East European plate and the Kazakh continent in the Late Carboniferous produced the Talitsa porphyry Mo deposit located in the East Uralian megaterrane.

Figure 1. Simplified tectonic scheme of the Middle and South Urals, and locations of porphyry deposits and occurrences, modified after (Petrov et al. 2007; Plotinskaya et al. 2017). Terranes: WU – West Uralian; CU – Central Uralian; T – Tagyil; M – Magnitogorsk; EU – East Uralian, TU – Trans Uralian (Va – Valerianovka volcanic terrane).
This paper presents first data on EMPA and LA-ICPMS study of molybdenite from selected Cu(Mo) deposits and attempts to discuss the obtained regularities in terms of trace element geochemistry of molybdenite and geotectonic settings of the deposits.

2 Analytical methods

The chemical compositions of ore and gangue minerals were determined using a Zeiss EVO 15LS scanning electron microscope with an Oxford Instruments X-Max EDX detector (Natural History Museum, London). X-ray mapping and point analyses of molybdenite were performed using a Cameca SX-100 electron microprobe with five WDX spectrometers (Natural History Museum, London, UK). Farther details are described in Plotinskaya et al. (2018). The trace element data of molybdenite were acquired using the New Wave 213UP laser coupled with the Thermo X Series2 quadrupole ICP-MS (IGEM RAS, Moscow). The following isotopes were measured: S33, V51, Fe57, Co59, Ni60, Cu65, Zn66, As75, Se77, Mo95, Ag107, Sn118, Cd111, Sb121, Te125, W182, Re185, Re187, Au197, Hg202, Tl205, Pb208, Bi209. Si29, Ti47, and Ca43 were measured in order to reveal mineral inclusions but were not calculated. External standards were in-house pyrrhotite for Re and MASS-1 for the remaining elements; S was used as internal standard based on molybdenite stoichiometry. The analyses were obtained from line profiles with laser diameter 30 and 40 μm, laser frequency of 15 Hz, 5-7mJ input power and 5 μm/s ablation speed.

3 Results

3.1 The Tomino ore field

The Tomino porphyry Cu deposit with 660 Mt @ 0.4% Cu (Russian Copper Company, 2019) consists of two diorite stocks, each ca. 2 km in diameter, dated as 427±6 Ma (U-Pb in zircons) (Grabezhev and Ronkin 2011), intruded into Ordovician basalts. The northern stock hosts the Tomino site, while the southern one – Kalinovskoe site. Molybdenite from the Kalinovskoe deposit was dated by Re-Os as 430.4 ± 2.0 Ma (Tessalina and Plotinskaya 2017; Plotinskaya et al. 2018).

EMPA study of molybdenite from the Kalinovskoe site revealed uneven distribution of Re within single grains of molybdenite with micron-scale zones where Re contents reach 0.95 wt.%. LA-ICPMS data show contents of Re as much as 8.7 to 4540 ppm, geom. mean 621 ppm), W (to 4.3 ppm, geom. mean 0.46 ppm), Se (32 to 350 ppm, geom. mean 146 ppm), Cu, Fe (tens to thousands ppm), Zn, Pb, Bi (several ppm to hundreds ppm), Co, Ni, As, Ag, Te, Au (up to tens ppm), Sb (up to several ppm) (Plotinskaya et al. 2018).

EMPA study of molybdenite from the Tomino site (1 sample) revealed Re-enriched growth zones (up to 0.68 wt.% of Re) within molybdenite flakes (Fig. 2). LA-ICP-MS data also show high contents of Re (2670 to 5800 ppm, geom. mean 3645 ppm), Se (194 to 410 ppm, geom. mean 271 ppm), low contents of W (1.5 to 5.8 ppm), as well as remarkable admixtures of Cu, Fe, Zn (tens to hundreds ppm), Ni, Te (tens ppm), As, Cd, Hg, Pb, (several ppm to tens ppm), Co, Ag, Sb, Au, Bi (up to several ppm).

3.2 The Mikheevskoe deposit

The Mikheevskoe porphyry Cu deposit, with 629 Mt @ 0.41% Cu (Russian Copper Company, 2019), is the economically most significant porphyry Cu deposit in the Urals. Mineralization is hosted by Late Devonian sandstones, tuffstones, basaltic andesites, overlain by Late Devonian to Early Carboniferous basaltic lavas, tuffs, sandstones. Intrusions are represented by quartz diorite stocks and numerous diorite and granodiorite porphyry dykes (Shargorodsky et al. 2005) dated as 356±6 Ma (U-Pb in zircons) (Grabezhev and Ronkin 2011). Molybdenite from the Mikheevskoe deposit was dated by Re-Os as 357.8±1.8 Ma and 356.1±1.4 (Tessalina and Plotinskaya 2017).

Previous EMPA study (Plotinskaya et al. 2015) revealed micron-scale zones with up 1.34 wt.% of Re. LA-ICPMS study revealed contents of Re (83 to 3440 ppm, geom. mean 967 ppm), W (1.0 to 4.9 ppm), Se (124 to 848 ppm, geom. mean 307 ppm), Cu, Fe (tens to thousands ppm), Zn, Pb, Bi (several ppm to hundreds ppm), Co, Ni, As, Ag, Te, Au (up to tens ppm), Sb (up to several ppm) (Plotinskaya et al. 2018).
3.3 The Benkala deposit

The Benkala porphyry Cu deposit (1.56 Mt Cu @ 0.42% Cu according to Frontier Mining (2012)) is associated with Early to Middle Carboniferous intrusions and dykes of the Sokolov-Sarbai diorite–granite complex (porphyritic quartz diorite and granodiorite, and plagiogranite porphyries) hosted by Lower Carboniferous volcano-sedimentary sequence (Gachkevich et al. 1986). Intrusions were dated as 334.7±2.9 Ma (U-Pb in zircons) (Grabezhev et al. 2017).

Molybdenite of the Benkala deposit (1 sample) contains Re (364 to 744 ppm, geom. mean 574 ppm), W (29.2 to 76.8 ppm, geom. mean 46.9 ppm), Se (72 to 120 ppm, geom. mean 96 ppm), Fe (thousands ppm), Cu (hundreds ppm), V, Zn, Pb (tens to hundreds ppm), As, (tens ppm), Co, Ag, Cd, (several ppm to tens ppm), Ni, Sb, Te, Au, Hg, Bi (up to several ppm).

3.4 The Talitsa deposit

The Talitsa Mo porphyry deposit is located in the western margin of the East Uralian megaterrane in the Middle Urals within a sub-alkaline intrusion of about 4 km² hosted by Devonian ultrabasic rocks and rhyolite-basalt volcanics. The Talitsa intrusion consists of granodiorite to quartz monzonites and minor monzodiorites cross-cut by granodiorite to quartz monzonite and granite porphyry stocks and dykes (Azovskova and Grabezhev 2008). The deposit was dated as 297.4±2.3 Ma (U-Pb in zircon) (Smirnov et al. 2017) and 298.3±1.3 Ma (Re-Os in molybdenite) (Tessalina and Plotinskaya 2017).

Molybdenite of the Talitsa deposit (5 samples, fig. 3) contains Re (40.8 to 388 ppm, geom. mean 109 ppm), W (6.0 to 232 ppm, geom. mean 17.4), Se (10 to 520 ppm, geom. mean 166 ppm), Fe, Cu, Zn, Sb, Pb, Bi (tens to thousands ppm), V, (tens to hundreds ppm), Ni, As, Cd, Ag, Te, Hg (up to hundreds ppm), Co (up to tens ppm), (several ppm to tens ppm), Au (up to several ppm).

4 Discussion

4.1 Trace elements incorporation in molybdenite

Most trace elements have positive correlations with each other (Fe, Co, Cu, Zn, Ni, As, Se, Ag, Cd, Sb, Te, Ti, Pb, and Bi) because they occur mainly as micro- to nanoscale mineral inclusions within molybdenite (Figs. 2, 3). Re and W usually have neither positive nor negative correlation with all other trace elements but show a weak negative correlation with each other (−0.26 for the whole dataset, −0.43 for the Mikheevskoe deposit). This means both Re and W substitute for Mo in the molybdenite structure. However in some LA-ICPMS profiles in molybdenite from the Talitsa deposit synchronous peaks of W182 and Ti47 indicate inclusions of rutile with W impurities (Fig. 3). Thus, the highest W contents observed in this study (over 60 ppm), are likely linked to mineral inclusions.

4.2 Sources of rhenium and other metals

It is noteworthy that both Re and W are inhomogeneously distributed even within single grains of molybdenite (Figs. 2, 3) and vary in an order of magnitude within a deposit. Despite this, molybdenite from the deposits studied shows a significant difference in both Re and W contents. Molybdenite from Tomino and Mikheevskoe is featured by the highest contents of Re (mostly over 400 ppm) and lowest contents of W (<10 ppm), while molybdenite from the Talitsa deposit has lowest contents of Re (mainly below 200 ppm) and significant admixtures of W (6 to 50 ppm).

Mao et al. (2013) proposed that <10 ppm Re in molybdenite indicates crustal sources, 10 to 100 ppm indicates a mixed mantle/crustal source and >100 ppm Re in molybdenite indicates molybdenite derived from mantle sources. Therefore, the high Re contents of most molybdenites from Tomino, Mikheevskoe and Benkala deposits may indicate a predominantly mantle source for the metals, while molybdenite from the Talitsa deposit indicates a mixed mantle/crustal source (Fig. 4). Remarkable input of mantle material is in good agreement with a subduction setting of porphyry Cu deposits. Controls of W contents in molybdenite are not well understood. However continental crust is known to be enriched in W relative to mantle (Holland and Turekian...
and it can be supposed that significant input of crustal material may reflect elevated contents of W in molybdenite. It explains low contents of W in molybdenite from porphyry copper deposits from oceanic arc settings (e.g. in Tomino) and higher W admixtures in molybdenite from deposits formed on continental crust, i.e. Benkala deposit formed within a continental margin and Talitsa deposit formed due to continent-continent collision.

Figure 4. Re vs. W contents in molybdenite from the porphyry Cu(Mo) deposits studied. Fields for mixed mantle/crustal and mantle Re sources are from Mao et al. (2013) and references therein.

5 Conclusions

(1) Most trace elements form mineral inclusions within molybdenite in all deposits studied here; only Re and W are most likely to be incorporated into the molybdenite lattice.

(2) Porphyry Cu deposits formed within oceanic arc settings are featured by high contents of Re (mostly over 400 ppm) and low contents of W (<10 ppm) in molybdenite.

(3) Porphyry Cu deposits from Andean-type geotectonic environment (Benkala) are featured by lower Re content (hundreds ppm) and high contents of W (tens ppm) in molybdenite.

(4) Molybdenite from porphyry deposits from collisional setting (Talitsa) has low content of Re and elevated W contents (tens ppm).

(5) These results demonstrate that the study of trace element geochemistry molybdenite is a useful tool to define source of metal components in porphyry Cu(Mo) deposits.

Acknowledgements

This study was supported by RFBR #19-05-00254, 19-05-00476 and by NHM (CERCAMS program). RS acknowledges funding under NERC Grant NE/P017452/1 “From arc magmas to ores (FAMOS): A mineral systems approach”.

References


Identifying a superimposed porphyry-epithermal system based on alteration-mineralization mapping: example from the Cretaceous Dongnan Cu deposit, Zijinshan ore district (SE China)

Gan Duan
School of Earth, Atmosphere and Environment, Monash University, Australia

Huayong Chen
Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, PRChina

Abstract. The temporal evolution of alteration in porphyry-epithermal systems has been well established based on a porphyry-centered system, with high-sulfidation (HS) epithermal deposits overlapping the porphyry system (telescoping), or adjacent to a deeper porphyry deposit. There is still conjecture on the origin of hydrothermal fluids responsible for telescoped deposits, especially where multiple hydrothermal events occur. The Dongnan Cu (-Mo) deposit with both HS and porphyry alteration, located around 1 km to the southeast of Zijinshan HS epithermal deposit and around 1.5 km to the southwest of Luoboling porphyry deposit within the Zijinshan ore district (ZOD), offers a window to investigate the origins of hydrothermal fluids responsible for these mineralization-alteration events in such porphyry-epithermal mineral systems. Detailed field and drill logging and alteration mineral mapping by shortwave infrared spectroscopy analysis (SWIR) show that HS-type alteration decreases from west to east in the ZOD, whilst the east part of ZOD is dominated by porphyry-type alteration. The distribution of alteration minerals indicates that the hydrothermal fluids for the porphyry-type and HS-type alteration at Dongnan deposit come separately from east and west, suggesting that multiple magmatic centers exist in the ZOD, which contributes to the understanding of ore genesis of this superimposed porphyry-epithermal system and supports further mineral exploration in the Zijinshan Ore district.

1 Introduction

The large-size Zijinshan porphyry-epithermal Cu-Au-Mo-Ag ore district is located in the southwestern Fujian Province of Southeast China (Fig. 1; So et al. 1998) and in the Circum-Pacific porphyry metallogenic domain (Gao et al. 2018). By the end of 2014, the proven reserves in the Zijinshan ore district comprise 400 t Au, 4.14 Mt Cu, 6339 t Ag and 0.11 Mt Mo (Zhang 2013). The Zijinshan Cu-Au mineralization, as the first recognized Cretaceous HS epithermal deposit in mainland China, hosts a reserve of 3 Mt Cu (0.36%) and 300 t Au (0.2g/t ~ 0.5g/t) (Zhang 2013). The Luoboling deposit is currently the largest porphyry deposit in the ZOD, with proven reserves of 1.4 Mt Cu (0.39%) and 0.11 Mt Mo (0.036%; Zhang, 2013). The newly discovered and currently explored Dongnan Cu (-Mo) deposit is located between the Zijinshan deposit and the Luoboling deposit (Duan et al. 2017), showing both HS epithermal deposit and porphyry deposit characteristics, with a current estimated reserve of about 0.1 Mt contained Cu metal at 0.4% and 3,000 t Mo at 0.012% (Zijin Mining Group Co. 2014).

Previous research has been mainly dedicated to the famous Zijinshan and Luoboling deposits (Huang et al., 2018; Zhong et al. 2018), which generated a great wealth of data on fluid inclusions, stable isotope geochemistry, geochronology and structural geology (So et al. 1998; Jiang et al. 2013; Piquer et al. 2017). It is now widely accepted that the Zijinshan deposit is a HS epithermal Cu-Au deposit, whilst the Luoboling deposit is a porphyry Cu-Mo deposit (Zhong et al. 2014; Zhong et al. 2018). However, a key question for the ZOD is whether the porphyry and HS mineralization processes are associated with a single fluid subjected to changing physical conditions, or by a series of superimposed events that involved multiple fluid sources from different magmatic centers (Blundy et al. 2015; Weis et al. 2012; Wilkinson 2013).

In this study, we used detailed drill hole logging data and alteration mineral SWIR mapping to refine the understanding of hydrothermal fluids responsible for both epithermal and porphyry characteristic minerals from Dongnan deposit. We consider that multiple magmatic fluids came separately from Zijinshan deposit and Luoboling deposit and resulted in telescoping of multiple alteration events at Dongnan deposit. It provides important clues not only to the relationships between porphyry and HS deposits, but also serves as an example where porphyry and epithermal deposits are spatially connected, yet they may ultimately originate from different magmatic-hydrothermal sources.

2 Regional geology

The ZOD is located in the Cathaysia Fold Belt, southeast China (Fig. 1a). Many different deposit types have been identified so far, such as the Zijinshan HS epithermal Cu-Au deposit (So et al. 1998; Zhang et al. 2003), the Luoboling porphyry Cu-Mo deposit (Zhong et al. 2011),
the Yueyang low-sulfidation (LS) epithermal Ag-Au-Cu deposit (Zhong et al. 2018), the Wuziqilong Cu deposit (Chen et al. 2011), the Erniaogou Cu-Au deposit (Lin et al. 2012), and the Longjiangting Cu deposit (Fig. 1b; Chen et al. 2015).

The exposed strata in the ZOD consist of Neoproterozoic phyllite and fine-grained meta-sandstone unconformably overlain by Devonian-Carboniferous clastic rocks and limestone (Fig. 1b). Early Cretaceous volcanic rocks crop out in the northwestern part of the ore district and in the Shanghang Volcanic Basin (Zhang et al. 2001). Middle to Late Jurassic and Early Cretaceous magmatic rocks dominate the ore district (Zhang et al. 2001; Jiang et al. 2013). The Middle Jurassic Zijinshan granite complex in the southeastern part of the ore district, which hosts the Zijinshan HS epithermal deposit, comprises the multiphase Jingmei, Wulongsi, and Jinglongqiao granitic plutons (Zhang et al. 2001). Late Jurassic Caixi monzogranite (Yu et al. 2013) in the northeastern part of the ore district intruded the Wulongsi pluton (Mao et al. 2004). The Early Cretaceous NNE-trending Sifang granodiorite (Jiang et al. 2013) exposed in the northeastern ZOD was emplaced into the Wulongsi and Caixi plutons (Zhang et al. 2001). The Cretaceous Luoboling granodiorite porphyry in the northeastern Zijinshan ore district intruded the Sifang granodiorite (Fig. 1c; Zhang et al. 2001).

3 Geology of the Dongnan deposit

The Dongnan deposit is located between the Zijinshan and Luoboling deposits (Fig. 1b), and NW- and NNE-trending faults are very common in the study area (Figs. 1b and 2a).

Figure 1. (A) Tectonic map showing the location of the study area (modified after Mao et al. 2013). (B) Regional tectonic framework of the ZOD (modified after Jiang et al. 2013).

Figure 2. (A) Geologic map of the Dongnan deposit (modified from the Zijin Mining Group, 2014). (B) The NE-trending sketch profile of the Dongnan deposit.

Two major magmatic episodes have been identified at Dongnan, including a Middle to Late Jurassic (ca. 165 – 150 Ma) and a Cretaceous one which can be further divided into late Early Cretaceous (ca. 110 – 105 Ma) and early Late Cretaceous (ca. 100 – 95 Ma). The Middle to Late Jurassic rocks include the Caixi monzogranite and Wulongsi granite. The late Early Cretaceous rocks include the Sifang granodiorite, Luoboling granodiorite porphyry, quartz diorite porphyry and dacite porphyry, whilst the early Late Cretaceous rocks include rhyodacite and rhyolite. These igneous rocks show clear temporal and spatial relationships in the Dongnan deposit area (Fig. 2). The plutons exposed are mainly the Wulongsi granite and its intruding Sifang granodiorite (Figs. 2a and 2b), with the latter being intruded by the Luoboling pluton at depth (Fig. 2b). Stocks of quartz diorite porphyry and dacite porphyry are also present, with the former intruding the Sifang granodiorite and the latter intruding all the Sifang granodiorite, the Wulongsi pluton and Luoboling granodiorite porphyry (Fig. 2b; Duan et al. 2017). It is noticeable that Wulongsi granite has been severely brecciated at west Dongnan deposit due to intense hydrothermal fluid events.

In order to outline mineralization and alteration distribution of Dongnan deposit, a total of ten drill holes (around 6.8 km length in total) were chosen for detailed mineralization and alteration logging. These drill holes are distributed almost evenly in Dongnan deposit (Fig. 2a), thus can outline main mineralization and alteration zonation within Dongnan deposit. Two alteration and mineralization types (porphyry and HS epithermal) were recognized from these drill holes in field, of which the porphyry-type occurs in the Luoboling granodiorite porphyry and Sifang granodiorite stocks, and the HS epithermal-type occurs in the Sifang granodiorite and the hydrothermal breccia at shallow level (Fig. 2b). Both porphyry-type and epithermal-type ores occur as lenses, in which the former is ca. 600 m long and 30 to 50 m wide, and the latter is ca. 200 m long and 50 m wide (Fig. 2b). Porphyry-type mineralization mainly occurs as disseminated ore and quartz-sulfide veins (quartz +
chalcopyrite + pyrite + molybdenite + muscovite ± anhydrite ± K-feldspar). HS epithermal-type mineralization mainly occurs as disseminated ore (covellite + digenite + pyrite ± dickite ± alunite ± pyrophyllite).

4 Distribution of alteration minerals based on SWIR analysis

Since hydrothermal alteration at the Dongnan deposit significantly overlaps with each other, it is hard to strictly separate different alteration minerals merely by field observation. In order to solve this problem, SWIR analysis was carried out to help identify different hydrothermal alteration minerals. Around 160 samples (systematically spaced at 10 m to 50 m intervals) from six drill holes in cross sections A-A’ and B-B’ were used for TerraSpec SWIR at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). More details about SWIR method see Hermann et al. (2001).

The dickite and kaolinite alteration zones overlap each other in the upper parts of the cross section, particularly in the Wulongsi pluton, hydrothermal breccia, dacite porphyry and part of the Sifang granodiorite. The kaolinite zone is much wider than the dickite zone, and it is difficult to distinguish hypogene kaolinite from supergene kaolinite. The pyrophyllite zone in section A-A’ lies below the dickite zone in the Sifang granodiorite, and partly overlaps the kaolinite zone. The pyrophyllite zone in section B-B’ lies slightly below but mainly overlaps the dickite zone. The alunite zone in section A-A’ comprises two parts: the upper part is closely associated with the hydrothermal breccia, and alunite occurring in this zone is also within the dickite zone; the lower part has close spatial relationships with pyrophyllite alteration. The alunite zone in section B-B’ also comprises two parts: the upper part (in ZK3220 and ZK4016) is closely associated with the hydrothermal breccia, whereas, the lower part (in ZK4806 and ZK5605) overlaps both the dickite and pyrophyllite zones.

Muscovite is disseminated in section A-A’ and section B-B’. In both sections, muscovite mainly occurs in the Wulongsi granodiorite and the Sifang granodiorite and is a minor phase in the Luoboling granodiorite, from the surface to ca. 500 m deep. The illite zone in the section A-A’ is narrow, and lies below the muscovite, pyrophyllite, dickite and kaolinite zones in the upper parts of the Luoboling granodiorite, with a minor illite zone in the upper parts of the dacite porphyry and the Sifang granodiorite. The illite zone from section B-B’ comprises two parts: the upper part in the Sifang granodiorite and the lower part in the Luoboling granodiorite. It is observed that in ZK5605 the pyrophyllite and alunite zones are located approximately between the two illite zones. The illite-montmorillonite zone is in the bottom of the sections in the Luoboling granodiorite porphyry and close to the illite zone of both sections. The illite-montmorillonite zone in the shallow quartz diorite porphyry is isolated and is likely unrelated to the illite-montmorillonite zone associated with deeper plutons.

5 Discussion

In Dongnan, porphyry type alteration characterized by phyllic alteration (muscovite + quartz + pyrite) is an early alteration stage. Detailed drill core logging and mapping show that the porphyry-type orebody at Dongnan stretches northeast into the Luoboling deposit and becomes part of the main orebody of the Luoboling deposit, which indicates that the deep porphyry-type orebody at Dongnan is a peripheral part of the Luoboling deposit. It is reasonable to suggest that Luoboling porphyry deposit is responsible for Dongnan porphyry-type alteration.

It is observed that high-sulfidation epithermal alteration (e.g. alunite, dickite and pyrophyllite) only occurs in the western part of the ZOD, superimposed on the original porphyry phyllic alteration and not in the eastern part. At least two HS alteration stages exist, one is responsible for dickite + alunite alteration and another is for alunite + pyrophyllite alteration, as pyrophyllite was overprinted by dickite. The hydrothermal fluid for the areas of HS epithermal alteration may come either from Zijinshan deposit or Luoboling porphyry deposit. The pyrophyllite alteration zone in Dongnan decreases sharply from southwest to northeast, directly suggesting that the related high-sulfidation fluid comes from the southwest direction of the Dongnan deposit. Even though pyrophyllite alteration is extensively superimposed by dickite alteration in the western surface of the Dongnan deposit, the telescoped extent decreased from west to east. This decreasing trend from west to east suggests that the fluid attributed to the HS stage at Dongnan was likely derived from the western Zijinshan HS epithermal deposit. In addition, the illite surrounds pyrophyllite in horizontal level in cross-section B-B’, suggesting that epithermal fluid for pyrophyllite from west in a horizontal direction rather than vertical direction. We suggest that the HS epithermal fluid from the Zijinshan deposit migrated in east direction to the Dongnan deposit and Luoboling deposit. It resulted in intense telescoping of HS alteration on the original Dongnan porphyry deposit and partly superimposed on west part of Luoboling deposit.

6 Exploration implications

The results of this study show that even though HS epithermal deposits and porphyry deposits may be different expressions of the same system, we found evidence that multiple magmatic centers may exist and are separately responsible for telescoped epithermal and porphyry mineralization systems. For the Zijinshan and Dongnan deposits, there is still considerable exploration potential for porphyry-style mineralization at depth. On a global or mining district scale, it is important to investigate whether porphyry-epithermal systems have formed from a single magmatic pluton, or separately with genetically unique magmatic centers, but subsequently telescoped. It is therefore necessary to investigate and explore for magmatic centers within high-sulfidation alteration zones (lithocaps) in known districts of porphyry mineralization.
Acknowledgements

We thank the staff of the Zijin Mining Co. Ltd. for their field assistance. This research was financially supported by the China National Funds for Distinguished Young Scientists (No.41725009).

References

So CS, Zhang DQ, Yun ST, Li DX (1998) Alteration mineralization zoning and fluid inclusions of the high sulfidation epithermal Cu-Au mineralization at Zijinshan, Fujian province, China. Econ Geol 93:961–980
Asynchronous formation of the adjacent epithermal Au-Cu and porphyry Cu-Mo deposits in the Zijinshan orefield, southeast China

Wenting Huang, Huaying Liang
Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences

Abstract. Adjacent high-sulfidation epithermal (HSE) and porphyry deposits often have similar Cu-Au metal associations, are co-genetic, and formed contemporaneously. The Zijinshan ore field (ZOF), the largest Au producer in China, contains a series of HSE Au-Cu and porphyry Cu-Mo deposits. The new age data indicate that the main HSE Au-Cu mineralizing event occurred at ca. 113 Ma. In comparison, the adjacent porphyry Cu-Mo mineralization formed at ca. 104 Ma, ca. 9 Myr after the HSE event. The volcanic rocks associated with the HSE Au-Cu mineralization yield zircon \(\epsilon_{Hf}(t)\) values from -4.1 to 0.3, whereas the Cu-Mo mineralized porphyry has lower zircon \(\epsilon_{Hf}(t)\) values (-4.5 to -1.2), suggesting that the magmas that formed the latter intrusion were derived from a source containing more crustal material than the magmas associated with the HSE mineralization. The differences in the timing of mineralization and the sources of the magmas indicate that the adjacent HSE and porphyry deposits in the ZOF formed from different magmatic-hydrothermal systems that controlled the different metal associations of the mineralizing systems. The results also show that not all adjacent porphyry and epithermal deposits, especially those with different metal associations, are co-genetic.

1 Introduction

Porphyry and high-sulfidation epithermal (HSE) mineralizing systems represent important sources of Cu, Mo, and Au (e.g. Heinrich et al. 1999) and are commonly closely spatially associated (e.g. Arribas et al. 1995). A genetic link has been proposed for these types of mineral deposits (e.g. Hedenquist and Lowenstern 1994). Co-genetic porphyry and HSE deposits usually have similar Cu and Au metal associations (e.g. Deyell and Hedenquist 2011) because both Cu and Au can be transported as stable chloride complexes in high-temperature saline fluids (Hemley and Hunt 1992) before they coprecipitate (e.g. Heinrich et al. 2004). Such co-genetic deposits form contemporaneously, as evidenced by ages that are within uncertainty of each other (e.g. Arribas et al. 1995).

The Zijinshan orefield (ZOF) is located in Fujian Province and is the richest Au-Cu mining area in southeast China (Zhang 2013). Several epithermal and porphyry deposits have been identified within the ZOF, including the Zijinshan HSE Au-Cu deposit, which is the largest epithermal deposit in China, and the Luoboling porphyry Cu-Mo deposit, which represents the largest porphyry deposit in southeast China (Zhang 2013). These two HSE and porphyry deposits are thought to be co-genetic, forming from the same magmatic-hydrothermal system (e.g. So et al. 1998; Zhang et al. 2001; Jiang et al. 2013). However, this co-genetic model for the ZOF is unlikely to be correct for a number of reasons. Firstly, the Zijinshan HSE deposit has an Au-Cu metal association, whereas the adjacent Luoboling porphyry deposit has a Cu-Mo metal association but contains low concentrations of Au (< 0.1 ppm). This pair of HSE Au-Cu and porphyry Cu-Mo deposits is different from the majority of adjacent and co-genetic HSE and porphyry deposits that have similar Au-Cu associations (Heinrich et al. 2004). Secondly, the co-genetic model is not supported by age data, as the porphyry mineralization is thought to have formed at ca. 104 Ma (e.g. Zhong et al. 2014), whereas the timing of epithermal mineralization remains poorly constrained.

This study presents a new robust zircon U-Pb age and muscovite \(^{40}\text{Ar}^{39}\text{Ar}\) ages for the Zijinshan HSE deposit to investigate the relationship between the deposits. We also determined the zircon Hf isotopic composition of a series of igneous rocks in the ZOF to understand variation in the sources of magmas associated with the deposits and their contrasting metal associations.

2 Geological setting

The ZOF is located in the eastern part of the Cathaysian fold belt in southeast China. There are two stages of magmatism, including the Late Jurassic and the Early Cretaceous, in the ZOF. The deposits in the ZOF were genetic-related with the Cretaceous magmatism (e.g. So et al. 1998; Jiang et al. 2013).

The ZOF contains numerous epithermal and porphyry deposits, including the giant Zijinshan HSE Au-Cu deposit, the large Longjiangting intermediate-sulfidation epithermal Cu-Ag-Au deposit, the large Yueyang low-sulfidation Ag-Au-Cu deposit, the small Wuziqilong Cu-Ag (Au) deposit, the large Luoboling porphyry Cu-Mo deposit, the small Jinmei porphyry Cu-Mo deposit and the Ermiaogou epithermal Cu-Au deposit. These deposits contain a total of 399 tons of Au, 6,400 thousand tons of Cu, 110 thousand tons of Ag, 4.137 million tons of Cu, and 110 thousand tons of Mo (Zhang 2013).

The Zijinshan HSE Au-Cu deposit is located in the central ZOF and is related to an early episode of Shimaoshan Group volcanism (So et al. 1998). The ore-hosting volcanic rocks have undergone pervasive hydrothermal alteration. In brief, there are four zones between the shallow and central alteration zones, and the
deeper alteration zones in the deposit, namely (1) a silicic-alteration (Q) zone, (2) an alunite-alteration (Alu-Q) zone, (3) a dickite alteration (Q-Alu-Di-Phy) zone, and (4) a sericite alteration (Phy) zone (So et al. 1998).

The Luoboling porphyry Cu-Mo deposit is located in the northeastern ZOF. Detailed geo-chronological research indicates the presence of two stages of mineralization-related granodiorite porphyry magmatism that yield zircon U-Pb ages of ca. 103 Ma and ca. 97 Ma (e.g. Huang et al. 2013).

### 3 Muscovite Ar-Ar ages

Sample ZJ-27 was collected from a quartz-muscovite-dickite-pyrite veinlet that is cut by quartz-alunite altered breccia (Fig. 1A) from the Q-Alu-Di-Phy zone. It yielded a flat age spectrum after stepwise laser heating. The main plateau consists of 16 successive steps (from steps 4 to 19) that represent 95.75% of the 39Ar released and yield a plateau age of 113.4 ± 1.1 Ma with a MSWD of 0.25 (Fig. 2A).

Sample LJ-04 was collected from an outcropping quartz-muscovite-pyrite veinlet that cuts an alunite-dickite altered rock (Fig. 1B). Removing the first and last few steps, data for muscovite sample LJ-04 yielded a total of 17 successive steps (4 to 20) that represent 82.74% of 39Ar released from the sample. These steps define the main plateau for this sample, yielding a plateau age of 110.4 ± 1.3 Ma with a MSWD of 0.12 (Fig. 2B).

Both samples yield initial 40Ar/39Ar values of 291 ± 14 and 292 ± 16, respectively, which are within uncertainty of the atmospheric argon value of 295.5 (Renne et al. 2009), indicating that the muscovite did not include inherited or excess 40Ar. Their plateau ages (113.4 ± 1.1 Ma and 110.4 ± 1.3 Ma) are therefore interpreted to represent the timing of crystallization of the muscovite.

### 4 Zircon U-Pb ages

Sample ZJ1505 is from the crypto-explosive breccia (Fig. 3) and yields zircon U-Pb ages from 108.5 to 630 Ma. Two spots with U-Pb ages of 628 and 630 Ma represent inherited zircons, and a further seven zircons yield U-Pb ages of 137 - 167 Ma that may represent fragments derived from Jurassic granites. The remaining seven zircons yield a U-Pb age for the crypto-explosive breccia of 112.9 ± 1.2 Ma with a MSWD of 0.96.

### 5 Zircon Hf isotopic compositions

Zircons within the crypto-explosive breccia (sample ZJ1502) yield 176Hf/177Hf ratios of 0.282718-0.282661 and εHf (t) values from -1.5 to 0.5. These zircons have associated two-stage Hf model ages (TDM2) of 1140 to 1268 Ma.

Zircons from the Luoboling granodiorite porphyry have 176Hf/177Hf ratios of 0.282583-0.282674, corresponding to εHf (t) values from -4.5 to -1.2. Their two-stage Hf model ages range from 1214 to 1447 Ma.

### 6 Discussions

#### 6.1 Asynchronous formation of porphyry and epithermal mineralization within the ZOF

Previous geochronological analysis of the Zijinshan deposit yielded four K-Ar ages on alunite from 82 to 111.7 Ma (Zhou and Chen 1996; Zhang et al. 2005), two Rb-Sr isochron ages on quartz-hosted fluid inclusions of 100 and 122 Ma (Zhou and Chen 1996), and three Rb-Sr isochron ages on whole-rock samples from 110 to 124 Ma (Chen 1996; Mao et al. 2002). The large range of these ages (from 124 to 82 Ma) suggests that both the alunite K-Ar system and the Rb-Sr system within these samples were disturbed by later hydrothermal events within the ZOF. Jiang et al. (2017) reported Re-Os model ages that range from 142 to 82 Ma for pyrite from the Zijinshan deposit (Jiang et al. 2017). This indicates that these pyrites formed over several stages of hydrothermal activity (Cardon et al. 2008).

Muscovite is a common mineral within the root zone of
porphyry Cu deposits (Seedorff et al. 2008) and in epithermal deposits. Muscovite has a radiogenic argon closure temperature of either 270°C - 325°C (Snee et al. 1988) or up to 410 °C (Hames and Bowring 1994; Kirschner et al. 1996). This means that muscovite 40Ar-39Ar results should more accurately record the mineralization age of an ore deposit that underwent multi-stage hydrothermal activity.

Some quartz-muscovite-pyrite veins cut the alunite-dickite alteration within the ZOF (Fig. 1B), indicating that the muscovite formed later than the alteration. This indicates that the 40Ar-39Ar plateau age (110.4 ± 1.3 Ma) of the muscovite represents a minimum age for the alunite-dickite alteration. This in turn indicates that the hydrothermal activity associated with the formation of the HSE Cu-Au mineralization occurred before ca. 110 Ma.

The Q-Alu-Di-Phy zone also contains disseminated muscovite and quartz-muscovite-dickite-pyrite veinlet in volcanic breccia (Fig. 1A). The planar crystal boundaries between muscovite and dickite suggest that these minerals formed contemporaneously. On a smaller scale, the quartz-muscovite-dickite-pyrite assemblage is cut by an alunite-altered breccia (Fig. 1A). These observations suggest that the epithermal mineralization-related muscovite formed contemporaneously with the dickite-alteration but earlier than the alunite-alteration. The 40Ar-39Ar plateau age (113.4 ± 1.1 Ma) of the muscovite therefore constrains the upper age of the alunite alteration to ca.113 Ma.

In addition, the crypto-explosive breccia, which containing clasts of hydrothermal sulfide mineralization (Fig. 3B), yields a zircon U-Pb age of 112.9 ± 1.2 Ma. It represents a minimum age for the hydrothermal sulfide ores within the deposit. The 40Ar-39Ar plateau age of the muscovite that is co-genetic with the dickite is within uncertainty of the zircon U-Pb age of the crypto-explosive breccia, again suggesting that the HSE Cu-Au mineralization formed at ca. 113 Ma.

Previously reported molybdenite Re-Os isochron ages of Luoboling porphyry Cu-Mo deposit is ca. 104 Ma (eg. Zhong et al. 2014). These age data indicate that the porphyry Cu-Mo mineralization formed ca. 9 Myr later than the main HSE mineralization. In other words, the adjacent HSE Au-Cu and porphyry Cu-Mo deposits within the ZOF are associated with two distinct episodes of magmatism and are not genetically linked.

6.2 Magmatic sources evolution and implications for metal associations

The various metal associations within the Zijinshan Cu-Au and Luoboling Cu-Mo deposits were originally thought to reflect metal zoning resulting from hydrothermal precipitation in a porphyry-epithermal system (e.g. Li and Jiang 2017). However, our new geo-chronological data indicate that these two deposits formed during distinct hydrothermal events. It means that their contrasting metal associations reflect different magmatic processes.

Magmatic-hydrothermal deposits have variable metal associations and Cu/Au ratios (eg. Halter et al. 2002; Richards 2011) that are controlled by the nature of the sources of magmas associated with the deposits. For example, the mantle contains higher concentrations of Cu (145 ppm; Gill, 1981) and Au (Rudnick and Gao 2003) than the bulk continental crust (Cu = 27 ppm; Rudnick and Gao 2003), whereas the majority of Mo is derived from continental crustal sources (eg. Klemm et al. 2008). This means that magmas derived from different sources are usually associated with mineral deposits with different metal compositions (e.g. Richards 2011). In addition, magmatic processes might also affect the metal associations and metal ratios within mineral deposits (e.g. Halter et al. 2002). Residual sulfide phases in sources or magma could affect the Cu/Au ratios of porphyry deposits because the partition coefficients for Au partitioning into sulfide phases relative to silicate melts (D(Au)_{sulfide/silicate~melt} = 2000-20,000, Li and Audétat 2013) are larger than those for both Cu (D(Cu)_{sulfide/silicate~melt} = 550-10,000; Jugo et al. 1999; Halter et al. 2002) and Mo (D(Mo)_{sulfide/silicate~melt} = 15-200, Li and Audétat 2012). However, the Cretaceous magmatism recorded within the ZOF is highly oxidized (eg. Xu et al. 2017), which could have suppressed the fractionation of sulfide during the evolution of magmas within this system. Consequently, the different metal associations within the Zijinshan and Luoboling deposits were possibly controlled by variations in magma source composition rather than the effect of residual sulfide phases.

The zircon εHf(t) values of the ZOF igneous rocks show a positive correlation with their zircon U-Pb ages, where crypto-explosive breccia associated with the Zijinshan HSE Au-Cu mineralization (112.9 ± 1.2 Ma) and the Luoboling granodiorite porphyry (103.8 ± 0.9 Ma) have εHf(t) values of -1.5 to -0.5 and -4.5 to -1.2, respectively. The ca. 103 Ma magmas associated with the porphyry Cu-Mo

Figure 4. Schematic diagrams showing a possible model for the genesis of Cretaceous igneous rocks and related mineralization within the ZOF. (A) Mantle-derived magmas mixed with crustal material to produce Au-Cu enriched magmas that were emplaced in the ZOF at ca. 113 Ma, forming the Zijinshan HSE Au-Cu deposit. (B) Continuing crust-mantle mixing added crustal materials into the magmas in this area, eventually generating the Cu-Mo enriched magmas that were emplaced at ca. 103 Ma and formed the Luoboling porphyry Cu-Mo deposit.

Magmatic hydrothermal systems: from Porphyry to Epithermal
mineralization were most likely derived from a source containing more crustal material (Fig. 4B) than the ca. 110 Ma magmas associated with the epithermal Au-Cu mineralization in the ZOF (Fig. 4A). These distinct source variations could be a controlling factor on the different metal associations present within the adjacent HSE Au-Cu and porphyry Cu-Mo deposits in the ZOF.

Acknowledgements

This work was financially supported by the Natural Science Foundation of China (grants 41502073 and 41772065) and the National Key R&D Program of China (grant 2016YFC0600407).

References


Mineralogical and geochemical evidence of late epithermal alteration in the Kışladağ porphyry gold deposit, Uşak, Western Turkey

Ömer Bozkaya, Gülcen Bozkaya
Pamukkale University, Turkey

Nurullah Hanilçi, Davut Laçin
Istanbul-Cerrahpaşa University, Turkey

David A. Banks
University of Leeds, United Kingdom

I. Tonguc Uysal
Australian Resources Research Center (ARRC), CSIRO, Australia

Abstract. The Kışladağ porphyry gold deposit is related to Miocene intrusive and sub-volcanic rocks that resulted from an extensional tectonic regime in western Anatolia. The main lithologies of the deposit are quartz-trachytes to quartz-latites and volcanoclastic rocks intruded by sub-volcanic porphyritic rocks. Three different intrusive phases which have been identified from their age, alteration grade and mineralization (IN-1: the oldest intrusion, intense potassic alteration, IN-2/2A: intense clay-quartz alteration, IN-3: the youngest intrusion, weak alteration). IN-1 contains quartz, illite and kaolinite, IN-2A has quartz, adularia, illite, kaolinite and smectite. Alunite, jarosite and tourmaline increase in IN-1 and IN-2A; whereas biotite and illite increase in IN-1 and IN-2A, respectively. The volcanoclastic rocks are composed of quartz, alunite and kaolinite/halloysite indicating advanced argillic alteration. Although the microscopic data confirms potassic and phyllic alterations in IN-1 and IN-2A, mineralogical (well crystallized 1M and poorly crystallized 1M illite, kaolinite/halloysite, alunite, jarosite) and geochemical (K/Ar age data for different grain-sized illite indicating late overprinting at least 5 Ma) data indicate that the early stage alteration phases were overprinted by the late stage epithermal alteration.

1 Introduction

The Kışladağ Au deposit is Europe’s largest porphyry type deposit (approximately 535.4 million tonnes total Au ore, 13 tonnes gold production per year, https://www.tuprag.com.tr) situated in western Turkey. The Kışladağ Au deposit is related to intrusive and sub-volcanic rocks of the Beydağ volcanic complex (17.3 to 12.2 Ma), resulting from extensional tectonics in western Anatolia (Figure 1; Karaoglu and Helvacı 2012). The main lithologies of the deposit area are quartz-trachyte to quartz-latite flows and volcanoclastic rocks that were intruded by a series of nested sub-volcanic alkali porphyritic intrusives (Figure 2; Juras et al. 2010; Baker et al. 2016).

Figure 1. Location of the Kışladağ gold deposit in relation to the boundaries of Tethyan Metallogenic Belt (Yiğit 2012) and geological map of the Uşak area (Karaoglu and Helvacı 2012).
The intrusions have a monzonitic character based on their mineralogy and chemistry and they have been subdivided according to cross-cutting relationships, alteration and mineralization as (i) intrusion 1 (IN-1), (ii) intrusion 2 (IN-2) and the altered equivalent of intrusion 2 (IN-2A), (iii) intrusion-3 (IN-3) (Baker et al. 2016). Gold mineralization occurs within the IN-1, IN-2 and IN-2A. Intrusive rocks which were intruded into the basement metamorphic rocks and overlain by Miocene volcanics. In this study, we have investigated late epithermal (argillic) alteration that overprints the initial potassic and phyllic (sericitic) alteration related to the porphyry system. Thus, it may be possible to evaluate the alteration mineralogy in combination with new radiogenic isotope data from clay and alunite from the alteration zones.

2 Geological Setting

The Kışladağ porphyry gold deposit is located in western Anatolia within the extension-related Neogene Uşak-Güre basin (Figure 1). The NE-SW-trending Uşak-Güre basin formed upon the Menderes metamorphic basement which was exhumed during extension (Karaoğlu et al. 2010). Basement units of the massif include augen gneisses, schist, and marble, and the structurally overlying Upper Cretaceous ophiolitic mélange rocks. The Kışladağ Au deposit occurs mainly within the intrusive rocks of the eroded Miocene Beydağı stratovolcano. Three different phases of intrusions (IN-1 to 3) have been identified from their cross-cutting relationships, alteration and mineralization (Figure 2, Baker et al. 2016). IN-1 is the oldest and best mineralized (0.86 g/t Au) intrusive phase and forms the core of the system. Alteration samples from IN-1 are characterized by tourmaline bearing quartz veins and fine-grained (sericitic) biotites (Figure 3a). IN-2 is a fine to medium-grained porphyritic rock, with intense pervasive clay-quartz alteration in IN-2A (Figure 3b) IN-2A samples (0.55 g/t Au) are characterized by an abundance of fine-grained (sericitic) white K-mica (illite) and completely sericitized feldspar phenocrysts. Intrusion IN-3, the youngest intrusive body (<5 to 200 ppb Au), is a fine-grained porphyritic rock and contains unaltered plagioclase, with rare quartz and biotite phenocrysts. The volcanoclastic rocks cover a wide area and show fine grained fragmental ash fall tuffs with pumice fragments and porphyritic flows.

3 Results

3.1 Optical Microscopy

Photomicrographs of the main alteration textures are shown in Figure 3. Feldspar phenocrysts are replaced by kaolinite in altered sub-volcanic rocks IN-1 and IN-2A which retains a primary porphyritic texture (Figure 3a, b). Kaolinites were developed replacing feldspars and also infilling pore spaces and cracks. Alunites are present as euhedral to subhedral prismatic crystal aggregates in alunite-bearing quartz veins (Figure 3c). In strongly silicified volcanoclastic rocks, a primary pyroclastic (vitroclastic) texture is evident and most of the samples are composed of hydrothermal quartz and partly pore-filling kaolinite. The textural evidence indicates that the advanced argillic alteration overprints the initial potassic and sericitic alteration.

3.2 Scanning Electron Microscopy

Scanning electron microscope data of altered samples from IN-1 show that fine-grained (<2 µm) illites are distinguished from coarse grained tabular illite/mica stacks (Figure 4a). Acicular rod-like adularia crystals are associated with flaky/tabular illites and coin-shaped alumina-silica phases in highly altered porphyry rocks from IN-2A (Figure 4b). Euhedral adularia crystals are found as formerly occurred phase and jarosite, illite and smectite crystals were subsequently developed as low-temperature phases (Figure 4c-d). The co-existence of fine and coarse grained (mica-like) platy illites indicate late epithermal (argillic) alteration overprinting the earlier phyllic and potassic alteration. In addition to this overprinting, the development of alunite and halloysite (Figure 4e-f) in highly silicified volcanoclastics from the outer parts of ore deposit, indicate a separate phase of argillic alteration.
3.3 X-ray Diffraction

Whole rock and clay fraction mineralogical compositions of the altered samples, obtained using a GNS APD 2000 X-ray diffractometer, are given in Table 1 and Figure 5. Quartz and feldspar (plagioclase) are the main minerals in almost all samples, Clay minerals are illite, kaolinite and smectite. The main clay mineral assemblage is illite + kaolinite ± smectite.

Table 1. X-ray diffraction whole-rock and clay fraction mineral composition of the samples from alteration zones (+: 20%, ± <5%).

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Whole Rock</th>
<th>Clay Fraction (&lt;2µm)</th>
<th>Ilt</th>
<th>Kln</th>
<th>Illt</th>
<th>Sme</th>
<th>K</th>
<th>Chl</th>
</tr>
</thead>
<tbody>
<tr>
<td>KD-3</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td></td>
<td></td>
<td>0.62</td>
<td>0.48</td>
</tr>
<tr>
<td>KD-5</td>
<td>++</td>
<td>±</td>
<td>Alu</td>
<td>++</td>
<td>+</td>
<td>±</td>
<td>0.68</td>
<td>0.45</td>
</tr>
<tr>
<td>KD-6</td>
<td>+</td>
<td>+</td>
<td>Alu</td>
<td>++</td>
<td>++</td>
<td>±</td>
<td>0.45</td>
<td>0.51</td>
</tr>
<tr>
<td>KD-7</td>
<td>+</td>
<td>+</td>
<td>Jrs</td>
<td>+</td>
<td>++</td>
<td>±</td>
<td>0.55</td>
<td>0.62</td>
</tr>
<tr>
<td>KD-8</td>
<td>+</td>
<td>+</td>
<td>Jrs</td>
<td>+</td>
<td>++</td>
<td>±</td>
<td>0.42</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Volcanoclastic rocks

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Whole Rock</th>
<th>Clay Fraction (&lt;2µm)</th>
<th>Ilt</th>
<th>Kln</th>
<th>Illt</th>
<th>Sme</th>
<th>K</th>
<th>Chl</th>
</tr>
</thead>
<tbody>
<tr>
<td>KD-13</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>±</td>
<td>0.50</td>
<td>0.51</td>
</tr>
<tr>
<td>KD-14</td>
<td>++</td>
<td>Alu</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>±</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KD-30</td>
<td>±</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>±</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Polytype data for illites of different grain-sizes, show that 1M illite is related with the coarse-grained size fraction (i.e. phyllic or potassic alteration stage), whereas 1Md illite is associated with the fine-grained fraction (i.e. late stage epithermal stage) (Figure 5a). The 10 Å illite peak decomposition data indicates that two types of illitic phases (well crystallized illite and poorly crystallized illite or R3 I-S) are present (Figure 5b). This data also confirms a late epithermal overprint.
3.4 Mineral chemistry and K/Ar age of illites

SEM-EDS analysis of illite/micas, evaluated on Si - Na+K and M' - 4Si - R²⁺ diagrams, indicate compositions between muscovite-phengite-illite (Figure 6). The wide range of illite/mica compositions results from different grain sized illitic phases, resulting from different origins (i.e. muscovite-phengite for the phyllic stage and illite for argillic stage).

K/Ar age data of different grain-size illites and one alunite, analysed at the CSIRO isotope laboratory, Australia, is given in Table 2 and Figure 7. K/Ar age data changes for different grain-sizes, the larger sizes, 2 -0.5 µm are always older than the smallest size fraction, i.e. 17-15 Ma for 0.5-0.2 µm grain size, whereas 14-13 Ma for <0.2 µm. The age of alunite from volcanoclastic rocks has been determined as 17.6±0.5 Ma. Our illite and alunite age data correlate with the literature data (age of host rocks and hydrothermal mineralization), the ages of coarse-grained illites are older than argillic alteration (Figure 7). This means coarser grains contain phyllic alteration related illitic phases because of the relatively higher temperature related occurrences. Two samples (KD-14 alunite and KD-17 illite 0.5-0.2 µm) have an older age and therefore they should be omitted for the evaluation. The younger ages for the fine grain size (<0.2 µm) illites represent a later and/or much younger thermal event and thus confirm the argillic alteration overprint of the potassic and sericitic/phyllic alterations (Figure 7).

![Figure 6. Distribution of illite/mica compositions on Si - Na+K and M' - 4Si - R²⁺ diagrams.](image)

![Figure 7. Chronological distribution of K/Ar age data from different sized illites and alunite.](image)

### Table 2. K/Ar ages of different size illites and alunite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral Lithology</th>
<th>Size (µm)</th>
<th>K (%)</th>
<th>Ar (%)</th>
<th>Age (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KD-17</td>
<td>Illite</td>
<td>&lt;0.2</td>
<td>6.54</td>
<td>7.2</td>
<td>14.2±0.9</td>
</tr>
<tr>
<td>KD-17</td>
<td>Illite</td>
<td>0.5-0.2</td>
<td>5.97</td>
<td>4.4</td>
<td>18.5±1.8</td>
</tr>
<tr>
<td>KD-17</td>
<td>Illite</td>
<td>2-0.5</td>
<td>5.25</td>
<td>2.3</td>
<td>18.9±3.3</td>
</tr>
<tr>
<td>KD-5</td>
<td>Illite</td>
<td>&lt;0.2</td>
<td>5.03</td>
<td>2.9</td>
<td>15.1±2.1</td>
</tr>
<tr>
<td>KD-5</td>
<td>Illite</td>
<td>0.5-0.2</td>
<td>4.94</td>
<td>3.4</td>
<td>16.2±2.1</td>
</tr>
<tr>
<td>KD-5</td>
<td>Illite</td>
<td>2-0.5</td>
<td>4.88</td>
<td>4.7</td>
<td>15.8±1.4</td>
</tr>
<tr>
<td>KD-7</td>
<td>Illite</td>
<td>&lt;0.2</td>
<td>5.91</td>
<td>36.7</td>
<td>12.7±0.3</td>
</tr>
<tr>
<td>KD-7</td>
<td>Illite</td>
<td>0.5-0.2</td>
<td>6.12</td>
<td>56.8</td>
<td>14.8±0.4</td>
</tr>
<tr>
<td>KD-7</td>
<td>Illite</td>
<td>2-0.5</td>
<td>6.36</td>
<td>57.0</td>
<td>14.5±0.3</td>
</tr>
<tr>
<td>KD-14</td>
<td>Alunite</td>
<td>&lt;2.0</td>
<td>5.49</td>
<td>27.2</td>
<td>17.6±0.5</td>
</tr>
</tbody>
</table>

4 Discussion and Conclusion

Three different intrusive phases are present in the Kışladağ deposit, each showing different types of alteration. IN-1, the oldest intrusion, is associated with intense potassic alteration, IN-2/2A, with intense clay-quartz alteration and IN-3, the youngest intrusion, is only weakly altered. Although the data confirms potassic and phyllic alterations in IN-1 and IN-2A, mineralogical (well crystallized 1M and poorly crystallized 1Md illite, kaolinite/halloysite, alunite, jarosite) and K/Ar ages indicate that the early stage alteration phases were overprinted by the later, much younger, epithermal alteration. Illite peak decomposition (well crystallized and poorly crystallized illites) and illite polytype data (1M illite for coarse-grains, 1Md illite for fine-grains), clearly indicate two different stages of alteration. Different types of illitic phases, well crystallized illite and poorly crystallized illite or R3 1-S, are found (Figure 5b).

The wide range of illite compositions and K/Ar ages confirm this interpretation. K/Ar dating of different grain-sizes of illites and alunite indicate that the epithermal overprint started shortly after the potassic and sericitic/phyllic alteration of the porphyry system. This shows the duration of hydrothermal activity and mineralization at Kışladağ was at least 5 Ma.

### References


Au-Ag-Te and Au-Ag-Se mineralizations as indicators of high- low sulfidation types of epithermal deposits of the Kurama volcanic-plutonic region (Uzbekistan)

Rustam Khalmatov,  
Centre for Advanced Technologies

Rustam Koneev  
National University of Uzbekistan, Tashkent, Uzbekistan

Margarita Kim  
Institute of Geology and Geophysics, Tashkent, Uzbekistan

Abstract. Geochemical and micro-nanomineralogical methods have been used to study the high sulfidation ores of the Kochbulak deposit and low sulfidation ores of Kyzylalmasay. The high sulfidation type is defined as Au-Ag-Te, gold-telluride-polymetallic, and low sulfidation Au-Ag-Se, electrum-selenide-sulfosalt. Such an approach enhances the capabilities of geochemical and mineralogical and geochemical methods in the search for, classification and evaluation of hidden gold mineralization.

1 Introduction

Current researchers of the epithermal deposits of volcanicogenic regions mainly follow the classification of J. Hedenquist et al. (1996). Two types of deposits are distinguished; High and Low sulfidation (HS and LS) differing in the composition of nonmetallic minerals: alunite, barite (HS), and sericite, adularia (LS). In the study of industrial deposits, the main focus should be on gold and ore elements (Te, Se, Ag, As, Sb, Bi, Hg), which determine its geochemistry, mineralogy and metallogeny. Gold compounds with the listed elements usually belong to rare, secondary ones however, in terms of frequency of occurrence and content in ores, they are not inferior and even exceed gold – the main economically valuable component. During the enrichment of ores, gold is extracted from concentrates of ore minerals. Nonmetallic – quartz, carbonates, feldspars, mica and others are waste products of enrichment and more often have a negative effect on gold recovery.

The purpose of research is the study of gold, related elements and minerals, to understand the genesis, develop search criteria, classify and evaluate new hidden deposits.

2 Methods

Polished thin sections and polystyrene briquettes with pressed concentrates have been studied. The studies were conducted on an Electron microprobe JXA Superprobe 8800R and a Zeiss electron microscope EVO/MA 10 (SEM-EDX). Geochemical analysis was performed on an Agilent Technologies ICP MS 7500 mass spectrometer. Considering that gold in primary sulfide ores is a typical micro-nanomineral (size from 100 to 0.000 μm), micro-nanomineralogical research methods have been applied (Koneev et al. 2010).

3 Geology

The Kurama region is the Eastern end of the Valeriano-Beltau-Kurama volcano-plutonic arc. Andesite volcanism and granitoid plutonism are commonly present in the region. The age of super-subduction magmatism is 320–289 Ma (U-Pb, SHRIMP), the age of epithermal pyrite mineralization is 298 Ma (Os-Re) (Dolgopolova et al. 2017). For comparative studies, two reference representatives of epithermal deposits were selected – HS type Kochbulak field and LS type Kyzylalmasay field. On Kochbulak, ore bodies are represented by steeply dipping veins, interfacial vein-metasomatic deposits, pipes of explosive breccia with gold content up to 20 000 g/t (Fig. 2 A). They are placed in bereitized and argilized dacites and andesites (C2), in sub-latitudinal and sub-meridional faults (Fig. 1 I). At Kyzylalmasay, ore bodies are represented by veins, interformational lodes in argilized and bereitized andesites, syenite-diorites (C2), granites (S2-D1) with a block of chlorite-sericite schist xenoliths (Fig. 2 B). The ore-enclosing structure is the 10 km-long Main ore-bearing zone formed by the Kyzylalmasay and Karabausky faults (Fig. 1 II).
4 Research results

Quartz, calcite, feldspars, alunite barite, pyrite, tetrahedrite, galena, sphalerite, chalcopyrite, bismuthinite dominate in ores of the Kochbulak deposit. The ratio Au:Ag is 10:1–1:10, Se:Te is 1:1–1:30. Geochemical leaders are Te, Au, Bi, Sb, Ag, Se, Cu, Pb (Kovalenker et al. 1997; Khalmatov et al. 2015) Micro-nanomineralogical studies have established a wide distribution of various tellurides, especially Au and Ag (Table 1). Gold has high fineness (800–1000‰). The relationship of gold and tellurides with matrix minerals is shown in figure 3, I.

Ores of the Kyzylalmasay deposit are represented by quartz, ankerite, sericite, adularia, pyrite, chalcopyrite, freibergite, acanthite (Khalmatov 2009). The ratio Au:Ag – 1:10–1:100, Se:Te – 10:1–1:10. Geochemical leaders are Ag, Au, Sb, Se, Cu, Te. A wide distribution in the upper and middle horizons of selenides were established (Table 1). The relationship of selenides and other Ag minerals are shown in figure 3, II. At deep levels, the concentration of Te, Bi, Pb and the corresponding compounds increases. Gold is represented by electrum, custelite and petrovskaite (AuAgS). The standard of 750 to 450% increases with depth. Silver in various minerals is often marked with Se impurity (0, n-2%).

On Kochbulak and Kyzylalmasay, except Au-Ag-Te and Au-Ag-Se types manifested early identical for both deposits Au-As, quartz-pyrite-arsenopyrite association, which occupies the bulk of the ore bodies. The gold is predominantly fine in there. Nickel minerals – gersdorffite, loellingite are also characteristic.
5 Discussion of the results and conclusions

The studies conducted on the Kochbulak and Kyzylalmasy deposits indicate that high- and low sulfidation types contrast well enough in their geochemical and mineralogical characteristics. We define HS type as Au-Ag-Te, gold-tellurium-polymetallic type. A distinctive feature of this type is the extensive development of Au, Ag, Pb, Sb, Bi, Hg tellurides with high-grade Au. In the wider Kurama region, in addition to Kochbulak, the deposits Kayragach, Samarchuk, Kauldy can be classified as this type.

The LS type corresponds to the Au-Ag-Se, electrum-telluride type. A distinctive feature of this type is the extensive development of A u-Ag-Se enhances the capabilities of geochemical methods of searching, classifying and estimating hidden ores. In combination with micro-nanomineralogical methods of research, they provide direct indications of the corresponding ores. Alunite barite, sericite, adularia minerals are convergent and are characteristics not only of epithermal gold deposits.

Acknowledgements

The research was supported by OT-F8-01 and IZ-0929142 grants of the Ministry of Innovation Development of the Republic of Uzbekistan.

References


Argillic alteration of the Mikheevskoe porphyry copper deposit (South Urals, Russia)

Oksana B. Azovskova, Mikhail Y. Rovnushkin
The Zavartsky Institute of Geology and Geochemistry, Ural Branch of Russian Academy of Sciences (IGG UB RAS)

Olga Y. Plotinskaya
Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences (IGEM RAS)

Vyacheslav A. Gemel
JSC Mikheevskiy GOK

Abstract. Geological setting and mineral composition of argillic alteration of the Mikheevskoe porphyry copper deposit have been examined. Typical argillic alteration occurs as steep-dipping zones, often associated with porphyry dikes. In the upper part of the deposit such zones have uneven lateral distribution and are classified as “loose sulphide ore” which requires a specific mineral processing treatment. Typical minerals of the argillic altered rocks are: quartz, illite/hydromica, kaolinite, chlorite, unoxidized sulphides (1-5%), often carbonates (calcite, dolomite, siderite), and low temperature bitumen of kerite range (0.1-0.5%). Argillic metasomatites of the central part of the deposit contain up to 5% of pyrophyllite. Major ore minerals are pyrite and chalcopyrite, minor ones are bornite and molybdenite. Molybdenite is characterized by quite uneven, patchy-spotted distribution of rhenium which in some point analyzes peaks at 1.72 wt%, with an average content of 0.43 wt%. Accompanying mineralization is represented by Co-Ni sulphoarsenides, Se-rich galena, and sphalerite. A distinguishing feature of argillic alteration is the presence of Au-Ag, Ag, and Pb selenides, often in association with tellurides and native gold of quite a diverse composition. Compositional variability and intensity of the accompanying mineralization is controlled by both intensity of argillic alteration and distribution of earlier alteration processes.

1 Introduction

The Mikheevskoe deposit is one of the most economically significant (Mo,Au)-Cu-porphyry in Russia. It is situated 250 km south of the city of Chelyabinsk and represents part of the Novonikolaevskii ore cluster. From the regional structural perspective this area is confined to the junction of two large structures - East- and Transuralian megazones (Grabezhev 2014; Puchkov 2010). Extensive network of faults in the area results in linear blocks with sheared east-west striking linear folds within the blocks. The geology of the area features Late Devonian volcanic and volcano-sedimentary basaltic andesite and basalt formations with terrigenous layers and small bodies of serpentinite, as well as granitoids of Ulyanovsk (Late Devonian) and Mikheevsky (Late Devonian to Eraly Carboniferous) complexes (Grabezhev and Belgorodskii 1992).

Porphyry molybdenum-copper mineralization is genetically linked to the Mikheevsky igneous complex. Re-Os age of the mineralization is 357.8±1.8 and 356.1±1.4 Ma (Tessalina and Plotinskaya 2017). Mineralization is associated with a belt of quartz-diorite and diorite dikes (mostly porphyritic) which stretches between two diorite stocks of the Mikheevsky complex (Fig. 1). There is an intensive rock alteration represented by the following main alteration types and associated ore minerals (modified after Plotinskaya et al. 2018):

1. actinolite±epidote, with magnetite, occasionally with garnet relics (andradite);
2. biotite+muscovite±K-feldspar (potassic alteration), with bornite and chalcopyrite;
3. chlorite+epidote+sericite (propylitisation), with pyrite or pyrite and chalcopyrite;
4. quartz+sericite (quartz-sericite or phyllic alteration), with chalcopyrite and molybdenite;
5. quartz+illite/hydromica+kaolinite (argillic alteration), predominantly with pyrite, ± chalcopyrite, bornite, molybdenite.

Most abundant are the intermediate varieties – chlorite-sericite metasomatites. Notably, carbonate (calcite, dolomite, siderite) is almost always present in altered rocks, often in the form of veinlets.

Typical argillic metasomatites can be observed in the existing open as steep-dipping zones with apparent thickness of up to 40 m or more, or series of closely located thinner zones. At the same time, there are quite frequent occurrences of weaker argillic alteration superimposed on other alteration types. In the upper section argillic metasomatites extend laterally, albeit extremely unevenly (Fig. 1). Thickness of such formations varies from 1.6 to 46 m, average thickness is 14 m. They are overlain by the weathering crust, often with a gradual boundary. As a result, they are considered as a specific ore type which requires a different mineral processing circuit (Russian Copper Company).

This study is aimed to describe mineralogical and geochemical features of argillic metasomatites from steep-dipping zones in the northern part of the deposit.
2 Sampling and analytical methods

Five sites of argillic metasomatites were sampled from the open pit; 4 sites were sampled in the northern portion of the deposit, and 1 site in the central portion of the deposit. Study was carried out in the Zavaritsky Institute of Geology and Geochemistry, Ural Branch of Russian Academy of Sciences, Yekaterinburg. Bulk mineral composition of altered rocks was studied using Shimadzu XRD-7000 X-ray diffractometer and PerkinElmer Diamond TG/DTA system (analysts: N.G. Petrishcheva, T.Ya. Gulyaeva and O.L. Galahova). Mineralogy was studied using (SEM) JSM-6390LV by Jeol with energy-dispersive detector INCA Energy 450 X-Max 80 by Oxford Instruments (analysts: S.P. Glavatskikh, I.A. Gottman, L.V. Leonova). Detailed studies of specific molybdenite and pyrite grains were carried out using a Cameca SX100 electron probe microanalyzer (analyst D.A. Zamyatin). Trace element composition of typical samples of argillic metasomatites were identified using ICP-MS method by Perkin Elmer ELAN-9000.

3 Results and discussion

Steep-dipping argillic alteration zones are often associated with quartz-diorite porphyry dikes and their external contacts. Typical argillic metasomatite is a whitish, light-grey, greenish, or yellowish rock that retains all of the structural and textural features of the primary rock. At the same time, it can be easily molded by hand, and 90-95% of the volume can be washed away by water. There are occasional areas and zones of silification. Most common minerals of the argillic rock are (according to X-Ray and TG/DTA analysis): fine grained quartz, illite/hydromica, kaolinite (0-15%) and unoxidized (newly formed) sulphides (1-5%). A third of the studied samples also feature low temperature bitumen (0.1-0.5%). There are also variable quantities of chlorite. ~ 50% of samples and veinlet zones contain carbonate: calcite, to a lesser extent dolomite and siderite (up to 2-3%, occasionally more). Argillic altered rock of the central part of the deposit often contains up to 5% pyrophyllite. Major ore minerals (in descending order) are: pyrite, chalcopyrite, copper sulphides, molybdenite; Co-Ni sulphoarsenides of cobaltine-gersdorffite range are typically present. There are minor amounts of galena and sphalerite.

Pyrite is the most abundant sulfide in the argillic metasomatites. It occurs, mostly, in cubic form and cube-based combinations, with grain size of ~0.01-~0.1 mm, rarely larger. SEM study of inclusions and ingrowths on the surface of pyrite grains was carried out in order to describe ore and accompanying mineralization in more detail.
277 pyrite grains from 8 samples from three areas in the northern part of the deposit have been studied to date. Site-1 is located in the central part of the main Cu-ore zone (Fig. 1), site-2 – in its western margin, and site-3 – outside of the ore boundary. The discovered inclusions and neogenesis represent the following mineral groups and types: 1) Native elements – gold and electrum, natural copper-zinc alloys (±Sn), iron; 2) Sulfides – chalcopyrite, bornite, molybdenite, galena (usually Se-rich), sphalerite and (Fe,Cu,Zn)S phase, rarely arsenopyrite and argentite; 3) Sulfoselenides of cobaltine- gersdorffite range (±Cu,Sb); 4) Sulfosalts – tennantite and tetrahedrite, very rarely in association with Bi- or Pb-Bi-sulfosalts; 5) Tellurides – hessite (predominant), Au-Ag-telluride which is close to petzite, coloradoite, altaite, tellurobismuthite; 6) Selenides and selenotellurides of Co-Ni – sulpharsenides of cobaltite-gersdorffite range (±Cu,Sb), unidentified phases or phase mixtures of Au-Ag-Se, Cu-Ag-Se, Ag-Pb-Se-(± Bi). Fine aggregates of selenides and tellurides are occasionally observed; sulfoselenides may be also present. Among the gangue minerals, most typical are newly formed monazite of variable composition, K/Na chlorides and more complex chloride compounds, inclusions and selvages of bitumen. The diagram (Fig. 2) shows comparative abundance of various inclusions in the three studied argillic alteration sites.

Pyrite from the central part of copper ore zone (site-1) is featured by the highest amount and variety of such inclusions; it is relatively enriched by Au-Ag minerals, and represents the only place where sulphosalts occur. Inclusions of molybdenite, monazite, and bitumen are more common in the periphery of the ore zone (site-2). The most “inclusion-poor” pyrite comes from argillic altered rock of site-3 which is outside of the main ore zone and, in particular, lacks any noble metal mineralization or selenides.

![Figure 2. Relative frequency occurrence of various inclusions and neogenesises on the surface of pyrite grains from argillic metasomatites of Mikheevskoe deposit.](image)

1, 2, and 3 – sampling areas in the northern part of the deposit. Key to mineral types and groups: Chp – chalcopyrite, Sf-Cu – copper sulphides (bornite ± chalcocite), Mo – molybdenite, Ga – galena, Sf-Zn – zinc sulphides (sphalerite, (Fe,Cu,Zn)S) phase, Co-Ni – sulpharsenides of cobaltite-gersdorffite range, Ss – sulfosalts, Au-Ag – native gold and electrum, (Au,Ag)-Te –gold and silver tellurides, Tel – other tellurides, Sel – selenides (mostly Au, Ag), Mz – monazite, Bit – bitumen

Native gold is present as micron-scale segregations ≤10 µm, both in polished thin sections of relatively intense argillic metasomatites, and on surface of pyrite from loose argillic metasomatites (Fig. 3 b,c). Unlike gold from the porphyry-style ore, this gold has a wide variation in fineness – from electrum and Hg-bearing electrum (fineness < 300, Hg up to 10 wt%) to quite high-fineness gold (Plotinskaya et al. 2018). Frequently there are intimate intergrowths of native gold and Au-Ag-tellurides and selenides. Cu-rich gold with 4-5 wt% of Cu and no Ag was noted in few specific cases; this, according to (Spiridonov and Pletnev 2002) suggests rather low-temperature conditions.

Molybdenite occurs in loose argillic metasomatites as platy parcel-like ~0.01–0.1 mm (Fig. 3 e), sometimes larger, grains – often intergrown with pyrite. There are occasional molybdenite enriched zones associated with
argillic altered porphyry dikes. Rhenium distribution in molybdenite is rather uneven, patchy-spotted, with some zonation (Fig 3 f) and considerable variation of Re content (average 0.43 wt%), which, on the whole, corresponds to molybdenite from porphyry-style ore (Grabezhev 2013; Plotinskaya et al. 2015). The only difference is somewhat higher rhenium content in specific spots – up to 1.72 wt%.

**Bitumen** traces were identified in a significant number of samples. By burn-off temperature (exo-effect peaks on DTA curves) the bitumen corresponds to low-middle kerite – T_max 305-375°C (Azovskova et al. 2015). Bitumen selvedges and inclusions observed on pyrite grains and other ore minerals are usually enriched by Cl, P, ± F, As. Sometimes they feature micro-inclusions of native gold, galena, native lead, and unidentified mineral phases (Fig. 3 c,d). Such mineralization is likely to be related to incomplete breakdown of organoelemental and chloride compounds and can indicate active involvement of organic matter in low-temperature process of argillic phase of mineralization-alteration.

### 4 Conclusions

Argillic metasomatites are present in variable volumes in most known porphyry copper deposits and can occur at different stages of porphyry system development (Sillitoe 2010). In the Mikheevskoe deposit such metasomatites are quite abundant, and even represent a special process type of ore in the upper section. They have distinctive ore-and accompanying mineralization (e.g. presence of Au-Ag, Ag, and Pb selenides, large variations of native gold composition, traces of low temperature bitumen etc.). Differences in mineral composition and the degree of accompanying mineralization between various areas of the deposit reflect element zonation which may be related both to argillic alteration and to earlier ore and alteration processes. Ore-bearing argillic rocks of Mikheevskoe deposit formed at the final epithermal stage of deposit formation however, certain influence of later endogenous processes during Late Mesozoic tectono-magmatic activation of Uralian structures cannot be excluded.

### Acknowledgements

This study was supported by the state assignment projects of IGG UB RAS (theme 0393-2018-0031) and Russian Foundation for Basic Research, project # 19-05-00254. I.A. Gottman, L.V. Leonova, D.A., Zamyatin (IGG UB RAS, Yekaterinburg) are warmly thanked for their assistance with SEM and microprobe analysis. N.G. Petrishcheva, T.Ya. Gulyaeva and O.L. Galahova (IGG UB RAS, Yekaterinburg) are acknowledged for X-ray and TG/DTA analysis.

### References


Fluid evolution and genesis of epithermal gold deposit hosted by a shear-zone: Banská Hodruša, Slovakia

Peter Koděra, Alexander Kubač, Peter Uhlík, Rastislav Vojtko, Martin Chovan
Faculty of Natural Sciences, Comenius University

Jaroslav Lexa, Rastislav Milovský
Earth Science Institute, Slovak Academy of Sciences

Oscar Laurent
Department of Earth Sciences, ETH Zürich

Anthony E. Fallick
Scottish Universities Environmental Research Centre

Abstract. The Banská Hodruša gold deposit is hosted by a low-angle shear zone in the centre of a Neogene stratovolcano. The deposit developed during five mineralisation stages and two stages of shear zone evolution. Fluid inclusion and stable isotope data showed that temperature, chemical and isotopic composition of fluids were nearly constant during all mineralisation stages in all parts of the deposit. Precipitation of ores was triggered by boiling and cooling of fluids. The dominant source of fluids was contracted magmatic vapour mixed with deep-convecting meteoric water. The genetic model includes sequence of events starting with the emplacement of a granodiorite pluton, associated with Pb-Zn-Cu stockwork mineralization and advanced argillic alteration. It followed a rapid exhumation of the granodiorite and the shear zone evolution, which was penetrated by fluids, represented by contracted magmatic vapour mixed with deep-convecting meteoric water. Ore mineralisation is related to focusing of fluids in areas with a dense network of dilatational structures, while the argillised upper boundary of the shear zone worked as a collector of hydrothermal fluids and gases resulting from boiling. The final evolution includes caldera subsidence and long-lasting resurgent horst uplift, hosting an extensive system of younger veins.

1 Introduction

The intermediate-sulfidation Au-Ag-Pb-Zn-Cu deposit at the Rozália mine in Banská Hodruša represents an unusual subhorizontal multi-stage vein system, hosted by a low-angle normal fault zone (LANF). The shear zone, hosting the vein system, is related to processes of exhumation of a subvolcanic granodiorite pluton, probably accompanied by a sector collapse of the hosting stratovolcano (Kubač et al. 2018). The unusual structural setting of the deposit resulted in several unique characteristics, including fluid properties of the hydrothermal system, distribution of ores and alteration patterns. The proposed genetic model is based on new and published fluid inclusion and stable isotope data, interpreted in accordance with available geological, mineralogical and structural information.

2 Banská Hodruša deposit

The deposit is hosted by the central zone of the large Middle Miocene Štiavnica stratovolcano, the largest stratovolcano in the Central Slovakia Volcanic Field, located on the inner side of the Carpathian arc. The stratovolcano includes an extensive caldera, a late-stage resurgent horst in the caldera centre and an extensive pre- to syn-caldera subvolcanic intrusive complex. The gold mineralization is hosted by pre-caldera anodesite, near to the flat roof of a pre-mineralisation subvolcanic granodiorite pluton. The veins are dismembered by a set of quartz-diorite porphyry sills and later steeply-dipping faults of the resurgent horst, mineralized with Cu-Pb-Zn epithermal ores.

The gold deposit occurs at the Rozália mine, 400–650 m below the surface. Epithermal gold ore has been exploited here since 1992, but in the past the Rozália mine was also used to exploit the horst-related Cu-Pb-Zn epithermal veins and base-metal stockwork mineralization. The stockwork mineralisation occurs some 1.5 km south of the Au-Ag deposit, hosted by apical porphyritic part of the granodiorite pluton and resembles a porphyry hydrothermal system including potassic alteration in the granodiorite, and advanced argillic alteration in the overlying andesite (Koděra et al. 2004).

The gold deposit consists of two parts, separated by a thick sill of post-mineralisation quartz-diorite porphyry. The western part has been already mined out but the eastern part is still exploited, with the annual production of ~30–45 kt of ore with 14 g/t Au, 17 g/t Ag, 0.6 wt% Zn, 0.45 wt% Pb, and 0.15 wt% Cu.

The deposit developed during five stages (Kubač et al. 2018). Stage 1 is related to hydraulic fracturing along subhorizontal structures dipping 20–30° to SE related to the underground cauldron subsidence and corresponds to the origin of low-grade silicified breccia at the base of the deposit. The major productive Stage 2 is related to the early evolution of the LANF with mostly southward movement of the downthrown block and is represented by a stockwork of steep veins (40–60° to S) with rhodonite-rhodochrosite (Stage 2a) and quartz-sulphide-carbonate (Stage 2b) assemblages with sphalerite, galena, chalcopyrite, pyrite, gold, rare hessite and
petzite. Locally, these veins are accompanied by quartz-gold veins resulting from complementary transmissive sinistral strike-slip movements (Stage 2c). Stage 3 is related to a renewed motion of the downthrown block towards the SE. The corresponding oriented vein systems consist of thin quartz-gold veins located on tension cracks inside the shear zone (dips ~45° to SE, Stage 3a), and complementary detachment-hosted quartz-base metals-gold veins (<30°; Stage 3b) located in the roof of the shear zone. Post-ore veins include rare barren quartz veins of variable orientation (Stage 4) and steep base metal veins with the NE-SW strike, related to the resurgent horst uplift (Stage 5).

Hydrothermal alteration occurs in a zonal arrangement (Koděra et al. 2017). Major veins are accompanied strong adularisation, quartz and illite. Strong argilisation occurs along the upper boundary of the shear zone there represented predominantly by illite, accompanied by quartz and pyrite. At the base of the deposit silicification of variable intensity is present, corresponding mostly to the Stage 1 mineralisation. Weak adularisation occurs in the hanging wall of silicites and close to minor ore veins. Propylitisation occurs distal to ore veins and in the hanging wall of the deposit (above the shear zone).

3 Methods

The new microthermometry on fluid inclusions was conducted on a Linkam THMSG-600 cooling-heating stage. LA-ICP-MS microanalyses of fluid inclusions were performed at the Department of Earth Sciences, ETH Zürich, with a Perkin Elmer NexION 2000 fast-scanning quadrupole ICP MS connected to a GeoLas 193 nm ArF excimer laser ablation system. The new $^{18}$O/$^{16}$O and $^{13}$C/$^{12}$C isotopic compositions were analysed at SUERC (Glasgow, UK), D/H at the Earth Sciences Institute of SAS in Banská Bystrica (Slovakia). For the stable isotope study of clays, the size fraction <2 μm or smaller was used, with mineralogy checked by XRD. The XRD analyses of clay fractions were also used for calculation of temperatures using expandability (smectite content in illite-smectites) and illite crystallinity (Kübler index – KI).

Data presentations and interpretations include fluid inclusion microthermometry and stable isotope data already published by Koděra et al. (2004, 2005) from the base metal stockwork mineralisation and epithermal mineralisation from the western part of the deposit.

4 Results

4.1 Fluid inclusions

Fluid inclusions from quartz, sphalerite and carbonates from the gold mineralisation are of low salinity (~1–3 wt.% NaCl eq.) and moderate homogenization temperatures (Th; ~250–310 °C) with frequent evidence of extensive boiling. No apparent differences occur between quartz data from both parts of the deposit, nor individual stages, except Stage 1 silicites which show slightly higher temperatures (up to 330 °C). Data from sphalerite show apparently lower mean Th values than quartz (~250–280 °C), but salinity is similar, so the changes in temperature can probably be explained by boiling (which is an endothermic process) rather than mixing. Sometimes carbonates from various stages also show lower Th values.

Fluid inclusions from the host-related veins (Stage 5) showed Th peaks at ~285 and 185 °C and salinities between 1 and 4 wt% NaCl eq., corresponding to two different substages in the vein filling. Evidence for boiling was observed locally (Koděra et al. 2005).

Hydrothermal minerals from the base metal stockwork mineralisation (epidote, sphalerite, calcite) host inclusions that showed progressive decrease in salinities (5 to 0.5 wt% NaCl eq.) and Th values (330 °C to 190 °C), indicative of fluid mixing. Data for massive silica from the overlying advanced argillic alteration (0.3–3.9 wt% NaCl eq., 240–360 °C) are consistent with the origin from magmatic condensates (Koděra et al. 2004).

The fluid inclusion populations with evidence for boiling were used to calculate fluid pressures and depths of formation. In the gold mineralization the highest fluid pressure was determined for Stage 1 inclusions (~85 bars), while the Stage 2 and Stage 3 inclusions showed very variable pressure estimates (45–80 bars). The highest pressure corresponds to initial opening of host fractures, when the hydrothermal system was governed by suprahydrostatic conditions, probably with a lack of connection to the surface. Local overpressure is indicated by frequent breccia textures in silicites. Variable pressures are indicative of local decompression in dilatational structures, with pressure release resulting in extensive boiling, followed by precipitation of gold, adularia and Mn-minerals. The calculated apparent paleodepths, corresponding to changes in fluid pressure, are also very variable due to the local suprahydrostatic conditions and possible variation in CO2 content. The probable paleodepth (550 ± 100 m) can be derived from the lowest fluid pressure value. Inclusions from Stage 5 steep horst-related veins produced pressures 60–68 bars, corresponding to 780 ± 60 m at hydrostatic conditions.

Results of LA ICPMS analyses of fluid inclusions from the gold deposit showed that (i) the same set of elements is systematically detected (Na, B, Cl, K, As, Rb, Sr, Sb, Cs ± Fe, Cu, Zn, Au, Pb); and (ii) the ratios of these elements to Na are fairly homogeneous, despite the low salinity and small size of most inclusions. Both are clear evidences that the fluids had a common, long-lasting source throughout the entire hydrothermal process and precipitation of ore mineralisation was mostly affected by pressure decrease and cooling rather than mixing of fluids. High B/Rb, B/Sr and As/Rb ratios indicate that contracted magmatic vapour was the dominant source of hydrothermal fluids, with no or little influence of fluid/rock reaction with sedimentary rocks (c.f. Large et al. 2016). Fluids in pre-mineralisation stages (1 and 2a) had probably a higher proportion of the contracted magmatic vapour compared to later stages, as indicated by their relatively higher B, As, Sb contents, Na/K values and lower Cl, Rb and K contents than later stages. This can be explained by the fact that both B, As and Sb are known to preferentially accumulate in vapour, while Rb and K are
The relatively higher proportion of contracted vapour in early stages also corresponds to their slightly lower salinity but higher Th values. Gold content in fluids typically ranges from 0.2 to 2 ppm; however, some individual inclusions have sometimes significantly higher concentrations up to 50 ppm. The increased gold contents were determined in fluid inclusions from all gold bearing stages (2b, 3a, 3b), as well as in Stage 5 host-related veins. Silver/gold ratio in fluid inclusions was similar to most gold ores at the deposit, i.e. close to 10.

4.2 Stable isotopes

Oxygen isotope data from vein quartz and illites associated with gold mineralisation suggest a relatively narrow range of δ¹⁸Ofluid values (-2 to 1 ‰) for all stages of veins and for both the western and eastern parts of the deposit. Fluids in equilibrium with illite are also very homogeneous in terms of hydrogen isotope ratio (-50 to -69‰ δDfluid). This indicates that the source fluid was quite homogeneous, which is consistent with the low variability of fluid inclusion data, including Th values and chemical composition, during all mineralisation stages in all studied parts of the deposit. Only the fluids associated with Stage 1 silicites and illites are isotopically slightly heavier (by ~1 ‰) compared to other stages. A somewhat different composition is only indicated by carbonates that show slightly lower δ¹⁸Ofluid values (-1.9 to -2.7 ‰).

Isotopic composition of epithermal fluids plotted in a δ¹⁸Ofluid vs. δDfluid diagram shows a mixed character of fluids falling between the fields of typical magmatic water dissolved in felsic melts and meteoric waters. The observed well homogenised fluid composition is consistent with mixing of the fluids outside of the deposit during ascent of magmatic fluids from depth, assuming a deep-convecting source of meteoric fluids.

The isotopic signature of the hydrothermal alteration of granodiorite that is associated with the base metal stockwork mineralisation was examined using epidote and chloride (0.4 to 1.1 ‰ δ¹⁸Ofluid, -22 to -46 ‰ δDfluid; Koděra et al. 2004). Fluids related to accompanying advanced argillic alteration were characterised by analyses of illite, illite-smectite and massive silica (-8.2 to 0.6 ‰ δ¹⁸Ofluid, -64 to -50 ‰ δDfluid). In contrast to epithermal veins, the data show a progressive mixing trend of magmatic fluids with δ¹⁸O-shifted meteoric waters. The isotopic composition of meteoric water in this system was roughly similar to that in the epithermal vein system and it is also similar to the present-day meteoric water. The mixing trend is probably related to a relatively shallow convection of meteoric water in the vicinity of a thermal anomaly of ascending, predominantly magmatic hydrothermal fluids in the apical part of the pluton. They include early magmatic vapour that has condensed in overlying andesite and resulted in advanced argillic alteration, and later supercritical magmatic fluid, responsible for the base metal stockwork mineralisation (Koděra et al. 2004). However, contracted magmatic vapour could be an alternative form of magmatic fluid source.

4.3 Illite geothermometry

The XRD analyses of clay fraction were used for calculation for crystallisation temperatures of clay minerals (illite, illite-smectite). Illite from the vicinity of veins provided KI values from ~0.4 to 0.6, corresponding to temperatures from 270 to 290 °C, which are similar to fluid inclusion homogenisation temperatures. Especially, the illite from the hanging-wall of the detachment-hosted vein system (Stage 3b) has a nearly constant crystallinity for all studied samples, similar to their oxygen isotope data. This indicates that there was no apparent thermal gradient along this horizon.

Clays from the stockwork-related advanced argillic alteration produced significantly higher KI values of illites (0.7 to 1.3) and high proportion of smectite in illite-smectite (25 %), resulting in much lower temperature range of their crystallisation (135–248 °C). This corresponds to the mixing trend determined for this system using the stable isotope data.

5 Genesis of the deposit

The available geological, structural, mineralogical and fluid properties data obtained in this study enable to present a genetic model of the epithermal gold deposit at the Rozália mine (Fig. 1). The sequence of events started with the emplacement of the granodiorite bell jar pluton at a minimum depth of ~2 km (Konečný et al. 2002). The emplacement was accompanied by advanced argillic alteration in the overlying andesite, resulting from condensation of magmatic vapour escaping from the crystallising granodiorite magma. Mixing with meteoric water in the vicinity of the upflow zone has also occurred. Following cooling and fracturing of the apical part of the pluton, Pb-Zn-Cu stockwork mineralization precipitated here due to the upflow of a deep-exsolved supercritical fluid or magmatic vapour contracted to aqueous liquid. Neither the advanced argillic nor the stockwork system contain gold and precipitation of base metals occurred by mixing with external meteoric water.

Shortly after its emplacement, the granodiorite pluton has experienced a very rapid exhumation, followed by unroofing and low-angle normal shear zone evolution, possibly enabled by argillised nature of the overlying andesite. The shear zone was penetrated by hydrothermal fluids forming the Au-Ag ± Pb-Zn-Cu veins, followed by emplacement of quartz-diorite porphyry dikes and sills into the same structures. As indicated by the fluid inclusion data, the source of fluids was predominantly vapour escaping from the parental differentiated magma chamber. Vapour has contracted to liquid and mixed with deep-convecting meteoric water.
before reaching the shear zone level. Some admixed proportion of brine could have been also present in the fluid. Enrichment of fluids in gold probably resulted from the ability of vapour to transport gold, and possibly due to the degassing of a mafic magma that could have penetrated the parental magma chamber, as indicated by the presence of mafic nodules in post-mineral quartz-diorite porphyry sills. Precipitation of ores was triggered by boiling of fluids evolving from suprahydrostatic to hydrostatic conditions at a depth of ~550 m. Precipitation of ores usually started with precipitation of sulphides due to cooling, as boiling is an endothermic process. Subsequent precipitation of gold resulted from the resulting lack of sulphur in the fluid as gold in epithermal systems is mostly transported in sulphur complexes.

The main migration of paleofluids occurred along low-angle normal faults of the shear zone from S-SE to NW, as indicated by the geological setting of the quartz-diorite porphyries that intruded the shear zone at the end of the hydrothermal activity from S-SE. Main ore mineralisation is related to focusing of fluids in areas with a dense network of dilatational structures, where both major boundaries of the shear zone were relatively close together, i.e. where the hanging-wall argillite was relatively close to foot-wall silicate (Koděra et al. 2017). Opening of dilatational structures enabled an active suction of fluids and their boiling due to the decreased pressure. The strongly argillised upper boundary of the shear zone probably worked as a collector of hydrothermal fluids flowing along the shear zone and producing the Stage 3b veins, as well as a collector of vapour and gases escaping from boiling fluids throughout the entire thickness of the shear zone. Thus, this horizon is quite important for future exploration as it marks areas with extensive boiling (and possibly associated gold mineralisation) in the footwall of this argillised horizon.

The fluid-mixing trends obtained from isotopic data point to a similar meteoric water isotopic composition both for the granodiorite-related hydrothermal system and for the epithermal gold system. This interpretation is consistent with the assumed very quick exhumation of the granodiorite followed by shear zone development, as there was no time for significant change in the isotopic composition of meteoric water through changes in climate. Recent U-Pb dating has confirms that the exhumation has occurred in less than 0.3 Ma (unpublished work).

The final evolution of the deposit includes caldera subsidence, followed by the long-lasting resurgent horst uplift producing the extensive system of horst-related veins (Stage 5). The gold deposit was overlain by new portions of differentiated andesite (caldera-fill and post-caldera), which explains deeper boiling depth of the horst related veins (~780 m), compared to gold veins (~550 m).

Acknowledgements

This work was supported by the grants VEGA No. 1/0560/15, APVV-15-0083 and the company Slovenská banská, spol. Ltd.

References


Geochronology, mineral chemistry, isotope and microthermometry features of the Wunuer deposit, Inner Mongolia, China: a porphyry-hydrothermal-epithermal system

Xiejun Fan
Faculty of Earth Resources, China University of Geosciences, China

Abstract. The Wunuer Pb-Zn-Mo deposit is a newly explored polymetallic ore deposit located in the middle segment of the Great Xing’an Range, Inner Mongolia, NE China. Three stages of mineralization, composed of an early porphyry stage, an intermediate hydrothermal stage, and a later epithermal stage, have been identified. Sphalerite is the principal mineral in both hydrothermal and epithermal stages, and thus two generations of sphalerite are separated, which show distinct textural and chemical characteristics. Detailed study of the texture, chemistry, fluid inclusion and sulfur isotope characteristics of these two generations of sphalerite were carried out to reveal ore forming conditions of the hydrothermal and epithermal mineralization stages. In addition, granite porphyry zircon U-Pb concordia, hydrothermal stage hydrothermal zircon U-Pb concordia and epithermal stage sphalerite (Sp2) Rb-Sr isochron ages were determined to constrain the chronology of the system and the duration of the porphyry to hydrothermal and to epithermal transition.

1 Brief introduction to deposit geology

The Wunuer Pb-Zn-Mo polymetallic deposit, located in the middle segment of the Great Xing’an Range, Inner Mongolia, NE China, is closely related to mesozoic volcanic-subvolcanic rocks (Fig. 1).

Wall rocks in the Wunuer deposit area are dominated by Upper Jurassic Manketouebo Formation terrestrial volcaniclastic rocks, which were intruded by a late-Jurassic granite porphyry closely related to ore forming (Fig. 1). Porphyry-stage mineralization occurred mainly in the apical portions of the granite porphyry intrusion (Fig. 1), forming molybdenite-magnetite-hematite-pyrite-bearing quartz veins (Fig. 2a). Hydrothermal stage mineralization occurred mainly in crypto-explosive breccia of granite porphyry and wall rocks adjacent to intrusion (Fig. 1), forming sphalerite-bearing breccias (Fig. 2b). Epithermal-stage mineralization occurred principally in the wall rocks at the top of the deposit (Fig. 1) and comprises brecciated, veined and stockwork lead-
zinc ores (Fig. 2c). Therefore, two generations of sphalerite, with the first-generation sphalerite (Sp1) precipitated in hydrothermal stage and the second-generation sphalerite (Sp2) precipitated in epithermal stage, were identified. Generally, porphyry mineralization was usually accompanied by potassic, silicic, and fluorite-bearing alteration, hydrothermal stage mineralization was usually accompanied by chlorite-, sericite-, zircon-, and rutile-bearing alteration, epithermal mineralization was mainly related to argillic, chlorite and carbonate alteration. The epithermal mineralization overprinted porphyry and hydrothermal mineralization, especially in the brecciated wall rocks near to the granite porphyry intrusion, where the hydrothermal stage sphalerite is widely replaced by the epithermal stage sphalerite.

Hydrothermal zircon, accompanied by sericite, pyrite, rutile and Sp1, is ubiquitous in hydrothermal stage mineralization. The occurrence of hydrothermal zircon is closely related to silicic, sericitic and chloritic alteration, generally in silicic granite porphyry (Fig. 3a, b), crypto-explosive breccias (Fig. 3c, d) and chlorite-bearing wall rocks (Fig. 3e, f).

Figure 3. (a) Silicic porphyry granite. (b) Hydrothermal zircon accompanied by Sp1, rutile and pyrite in sample Fig. 3a. (c) Crypto-explosive breccia of granite porphyry. (d) Hydrothermal zircon accompanied by rutile and pyrite in sample Fig. 3c. (e) Chlorite-bearing wall rock. (f) Hydrothermal zircon accompanied by Sp1, sericite, rutile, and pyrite in sample Fig. 3e.

2 Ore forming conditions

2.1 Implications of sphalerite texture and chemistry

Two generations of sphalerite show different crystal texture, transparency, colour, mineral inclusions and paragenetic relationship. The first-generation sphalerite (Sp1) is generally euhedral and light colored (yellow to brown in transmitted light), with rhombic dodecahedron structure (Fig. 2d). In general, this transparent sphalerite is free of mineral micro-inclusions, and is usually replaced by the second-generation sphalerite (Sp2) as well as by other sulfides along fractures or on crystal surfaces (Fig. 2d, f, h). The second-generation sphalerite (Sp2) is generally anhedral, opaque and black in colour (Fig. 2e, g, i). The black Sp2 contains abundant micro-inclusions, such as chalcopyrite “disease” (Fig. 2e, h).

These two generations of sphalerite have different chemical compositions. Element correlations, especially between Zn and Fe, Zn and Cu, Cu and Fe, and Cu and In, show different trends for Sp1 and Sp2. Fe shows negative linear correlation with Zn in both Sp1 and Sp2, but with a molar slope of -1 for Sp1 and -1.8 for Sp2, respectively (Fig. 4a). Cu is limited in Sp1, but is elevated in Sp2 and shows a negative linear correlation with Zn with a molar slope of -1.98 (Fig. 4b), as well as shows a positive linear correlation with Cu with a molar slope of 0.96 (Fig. 4c). In is limited in Sp2, but is elevated in Sp2 and reaches to hundreds of ppm (Fig. 4d).

Figure 4. Binary plots of major element contents by EPMA and trace element contents by LA-ICP-MS for sphalerite from the Wunuer deposit.

2.2 Fluid inclusions

Primary fluid inclusions trapped in a quartz vein from the early porphyry stage preserve information on the conditions of potassic-silicic alteration condition. This stage was characterized by high temperature and moderate salinity fluids (Fig. 5). The first-generation sphalerite (Sp1) is transparent and hence is ideal for fluid inclusion studies. Primary fluid inclusions trapped in Sp1 imply a moderate temperature and low salinity fluid in hydrothermal stage mineralization (Fig. 5). Unfortunately, it was not possible to observe fluid inclusions in Sp2 as it is opaque. Thus, we studied primary fluid inclusions in quartz in apparent textural equilibrium with Sp2 to infer its conditions of precipitation. The fluid inclusions measured are characterized by low homogenization temperature and salinity (Fig. 5).
3 Ore forming ages

3.1 Intrusion age

Magmatic zircons were hand-picked from a crushed sample of the ore-related granite porphyry intrusion, and were analyzed using LA-ICP-MS to obtain the zircon U-Pb age. As shown in Figure 6, the U-Pb concordia age implies that the granite porphyry was emplaced at 144.5 ± 0.6 Ma.

3.2 Hydrothermal zircon concordia age

In-situ LA-ICP-MS analysis of hydrothermal zircon was conducted to constrain the age of hydrothermal activity. As shown in Fig. 7, the hydrothermal zircon U-Pb concordia age is 138.8 ± 1.1 Ma out of 10 samples.

3.3 Sphalerite Rb-Sr isochron age

Seven Sp2 samples from the Wunuer deposit were picked out to conduct Rb-Sr isotopic analyses and calculate the Rb-Sr isochron age. As shown in Fig. 8, the age obtained is 121 ± 2.3 Ma based on five out of seven analyses.

4 Sulfur source

In-situ sulfur isotope analysis of sphalerite was carried out using the LA-MC-ICP-MS technique. The two generations of sphalerite from the Wunuer deposit have similar sulfur isotope compositions, which range from 1.0‰ to 4.0‰ δ^{34}S_V-CDT (Fig. 9).
5 Discussion

The Wunuer deposit had successively sulfured three stages of mineralization, an early porphyry stage, an intermediate hydrothermal stage, and a later epithermal stage. And two generations of sphalerite, with the first-generation sphalerite (Sp1) precipitated in hydrothermal stage and the second-generation sphalerite (Sp2) precipitated in epithermal stage, were identified.

The negative linear correlation between Fe and Zn in Sp1, with a molar slope of approximately -1 (Fig. 4a), implies an isovalent substitution of Fe$^{2+}$→Zn$^{2+}$ into crystal structure of Sp1. Negative linear correlations between Fe and Zn, Cu and Zn also exists in Sp2, both with a molar slope of approximately -2 (Fig. 4a, b). Fe in Sp2 shows a positive correlation with Cu, with a molar slope of approximately +1 (Fig. 4c). Therefore, it can be concluded that Cu, and most of Fe concentrated in Sp2 are mainly attribute to the ubiquitous chalcopyrite (CuFeS$_2$) inclusions in Sp2 (Bortnikov et al. 1991). Notably different Cu, In contents of Sp1 and Sp2 imply a Cu-depleted and In-rich fluid in hydrothermal stage, whereas a Cu-rich and In-depleted fluid in epithermal stage.

Fluid inclusion study reveals that from porphyry to hydrothermal and to epithermal mineralization, ore-forming fluids changed gradually from high temperature and moderate salinity to low temperature and low salinity (Fig. 5).

Magmatic zircon U-Pb concordia age of the ore-related granite porphyry, obtained as 144.5 ± 0.6 Ma (Fig. 6), can approximately represent the porphyry stage molybdenum-mineralization age. Hydrothermal zircons, formed during hydrothermal stage alteration, whose U-Pb concordia age (Fig. 7) thus can represent the hydrothermal stage zinc-mineralization age (121 ± 2.3 Ma). Rb-Sr isochron age of Sp2 (Fig. 8) implies that the epithermal stage lead-zinc-mineralization occurred at 121 ± 2.3 Ma (Yin et al. 2009).

Sp1 and Sp2 have similar positive sulfur isotope compositions (Fig. 9), which can be explained by the leaching of sulfur and potentially metals (Fe, Mo, Zn, Pb, etc.) from the granite porphyry for both hydrothermal and epithermal stages of sphalerite mineralization (Ripley et al. 1999; Staude et al. 2011).

6 Conclusions

In the late Jurassic epoch (144.5 ± 0.6 Ma), felsic magma intruded and cooled to form the porphyry, and then induced the porphyry molybdenum-mineralization. Subsequently (138.8 ± 1.1 Ma), the high temperature and Cu-depleted fluids, which leached metal materials from the ore-forming related granite porphyry, induced the hydrothermal zinc-mineralization with the formation of Sp1. A long time after porphyry and hydrothermal mineralization (121 ± 2.3 Ma), low temperature and Cu-Pb-rich fluids resulted in the epithermal lead-zinc-mineralization with the formation of Sp2, galena and chalcopyrite. Finally, these three stages of mineralization composed the Wunuer porphyry-hydrothermal-epithermal system.

Acknowledgements

We acknowledge the financial support for the project from the Inner Mongolia Autonomous Region Geological Prospecting Fund Management Center [Grant number: NMKD2014-23]. We greatly acknowledge the fieldwork help of the Sixth Survey and Development Institute of Geology and Mineral in Inner Mongolia. Thanks to teacher Meijun Yang of WUT for helping me conduct the EPMA analyses.

References


Hydrothermal alteration of granitic rocks and geophysical properties in “K-48-22-V” sheet in South Gobi, Mongolia

In-Joon Kim, Sang-Gun No*, Otgon-Erdene Davaasuren, Bum-Han Lee
Korea Institute of Geoscience and Mineral Resources

Abstract. The study area is located within the Gurvansayhan island arc terrane, Mongolia, which includes the Oyu Tolgoi, Kharmagtai, and Tsagaan suvarga porphyry type deposits. Intrusive rocks of the study area consist of granite, granite porphyry, acidic dyke, intermediate dyke, and aplite. In the study area chalcopyrite, bornite and/or malachite bearing veins have been discovered in granite, granite porphyry, and aplite. Copper mineralization is mainly observed in granite which consists of quartz, alkali-feldspars, plagioclase, biotite and minor hornblende. The mineralization occurs as vein, breccia, disseminated, and fissure filling types. Alterations related to the Cu bearing veins were observed as alkali metasomatism, phyllic alteration, and prophylitic alteration. The alterations were recognized by the changing color of the host granite due to the altered minerals such as alkali feldspar, epidote, and sericite. The chargeability obtained from the IP survey shows that there is a high anomaly point in the area where the content of Cu, Au, and Ag are high in the surface, especially in the underlying part bornite, covellite and chalcocite are observed.

1 Introduction

The “K-48-22-V” Cu area is located in the South Gobi region of Mongolia (Fig. 1), approximately 730 km south of the capital city of Ulaanbaatar and is in Omnogobi Province. The area has an average elevation of 1,345 m above sea level and relatively flat to gently undulating topography that is typical of the Gobi Desert of the southern Mongolia-Inner Mongolia plateau (Sung-Chiao, 1984). The term “Gobi” in Mongolian denotes all the deserts and semi deserts in the Mongolian plateau (Sung-Chiao, 1984), and locals use the term to refer to the windblown sand mounds around low bushes common in the region. The study area has been a subject of many systematic geological explorations since the last century. Expeditions of the Soviet Union have resulted in mapping and surveying of the region. Occurrences of copper and other minerals have been discovered during a 1:200,000 scale mapping expedition (Goldenberg et al., 1978), and identified as prospective. Many of the previous studies focused on Cu mineral areas and marked these areas as prospects.

Copper is one of the main metals produced in Mongolia. There are three primary belts across Mongolia where copper mineral deposits exists: South Mongolia, Central Mongolia and North Mongolian. The South Mongolian copper belt occupies nearly the entire area of the Gurvansaikhan island arc terrane, and is a 600 km x 200 km arcuate belt that formed when Middle to Late Palaeozoic volcanic and sedimentary rocks were intruded by Late Devonian and Carboniferous granitoids. The South Mongolian copper belt hosts most of the known porphyry and intrusion-related mineralization in the South Gobi region, including the giant Oyu Tolgoi copper-gold mine (2.4Bt @ 0.78% Cu & 0.33 g/t Au), the Tsagaan Suvarga copper molybdenum deposits (240 Mt @ 0.53% Cu & 0.018% Mo), Shuteen, Kharmagtai, and more than 45 additional deposits. The Early Mesozoic North Belt formed within a continental magmatic arc on the margin of the Siberian Craton. The arc developed in response to the closing of the Mongol-Okhotsk Sea and the subduction of the palaeo-Pacific ocean beneath the Siberian Craton. This belt hosts the giant Erdenet deposit (1.78Bt @ 0.62% Cu, 0.025% Mo), which is Mongolia’s largest producing porphyry copper-molybdenum deposit.

Figure 1. Location map of Tsogttsetsi area and Oyu Tolgoi Cu-Au (Mo) deposit.

2 Geological setting

The geology of the Tsoigtsetsi area (Fig. 2) consists of the Lower Carboniferous Sainshand Khudag Formation which is the dominant formation in the southeastern and northeastern parts of the survey area and consists of andesite, andesite-basalt, basalt, and tuff with a total thickness of approximately 2000 m (Suetenko, 1973; Durante et al., 1976). The formation can be divided into an upper and lower series, and fossils of fauna and flora are locally observed. Goldenberg et al. (1978) reported a Lower Carboniferous age for the Sainshand Khudag Formation, based on fossils present within the strata. The Permian Argalant Formation, the lowest sequence in the survey area and consists of basalt, basalt, and tuff with a total thickness of approximately 200 m (Suetenko, 1973; Durante et al., 1976). The formation can be divided into an upper and lower series, and fossils of fauna and flora are locally observed. Goldenberg et al. (1978) reported a Lower Carboniferous age for the Sainshand Khudag Formation, based on fossils present within the strata. The Permian Argalant Formation, the lowest sequence in the survey area, consists of rhyolite, trachyrhyolite, basalt, andtouriste, dacite, andesite, tuff and tuffaceous, with a total thickness of 1800-1900 m. The Argalant Formation is cut through to the Sainshand Khudag
Formation. The Lower Cretaceous Bayanshiree Formation is present across most of the survey area and consists of red colored clay-sand, sandstone, conglomerate, gravilite, and aleurolite. This formation overlies an unconformity above Paleozoic and lower Mesozoic rocks rich in in Uvurkhangai, South-Gobi, and East-Gobi and a sheeted disconformity between the Bayanzag and Baruungoyot Formations. The multistage Permian intrusive complex is in the central and northern parts of the Tsogttsetsii area, and consists of granite, biotite-amphibole granite, hornblende-biotite, and granodiorite. Older, cross-cutting stocks and dikes are common in the survey area. Early dikes are possibly related to andesitic volcanism because the dikes intrude volcanic and volcano-sedimentary sequences of the Sainshand Khudag Formation. The multistage Permian intrusive complex is in the central and northern parts of the Tsogttsetsii area, and consists of granite, biotite-amphibole granite, hornblende-biotite, and granodiorite. Older, cross-cutting stocks and dikes are common in the survey area. Early dikes are possibly related to andesitic volcanism because the dikes intrude volcanic and volcano-sedimentary sequences of the Sainshand Khudag Formation. The dikes are monzodiorite and dacite porphyry, as well as rhyolite. Granodiorite and granite dikes that intruded later cut the Permian intrusive complex. Aplitic and andesitic dikes then intruded the granitic dikes. Based on regional tectonic constraints and the present-day erosion, two sets of faults (WNW trending and NW-trending) are recognized in the area. The W-NW trending lineaments are dikes, faults, and alteration zones (Otgon et al., 2016).

3 Mineralization and alteration

Vein type is easily observed in field exploration. The veins are mainly extended in the NW-SE direction, and found within a rectangular area (500 m X 2km). The veins consist of different mineral assemblage such as magnetite + hematite + quartz + epidote + chalcopyrite + bornite + pyrite and quartz + epidote + chalcopyrite + pyrite (Fig. 3). The primary ore minerals containing copper are chalcopyrite, malachite, bornite, and chrysocolla. In some samples, bornite has relatively high sulfur content.

Figure 2. Geological map of the Tsogttsetsii area (modified after Jamiyandoj and Zoljargal, 2010).

Alterations related with the Cu-bearing veins were observed as alkali metasomatism, phyllic alteration, and prophylitic alteration (Fig. 4). The alterations were recognized by the changing the color of the host granite due to the altered minerals such as alkali feldspar, epidote, and sericite. The chargeability obtained from the IP survey shows that there is a high anomaly point in the area where the content of Cu, Au, and Ag are high in the surface, especially in the below part the bornite, covellite and chalcocite are observed.

Figure 3. The Cu mineralization types from study area.

Figure 4. The alteration types associated with each Cu bearing veins.

The host granite has 10-10,000 (upper detection limit) ppm Cu, 4-64 ppb Au, and 0.5-23.9 ppm Ag (Fig. 5). High anomalies of Cu, Au, and Ag show similar NW-SE patterns on the anomaly map. The location points showing highest values of Cu, Au, and Ag are matched with the points of the bornite occurrences.
The chargeability obtained from the IP survey shows that there is a high anomaly point in the area (Fig. 6) where the content of Cu, Au, and Ag are high in the surface, especially in the below part the bornite, covellite and chalcocite are observed.

4 Conclusion

We conclude that the mineral assemblages of the veins, along with the geochemical properties and alteration characteristics of the host rock, show that the study area has the potential for porphyry-related mineralization. Also, the results of chargeability surveys show NW-SE trending anomalies.

Acknowledgements

This research was supported by the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (Project No 19-3211-1) funded by the Ministry of Science, ICT and Future Planning of Korea.

References


Constraining the relation of the Erdenet Porphyry Cu-Mo deposit to the Tsagaan Chuluut lithocap in Northern Mongolia

Leslie Logan, Albrecht Von Quadt, Thomas Driesner
Institute of Isotope Geochemistry and Mineral Resources, ETH Zurich, Zurich, Switzerland
Irena Peytcheva
Geological Institute, Bulgarian Academy of Science, Sofia, Bulgaria

Abstract. Erdenet porphyry Cu-Mo deposit is situated in the Central Asian Orogenic Belt, located north of the Tethyan tectonic domain, which formed as a result of multiple oceanic subduction events and collisions (Liu et al. 2015). Arc-magmatism resulted from the closure and subduction of the Mongol-Okhotsk Ocean under the Siberian Craton during the late Permian and early Triassic. The deposit is the second largest copper producer in Mongolia (26 million tons of ore per year) and is ~240 Ma (Watanabe and Stein 2000; Jiang et al. 2010; Kavalieris et al. 2017). Erdenet is spatially related to the Tsagaan Chuluut lithocap approximately 2 km NW of Erdenet open pit, however, recent 40Ar/39Ar dating on alunite from the lithocap suggests it is 16 Ma younger than the porphyry system (224 ± 2 Ma; Kavalieris et al. 2017). To constrain the relationship between the lithocap and Erdenet porphyry deposit and assess the future exploration potential of the region, new zircon U-Pb LA-ICP-MS and ID-TIMS age data, and trace element geochemistry were obtained on selected host and younger cross-cutting dikes in both the deposit and the lithocap.

1 Introduction

Magmatic-hydrothermal ore systems form from focused and expelled magmatic fluid as a result of progressive crystallization of hydrous silicate melt. When the fluids originate from a fertile magma chamber and carry metal complexes, the interaction of such fluids and volatiles with wall rocks and local meteoric water can create porphyry Cu (Au-Ag-Mo) deposits together with an important halo of characteristic alteration zones (Heinrich and Candela 2014). In the shallowest manifestations of such alteration zones, advanced argillic alteration commonly forms an erosion-resistant cap, termed lithocap, composed of quartz, alunite, and argillie minerals (Hedenquist and Taran 2013), which can also be hosts to high-sulfidation epithermal massive-sulfide or Au-Ag deposits.

Mongolia's second largest porphyry Cu deposit is the locally-owned Triassic age Erdenetii Ovoo (referred to as Erdenet) porphyry Cu-Mo deposit in north central Mongolia which currently produces 530,000 tons of copper concentrate and 4,500 tons of molybdenum concentrate per year (Erdenet Mining Corporation 2017). Approximately 2 km northwest of Erdenet deposit, the Tsagaan Chuluut lithocap outcrops in the form of resistant ridges of quartz-alunite and residual quartz. While a body of literature (mostly Russian and Asian) exists for Erdenet deposit from the last 40 years, only recently has the Tsagaan Chuluut lithocap been shown to be enigmatic in its relation to Erdenet porphyry (Kavalieris et al. 2017). Kavalieris et al. (2017) published a 40Ar/39Ar date on K-alunite from the lithocap indicating the timing of its formation was 223.5 ± 1.9 Ma, which is 16 Ma younger than the accepted age of the porphyry (~240 Ma; Watanabe and Stein 2000; Jiang et al. 2010; Kavalieris et al. 2017). This age discrepancy implies the fluid source for the Tsagaan Chuluut lithocap at 223.5 ± 1.9 Ma is not related to the fluids that formed the Erdenet porphyry intrusion at 240 Ma, which carries important economic and future exploration implications for the region. To further investigate whether the lithocap is related to either the adjacent Erdenet deposit or subjacent, still undiscovered porphyry mineralization, new zircon U-Pb laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and ion dilution thermal ionization mass spectrometry (ID-TIMS) age data, and trace element geochemistry were obtained on key geologic samples that bracket the timing of porphyry and lithocap formation.

2 Background

Erdenet porphyry Cu-Mo deposit is related to the formation of the Central Asian Orogenic Belt (CAOB), which extends from the present day Ural Mountains in the west to the Sea of Okhotsk in the east. The CAOB has a multi-phase tectonic history, including the subduction of the Mongol-Okhotsk Ocean (Liu et al. 2015) which drove the arc-magmatism responsible for the Erdenet porphyritic granodiorite that hosts the Cu-Mo mineralization. The Erdenet ore district is a 20 km long NW-SE trending line of ore prospects (Fig. 1a) which occur as magnetic-low anomalies in a reduced-to-pole magnetization map (Fig. 1b) due to the associated magnetite-destructive sericitic alteration. Notably, to the northwest of the currently mined Erdenet open pit, and running in the same trend as the other prospects in the district, is a hitherto unexploited magnetic-low anomaly (Power Station anomaly), which lies directly under a local Erdenet neighborhood. This is the closest magnetic-low anomaly to the Tsagaan Chuluut lithocap.

The currently accepted age data for Erdenet porphyry come from a Re-Os date on molybdenite (Watanabe and...
A U-Pb date on host quartz diorite zircons (Jiang et al. 2010), and a 40Ar/39Ar date on muscovite from the sericitic alteration zone exposed in the open pit (Kavalieris et al. 2017). These dates bracket the timing of both intrusion and mineralization at ca. 240 Ma. The current study contributes new U-Pb LA-ICP-MS and first- time ID-TIMS zircon age data for pre-mineralization granodiorite host rocks, syn-mineralization porphyritic granodiorite, post-mineralization cross-cutting trachyandesite dikes in the open pit, and cross-cutting porphyritic andesite dikes in the lithocap. Samples were selected in order to bracket the latest timing of mineralization in the open pit (from the trachyandesite dikes) and compare it to the latest possible timing of the Tsagaan Chuluut lithocap (based on the porphyritic andesite dikes).

3 Results and discussion

3.1 Zircon geochronology – LA-ICP-MS

Weighted average 206Pb/238U ages give a first order approximation for the timing of the zircon crystallization in each of the respective samples (Table 1). The U-Pb data of the zircons of the pre-mineralization samples vary in age but are generally >250 Ma, in agreement with early stage magmatism in the region (Sotnikov et al. 2005). The syn-mineralization samples indicate protracted zircon crystallization, with weighted average ages around ~237 Ma, and within error of previously published dates for the deposit (Watanabe and Stein 2000; Jiang et al. 2010; Kavalieris et al. 2017). The post-mineralization samples bracket the timing of mineralization and alteration seen at Erdenet open pit and the Tsagaan Chuluut lithocap, respectively. Sample 376 (trachyandesite dike) gives a weighted average age of 240.3 ± 3.6 Ma, suggesting the dike could be coeval with the Erdenet magmatism. However, trace element discrimination diagrams and cathodoluminescent imaging argue that these zircons were not inherited from Erdenet porphyry rocks (Section 3.3). Sample 287 (porphyritic andesite dike) gives a weighted average age of 229.3 ± 3.4 Ma, and is within error of the alunite 40Ar/39Ar inverse isochron age of 224 ± 2 Ma from the lithocap (Kavalieris et al. 2017).

Table 1. Weighted average 206Pb/238U ages for Erdenet pre- syn- and post-mineralization samples based on LA-ICP-MS analysis and calculated using Isoplot (Ludwig 2003).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock Type</th>
<th>Relative Timing</th>
<th>206Pb/238U aU</th>
<th>Error*</th>
</tr>
</thead>
<tbody>
<tr>
<td>245</td>
<td>QDi</td>
<td>Pre-min.</td>
<td>258.3 ± 3.9</td>
<td></td>
</tr>
<tr>
<td>259</td>
<td>Gd</td>
<td>Pre-min.</td>
<td>255.7 ± 3.8</td>
<td></td>
</tr>
<tr>
<td>379.3</td>
<td>EgGr</td>
<td>Pre-syn-min.</td>
<td>237.4 ± 3.6</td>
<td></td>
</tr>
<tr>
<td>379.3</td>
<td>AP</td>
<td>Pre-syn-min.</td>
<td>237.7 ± 3.6</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>EGrG</td>
<td>Pre-syn-min.</td>
<td>235.7 ± 3.5</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>Gd brc</td>
<td>Pre-syn-min.</td>
<td>236.6 ± 3.5</td>
<td></td>
</tr>
<tr>
<td>376</td>
<td>TA dke</td>
<td>Post-min.</td>
<td>240.3 ± 3.6</td>
<td></td>
</tr>
<tr>
<td>287</td>
<td>An dke</td>
<td>Post-min.</td>
<td>229.3 ± 3.4</td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: QDi: quartz diorite, Gd: granodiorite, brc: breccia, TA: trachyandesite, An: andesite, dke: dike, min: mineralization. *propagated systematic error (1.5%).

3.2 Zircon geochronology – ID-TIMS

Zircons from three samples were selected for further ID-TIMS U-Pb zircon analysis: an altered pre- to syn-mineralization porphyritic granodiorite (379.3 AP), a post-mineralization trachyandesite dike (376), and a porphyritic andesite dike (287) that cross-cuts the lithocap (Fig. 2). Results from the host granodiorite and cutting trachyandesite dike help constrain the latest
timing of porphyry mineralization in the open pit. While the results indicate the weighted average ID-TIMS age for the cross-cutting trachyandesite dike is older than the hosting (and mineralized) granodiorite, it is likely that analytical uncertainty and zircon grain selection causes this slight discrepancy. Though data is limited, utilizing the youngest zircons of both 376 (trachyandesite dike) and 379.3 AP (granodiorite), it can be suggested that at least 240,000 yr passed at Erdenet porphyry deposit before the emplacement of the dike.

Zircons from the porphyritic andesite dike (287) that cross-cuts the lithocap show a weighted average ID-TIMS age of 230.219 ± 0.095 Ma (Fig. 2); importantly being older than and contradicting the currently published 40Ar/39Ar K-alunite age obtained for the lithocap (223.5 ± 1.9 Ma; Kavalieris et al. 2017). The lack of overlapping errors between the two ages suggests the 40Ar/39Ar age is not representative of the true timing of formation of the Tsagaan Chuluut lithocap and that the alunite measured for 40Ar/39Ar analysis did not remain in a closed isotopic system in its history. Additional microscopic and X-ray diffraction evidence from this study indicates plagioclase crystals in the porphyritic andesite samples have been altered to epidote, clays, and chlorite, corroborating that the dike and the lithocap were altered by relatively hot fluids after the dike’s emplacement.

3.3 Zircon trace element geochemistry

Zircon trace element geochemistry was used to distinguish and compare the dated pre-, syn-, and post-
mineralization samples and to provide insight into the processes forming each rock type. In general, zircons from the trachyandesite dike that cross-cuts the Erdenet porphyry (376) shows least-evolved signatures (relative to the other analyzed samples) especially noted in the plot of Yb/Gd (chondrite normalized, CN) versus Ce/Sm (CN; Fig. 3a). This suggests that even though the U-Pb geochronology indicates the trachyandesite dike is approximately coeval with the granodiorite host rocks, it has significantly more primitive trace element signatures and therefore should be related to late-post-ore replenishment of the upper crustal magma chamber. Additionally, these primitive signatures discriminate these zircons from Erdenet porphyry rocks excluding the possibility that they were inherited from the late stage Erdenet magma. On the other hand, the cross-cutting dike in the lithocap (287) shows the most evolved signatures in trace elements comparisons. It has previously been shown that fertile porphyry Cu ± Mo ± Au deposits can be traced by Eu/Eu* (Eu/sqrt(Sm*Gd), CN values), Ce/Nd, Dy/Yb, and Y comparisons of zircon compositional data, with Eu/Eu* values >0.03, (Ce/Nd)/Y >0.01, Dy/Yb <0.3 (Lu et al. 2016). Using these values to compare Erdenet and Tsagaan Chuluut zircon data (Fig. 3b-d) reveals that the dike that cross-cuts the lithocap (287) has a fertile magma chamber signature, despite being ca. 10 Ma younger than Erdenet deposit. Importantly, this suggests that magmatism sourcing from a fertile magma chamber occurred 10 Ma after Erdenet deposit was formed, and these dikes may belong to a yet undiscovered porphyry deposit. Additionally, such magmatism may be an explanation for an isotopic resetting of the younger alunite $^{40}$Ar/$^{39}$Ar age obtained by Kavalieris et al. (2017).

### 4 Implications

The recent $^{40}$Ar/$^{39}$Ar alunite age published by Kavalieris et al. (2017) raises an important question about the relationship of Tsagaan Chuluut lithocap to the Erdenet porphyry Cu deposit with significant economic implications. The $^{206}$Pb/$^{238}$U ID-TIMS youngest zircon age (230.079 ± 0.150 Ma) of the cross-cutting porphyritic andesite dike in the lithocap contradicts the 16 Ma younger $^{40}$Ar/$^{39}$Ar alunite age and indicates the lithocap cannot be younger than ca. 230 Ma. However, zircon trace element geochemistry (Fig. 3) indicates the zircons from this dike source from a similar (and fertile) magma chamber as the Erdenet porphyry host rocks $^{206}$Pb/$^{238}$U ID-TIMS youngest zircon age of 240.601 ± 0.395 Ma). The 10 Ma gap between these rocks suggests another similar and fertile magmatic system was occurring after the formation of Erdenet porphyry Cu-Mo deposit and may be related to the isotopic resetting and/or later formation of alunite in the Tsagaan Chuluut lithocap. Further geochronology and characterization of Tsagaan Chuluut lithocap is needed to fully assess the exploration potential of Erdenet ore district.

### Acknowledgements

This project was carried out at and supported by the Institute of Isotope Geochemistry and Mineral Resources at ETH Zurich. The authors thank Erdenet Mining Corporation, Imants Kavaleris, and Bat-Erdene Khashgerel for their collaboration and guidance during the field work in this project.

### References


Abstract. Tiegelongnan is located in Bangongco-Nujiang metallogenic belt, Tibet. It is the largest porphyry-epithermal Cu deposit in Duolong ore cluster with over 2.0 Gt @ 0.53% copper. The deposit is hosted in the Jurassic sandstones (Sewa Formation), and is related to Cretaceous intermediated-felsic intrusions (diorite and granodiorite), covered and protected by post-ore andesitic volcanic rocks of the Abushan Formation (Fig. 1; Lin et al. 2017a). This study aims to reveal the alteration, mineralization, diagenesis and ore-forming processes of this giant deposit according to the detailed geological core-logging, geochronology and fluid inclusions.

1 Geology

Based on the detailed field geological survey, drilling logging and microscopy, two kinds of mineralization were identified, with the early porphyry mineralization overprinted by later epithermal mineralization (Lin et al. 2019). Veinlet, vein and disseminated pyrite, chalcopyrite, bornite and minor molybdenite, etc. were the typical mineralization in the deep and outer zones (Lin et al. 2017a). Potassic, prophylitic, and phyllic were the main alteration styles and A, B, D veins occurred during the porphyry mineralization. Epithermal mineralization is mainly produced in the shallow parts of the system, superimposed onto the porphyry mineralization with disseminated and vein pyrite, enargite, bornite, covellite, digenite, eng-Enargite, Hem-hematite, Kao-kaolinite, lim-limonite, Mo-molybdenite, Py-pyrite, Q-quartz, Ser- sericite, Ten-tennattite, W-well crystallization, P-poor crystallization.

2 Results and Discussion

The diorite porphyry was intruded in the western of Tiegelongnan, as a concealed dike. Strong prophylitic alteration and minor veinlet chalcopyrite, pyrite and/or hematite are occurred in diorite porphyry, locally. Twenty LA-ICP-MS ages of zircons were used to determine the crystal age of diorite porphyry. Its weighted average age was 123.1±1.7 Ma (MSWD=0.7) (Lin et al., 2017a), represented the initial magmatism in Tiegelongnan deposit.

The granodiorite porphyry was emplaced in the center of Tiegelongnan, showing the closely relationship with copper mineralization and potassic, phyllic and advanced argillic alteration. The LA-ICP-MS weighted average ages of three different granodiorite porphyry samples (4804, 3204 and 2404) were 121.5±1.5Ma (n= 27, MSWD=0.8), 122.1±1.0Ma (n= 23, MSWD=0.4) and 120.4±1.3Ma (n= 25, MSWD=0.9), respectively. The SHRIMP weighted average age of another granodiorite porphyry sample...
(4004) was 121.2±2.4 Ma (n=9, MSWD=1.3), conceded with the LA-ICP-MS ages within the error. The volcanic rocks, andesite and dacite of Meiriqiecuo Formation covered the intrusions obviously, indicated that they erupted later, as the end of magmatism in Tiegelongnan. The LA-ICP-MS weighted average ages of two samples of andesite (3220, 2404) were 111.8±1.5 Ma (n=21, MSWD=1.6), 110.1±0.7 Ma (n=18, MSWD=2.3) (Wang et al., 2015), respectively, which were conceded with the SHRIMP age of another sample (3204), 111.7±2.1 Ma (n=10, MSWD=1.3).

The Re-Os ages of eight molybdenite samples from ore-bearing porphyry were in the range of 120.8±1.7 Ma to 121.7±1.7 Ma and a weighted average age of 121.2±0.6 Ma (MSWD=0.1) (Lin et al., 2017a) in agreement with previously published dates of 119±1.4 Ma (Fang et al., 2015). These data represented the porphyry mineralization age. Eight pyrite samples from the advanced alteration zone were used to do the Rb-Sr dating, and yielded an isochron age of 117±1.8 Ma (MSWD=1.3), representing the age of high-sulfidation epithermal mineralization (Line et al., 2017b).

40Ar-39Ar ages of biotite from potassic zone, sericite from phyllic zone were 121.1±0.5 Ma, 120.8±0.9 Ma, respectively (Lin et al., 2017b), which were coincided with Re-Os ages (121.2±1.2 Ma) of molybdenite from the porphyry mineralization (Lin et al., 2017a). In addition, An 40Ar-39Ar age of alunite from advanced argillic zone is 117.9±1.6 Ma, which coincided with the Rb-Sr age (117.5±1.8 Ma) of pyrite from epithermal mineralization (Fig. 3) (Lin et al., 2017b). These ages showed the delicate temporal framework of different alteration and mineralization, and were useful to reveal the ore-forming process of Tiegelongnan giant deposit.

In summary, the ore-forming process of the Tiegelongnan giant deposit can be divided into three stages: A) Porphyry mineralization (123 to 119 Ma): diorite and granodiorite porphyries intruded successively and formed the porphyry alteration and mineralization. B) Epithermal mineralization (118 to 117 Ma): magmatic vapour and hydrothermal fluid mixed with groundwater, superimposed and reformed the early porphyry alterations and mineralization, and formed the advanced argillic alteration and high-sulfidation copper polymetallic mineralization. C) Post mineralization volcanic cover (111 to 110 Ma): the large volume of andesite and dacite were erupted after a significant period of erosion of the porphyry-epithermal ore-body (~7 Ma) (Fig. 4), and protected the deposit up to now.

Acknowledgements

This work was jointly sponsored by the Public Science and Technology Research Funds Projects, National Key R&D Pro-gram of China, Deep Resources Exploration And Mining (project No.2018YFC0604101 and 2018YFC0604106).

References

Constraints of Re-Os-S-Pb isotopes and trace elements geochemistry on the genesis of the Larong W-Mo deposit, eastern Tibet

Jun Liu, Wenchang Li
Faculty of Earth Resources, China University of Geosciences, Wuhan, China

Wenchang Li, Xiangping Zhu, Baodi Wang
Chengdu Center of China Geological Survey, China

Fucheng Yang
Kunming University of Science and Technology, China

Abstract. The Larong W-Mo deposit is the first giant porphyry W-Mo deposit discovered in eastern Tibet. The W-Mo orebodies are mainly hosted in the monzogranite porphyry, the granodiorite porphyry and the surrounding quartz schist. Re-Os isotopic dating of six molybdenite samples yielded a weighted mean age of 91.8 ± 0.5 Ma. The results of in-situ trace elements analyses of pyrite, molybdenite and chalcopyrite are consistent with the mineralization characteristics of the Larong deposit, in which the main metallogenic elements are W and Mo, accompanied by Bi, Sn and Cu. The δ³⁴S_VCDT values of sulfides range from 0.25‰ to 6.37‰, with a mean of 2.15‰, suggesting a predominant magmatic sulfur origin. Molybdenite has high Pb isotopic composition (²⁰⁸Pb/²⁰⁴Pb = 39.356-39.908, ²⁰⁷Pb/²⁰⁴Pb = 15.747-15.928, ²⁰⁶Pb/²⁰⁴Pb = 18.843-20.1), but low Ni and Re contents, implying that the ore-forming materials in the Larong deposit were derived mainly from the upper crust. The W-Mo mineralization is genetically related to the Late Cretaceous monzogranite porphyry. With the decrease of temperature and oxygen fugacity of ore-forming fluid exsolved from magma, the mineralization of tungsten and molybdenum was formed successively.

1 Introduction

The Leiwuqi-Zogang metallogenic belt (LZMB) is an important non-ferrous metallogenic belt in Sanjiang area of southwestern China (Fig. 1). Previously discovered deposits in this belt mainly consist of Pb-Zn deposits and Fe deposits. The discoveries of the Saibeinong Sn deposit, Larong W-Mo deposit and Dongpulu Cu-W-Sn deposit in recent years indicate that the LZMB is expected to become another important W-Sn-Mo-Cu mineral resource base in southwest China. The Larong W-Mo deposit is situated in the southeastern part of the LZMB (Fig. 1). So far only a general study on the geological characteristics and metallogenic background of this deposit has been carried out. The formation age of the Larong deposit is unclear, the sources of ore-forming materials and the genesis of the deposit are not constrained.

Here Re-Os isotopic dating of molybdenite, in-situ sulfur and lead isotopic and trace elemental analyses of sulfides from the Larong deposit are carried out in order to determine the mineralization age, reveal the sources of ore-forming materials and provide critical information for the metallogenic process of the Larong deposit.

Figure 1. (A) Tectonic subdivision of the Tibetan Plateau-Sanjiang Region (Metcalfe 2013); (B) Geological map of the Leiwuqi-Zogang belt in eastern Tibet.

2 Geology of the ore deposit

The Youxi Group is the main ore-bearing strata (Fig. 2), which predominantly comprises a set of quartz schist, and metamorphic quartz sandstone. The faults are well developed in this deposit, mainly consisting of two groups of fault structures in directions of NW and nearly W-E (Fig. 2). The magmatic rocks in the deposit are mainly hypabyssal intrusive rocks. The granodiorite porphyry is located in the shallow part of the deposit, the monzogranite porphyry is situated in the deep part of this deposit, and both of them are ore-bearing intrusions. LA-ICP-MS zircon U-Pb dating reveals that the Larong
granodiorite porphyry and monzogranite porphyry were emplaced at 213.8 ± 1.3 Ma and 93.9 ± 1.3 Ma, respectively.

The Larong W-Mo deposit includes four orebodies (Fig. 2) which occur as banded structures along the NW direction and holds more than 11.48 Mt WO₃ and 2.6 Mt Mo. The NO. I main orebody is mainly hosted in the monzogranite porphyry, the granodiorite porphyry and the surrounding quartz schist. The ore minerals mostly consist of scheelite, molybdenite, pyrite and a small amount of chalcopyrite (Fig. 3). The gangue minerals are commonly composed of quartz, alkaline feldspar, sericite, muscovite, fluorite, chlorite, epidote and calcite. The Larong deposit has the alteration characteristics of typical porphyry W deposits. The alteration zonations from the inside to the outside can be roughly divided into potassium zone, strong quartz-sericite (muscovite) zone, weak quartz-sericite-chlorite zone. The Larong W-Mo mineralization can be divided into three paragenetic stages: Stage I is the main W-mineralization stage, the main mineral assemblages are quartz, alkaline feldspar, scheelite and muscovite (sericite). Stage II (quartz-sulfide stage) is dominated by molybdenite, pyrite and chalcopyrite, which have close relationships with silicidation, sericitization or muscovitization. This stage can be further subdivided into quartz + molybdenite + pyrite +chalcopyrite + scheelite stage (Stage II-1), quartz + molybdenite + pyrite stage (Stage II-2) and pyrite + molybdenite stage (Stage II-3). The paragenetic Stage III (quartz vein stage) is dominated by the quartz veins, with no or little pyrite, and this stage is closely related to chloritization and carbonatization.

3 Analytical results

3.1 Molybdenite Re-Os ages

The concentrations of ¹⁸⁷Re and ¹⁸⁷Os of the molybdenite samples from the Larong deposit range from 33.33 to 54.14 ppb to 51.03 to 82.64 ppm, respectively. Six samples yielded restricted model ages of 91.5 to 92.3 Ma with a weighted mean age of 91.8 ± 0.5 Ma (Fig. 4B), which is consistent with the isochron age of 90.6 ± 2.1 Ma (Fig. 4A).

3.2 LA-ICP-MS trace element compositions

Upper crust-normalized trace element variation of sulfides are shown in Fig. 5.
Pyrite in the Larong deposit is characterized by enrichment of As, Se, Co and Bi; Molybdenite is extremely rich in Pb, W, Bi, Sb, Se and Re; Chalcopyrite is characterized by enrichment in Se, Sn and Bi.

3.3 In-situ sulfur isotopic compositions

Except for individual grains of pyrite with higher values, the majority of \( \delta^{34}S_{VCDDT} \) values of sulfides are concentrated in the range of 0.25-2.68‰ and different sulfides are in the order: molybdenite (1.74-2.68‰, average 2.21‰) > pyrite (0.25-2.63‰, average 1.62‰) > chalcopyrite (0.46‰), indicating that sulfur isotopic fractionation had reached a balance between various sulfides and \( H_2S \) in hydrothermal ore-forming solution of the Larong deposit. Among them, \( \delta^{34}S_{VCDDT} \) values of the Stage II-1 pyrite are concentrated between 0.25‰ and 0.47‰, which are consistent with that of chalcopyrite (0.46‰); The Stage II-2 pyrite has \( \delta^{34}S_{VCDDT} \) values ranging from 0.72‰ to 2.5‰, which are basically consistent with those of molybdenum (1.74‰-2.68‰); The Stage II-3 pyrite has a wide range of \( \delta^{34}S_{VCDDT} \) values of 4.52‰-6.37‰.

3.4 In-situ lead isotopic compositions

All molybdenite samples have similar Pb isotopic compositions (Fig. 7) with \( ^{208}\text{Pb} / ^{204}\text{Pb}, ^{207}\text{Pb} / ^{204}\text{Pb} \) and \( ^{206}\text{Pb} / ^{204}\text{Pb} \) values of 39.356-39.908, 15.747-15.928 and 18.843-20.120, respectively. And they all have high \( \mu, \omega \) and Th/U values of 9.66-10.01, 35.26-40.90 and 3.47-3.97, respectively.

4 Discussion and conclusions

4.1 Timing the Larong W-Mo deposit

The Re-Os isochron age of 90.6 ± 2.1 Ma (Fig. 4A) is consistent with the weighted average age of 91.8 ± 0.5 Ma (Fig. 4B), indicating that the Larong W-Mo deposit was formed in the Late Cretaceous. This age is close to the K-Ar age of 99.16 Ma from the Saibeinong Sn deposit (Shentu and Wang 1991), suggesting that there exist a Late Cretaceous W-Sn-Mo metallogenic event in the LZMB.

4.2 Sources of ore-forming materials

The Larong deposit is free of sulphate minerals, and mainly composed of molybdenum, pyrite and chalcopyrite, indicating a relatively low oxygen fugacity, then the \( \delta^{34}S \) values of the sulfides are roughly equivalent to the total \( \delta^{34}S \) values of the hydrothermal fluid (Ohmoto 1972). The \( \delta^{34}S_{VCDDT} \) values of sulfides in the Larong deposit range from 0.25‰ to 6.37‰, with a mean of 2.15‰. Unlike sedimentary rocks, which usually have a negative or wide range of \( \delta^{34}S_{VCDDT} \) values, the \( \delta^{34}S_{VCDDT} \) values of sulfides in the Larong deposit are relatively concentrated, and slightly above the range of the mantle sulfur (0 ± 2‰), indicating a predominant magmatic sulfur origin. From Stage II-1, Stage II-2 to Stage II-3, the average \( \delta^{34}S \) values of pyrite change from +0.33‰ to 1.88‰ and to 5.34‰ (Fig. 6). It is possible that the increasing trend of \( \delta^{34}S \) values may reflect the gradually decreasing of oxygen fugacity and temperature during the ore-forming process (Herlec. 2010).

The \( \mu \) values of molybdenite in the Larong deposit are relatively concentrated (9.66-10.01), higher than the average value of upper crust (9.58), indicating a predominant upper crustal lead source. This argument is also supported by the fact that almost all molybdenite samples plot in the fields of the upper crust in the \( ^{207}\text{Pb} / ^{204}\text{Pb}, ^{206}\text{Pb} / ^{204}\text{Pb} \) diagram (Fig. 7A) and the \( \Delta\beta - \Delta\gamma \) lead parameters diagram (Fig. 7B). The \( \omega \) values of molybdenite are between 35.26 and 40.90, and the great majority of them are higher than the average value of the upper crust (36.84). The Th/U ratios of molybdenite vary from 3.47 to 3.97, between the average values of the mantle (3.45) and the upper crust (3.88), and are closed to the upper crustal reservoir, indicating that the lead of the Larong deposit was mainly derived form the upper crust.
source.

The Ni contents of pyrite can also provide important information for the sources of ore-forming materials. For example, the Ni contents in the mantle rocks can be up to 2200 ± 500 ppm (Palme and O'Neill 2003), therefore, if Ni in pyrite is derived from basic-ultrabasic rocks, then the Ni contents should be relatively high. In contrast, Ni in pyrite derived from felsic rocks such as highly differentiated granite usually has very low contents. In this study, the contents of Ni in most pyrites are less than the average value of continental crust (59 ppm; Rudnick and Gao 2003), indicating that the ore-forming materials were mainly derived from the continental crust.

4.3 Implications for ore-forming process

The Re-Os weighted average age (91.8 Ma) from the Larong deposit is consistent with the zircon U-Pb age (93.9 Ma) of the monzogranite porphyry, and high-temperature alteration and disseminated mineralization are well developed in the monzogranite porphyry. Hence, we propose that the Larong W-Mo deposit is genetically related to the monzogranite porphyry and the ore-forming processes are as below.

During the Later Cretaceous, fault-controlled emplacement of magma generated the Larong monzogranite porphyry, and it continued to cool and crystallize to form the W- and Mo-rich fluid.

2) In the ascending process, the fluid filtered through and reacted with the cooling porphyry rocks, causing K-silicate alterations. Then the alteration of plagioclase into K-feldspar released abundant Ca^{2+}, which combined with HWO_{4}^{2-} or WO_{4}^{2-} to form scheelite during Stage I. However, the Stage I fluid was relatively high-temperature, oxidizing and poor in S^{2-}, thus unfavorable for sulfide deposition (Yang et al. 2012).

3) As the water-rock reaction continued, the fluid became more acidic, reducing, lower-temperature and rich in S^{2-}. This change facilitated the deposition of sulfides such as molybdenite, together with quartz, forming the Stage II quartz-molybdenite stockworks. Meanwhile, plagioclase was altered to sericite or muscovite and released abundant Ca^{2+}, then combined with remaining HWO_{4}^{2-} or WO_{4}^{2-} to form a small quantity of scheelite.

4) Finally, after precipitation of scheelite and molybdenite, a small amount of pyrite was formed in the later stage (Stage III).

Acknowledgements

This research was supported by the Commonweal Project from Yunnan Science and Technology Award-Outstanding Contribution Award (2017001), China Geological Survey (DD20179604 and DD20160016) and the International Megascience Research Program of Chengdu Center of China Geological Survey. We are grateful to Dr. Kaiyun Chen and Dr. Zhihui Dai from the Institute of Geochemistry, Chinese Academy of Sciences for her assistance on the LA-ICP-MS trace element analysis of sulfides. We also appreciate the kind help of Wanhua Cheng from the Chengdu Center of China Geological Survey for his immense help on sample preparation.

References


Geology and exploration of the Sinongduo Ag polymetallic low-sulfidation epithermal deposit in Tibet, China

Juxing Tang  
*MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, CAGS, Beijing, China*

Zongyao Yang  
*Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu, China*

Xinghai Lang, Chonghai Zhang  
*College of Earth Science, Chengdu University of Technology, Chengdu, China*

Guyue Hu, Zhuang Li  
*MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, CAGS, Beijing, China*

**Abstract.** Sinongduo Ag polymetallic deposit explored in recent years is considered to be the first discovery of the low sulfidation epithermal deposit type in the Linzizong Group volcanic rocks. It contains >0.5 Mt of Pb+Zn grading at about 8% and 500 tons of Ag grading at about 80 g/t. We take the Sinongduo as a type example to study the mineralization in the Linzizong Group volcanic rocks and based on the geological study of Sinongduo, we find another gold prospect area in Woruo, which is about 2 km to the north of Sinongduo. 6 orebodies were found on the surface of Woruo and the grades of Au and Ag are approximately 0.9 g/t and 90 g/t respectively. Despite of the low grade of Au, we still believe there are potentially other high grade orebodies beneath the lithocap of Woruo.

**1 Introduction**

Tibet Plateau, is a result of the India–Eurasia collision, and is the Earth’s largest ongoing orogen. There are two important metallogenic belts named Gangdese Metallogenic Belt and the newly delimited Bangong-Nujiang Metallogenic Belt, which are prospective. Benefit from the abundant resource exploration projects and basic geological surveys supported by the Chinese government and mining companies recently years, so many large or giant deposits have been found such as the Duolong (Lin et al. 2019), Jiamu (Zheng et al. 2016) and Xiongcon (Lang et al. 2014; Tang et al. 2015; Yang et al. 2017). Although the amount of copper resources controlled at present is more than 60 Mt and the associated gold is more than 10 Mt, the prospective resources of copper are still more than 15 Mt (Tang et al. 2017).

The Linzizong volcanic rocks, which are widely distributed in the southern margin of Gangdese Metallogenic Belt in central Tibet, are the geological records of the India–Eurasia collision (Mo et al., 2008). It is mainly composed of a series of calc-alkaline subaerial volcanic rocks erupted from about 69 Ma to 40 Ma which are the main host rocks of the epithermal deposit around the word. Compared to the large number of epithermal deposits found in the subaerial volcanic rocks of the Andean metallogenic belt in South America, however, there is rare report of epithermal deposits in the Tethyan metallogenic belt. We can’t help asking that are these deposits denudated or even not exist? The answer is absolutely not, but those deposits just not have been found yet. Previous point is that the subaerial volcanic rocks of the Linzizong Group are with poor potential for prospect. However, the discoveries of the Sinongduo, Narusongduo, Luobuzhen, Lazong and Chagelei recently years which are related to the Linzizong volcanic rocks prove that it’s controversial for prospecting. On the contrary, the erosion of the Linzizong volcanic rocks is slightly, and that means the preservation of the deposit is in good condition.

**2 Geology**

The research area is the central part of the south Gangdese Metallogenic Belt (Fig 1). There are many Pb-Zn deposits in this area, which include Sinongduo, S-Sinongduo (>0.6 Mt of Pb and Zn grading at 12%), Narusongduo (>1 Mt at 10% Pb and Zn), Woruo (potential of more than 30 t Au, 1000 t Ag and 1 Mt Pb and Zn), Lazong, Zhazhalong, Chagelei, Xuebie, Luobuzhen and Chaji. The controlled Pb and Zn metal resources are more than 3 Mt as so far and it has been predicted that there are still a large amount of deposits remain to be discovered.

The host rocks of Sinongduo Ag polymetallic deposit are volcanic breccia and crystal tuff. Vein and hydrothermal brecciated ore column are the main type orebodies. Particularly, there are independent Ag vein orebodies (grading from about 50 g/t to 6000 g/t) over the Ag-Pb-Zn orebodies different from other Pb-Zn deposits nearby. The main structures include veined sturcture, brecciated (Fig 2e), mesh-veined, banded and laminated, crustified, massive and disseminated structures, which show an open space environment. The ore textures of this deposit are developed on the basis of crystallization, metasomatism and exsolution.
The volcanic-intrusive rocks in Sinongduo area were formed in Paleocene 65-62 Ma (Ding et al. 2017). The volcanic rocks belong to the high potassium peraluminous rocks and have the arc volcanoes geochemical characteristics. The $^{40}$Ar-$^{39}$Ar data of altered illite limited the deposit metallogenic age are about 62 Ma (unpublished yet), consistent with the eruption of volcanic rocks. The major metallic minerals are galena, sphalerite, and argentite, pearceite, and pyrite together with rare chalcopyrite. The silver minerals mainly include peaceite, argentite, pyrargyrite, akanthite and native silver, which occur in the fissures of the Fe-Mn carbonates, jasper and the early sulfides (Li et al. 2017).

We first considered the Sinongduo Ag polymetallic as a low sulfidation epithermal deposit because of the typical alteration and its tectonic setting. The major altered minerals are illite (Fig 2c, 2d), chalcedony (Fig 2b), adularia (Fig 2a), sericite, fluorite and carbonates such as rhodochrosite, siderite and calcite (Fig 2c, 2f, 2g). After 4 years of exploration, we convince that it is the first discovery of low sulfidation epithermal deposit in Linzizong Group volcanic rocks according to the fluid inclusion (Li et al. 2017), alteration, textures and ore mineralogy.

Figure 1. Geological map of the Sinongduo area showing the position of deposit.

Figure 2. a. Adularia and carbonates vein. b. Chalcedony stockwork. c. Siderite in illite. d. Illite in volcanic breccia. e. Sulfides cemented breccia. f. Rhodochrosite cemented breccia. g. Quartz after bladed calcite in ore.
3 Exploration in Linzizong Group

In order to give some exploration advices for Zhongrui Mining, we chose rock and soil geochemical survey to study the metallogenic elements anomaly. A total of about 20 thousand samples (9235 samples are collected by our group members) were taken from the surface in Sinongduo area for prospecting. Based on the rock survey in Sinongduo area, we found that there are strong anomalies of Au, Ag, As, Sb, Pb, Zn and Mo. The strongest anomalous area is about 1 km² and 2 km to the north of Sinongduo Ag polymetallic low sulfidation epithermal deposit named Woruo (Fig 1). The level of Au range from 20×10⁻⁹ to 130×10⁻⁹, and Ag is 30×10⁻⁶ to 100×10⁻⁶. All these anomalous elements coordinate with each other completely in good zoning.

![Figure 3. a. Vuggy quartz. b. Black sulfides-quartz cemented hydrothermal breccia. c. Hydrothermal breccia in drillhole WZK0001](image)

In addition, geological survey helped us to circle out the rudiment of the gold orebodies. According to the geological survey, 5 main orebodies were found hosted in the tuff. The orebodies strike to the north and the dip is very high. Main orebodies are formed with echelon structure. The stockwork ore and vein ore are distributed on both sides of the 5 main ores. Black materials cement the tuff and chaledony breccias forming the hydrothermal eruption breccia (Fig 3b, 3c). These kinds of black materials are composed of chaledony, quartz, fine-grained pyrite and other sulfides, which is the cause of black based on the microscopic features. Furthermore, pyritohedron pyrite is always visible under the hand lens, which is considered to be the indicator of the ore-hunting of gold. The crudely banded veins have many crystalized zonings which are black sulfides, quartz (chaledony), fine-grained pyrite and quartz core from the external to the central. Siliceous veins, massive quartz and comb quartz are the most typical characteristics.

4 Discussion

The evolution of the Neo-Tethyan Ocean and the process of India plate and Eurasia plate collision have been studied for decades. Although there are many patterns published, but the controversy still exist. Firstly, the ore-forming ages of Pb-Zn deposits in south Gangdese Metallogenic Belt are correspondence with the ages of Linzizong Group volcanic rocks (Wang et al. 2015). That could be an implication of the relationship between the Pb-Zn mineralization and Linzizong Group volcanic rocks, but not the Lhasa terranne basement. Secondly, the large amount of metal (more than 3 Mt Pb and Zn in our research area) also couldn’t be remelted out from the Lhasa terranne basement. According to the possible tectonic setting during that time, our evidences (unpublished yet) tend to owe the metallogenic materials to the subduction of some micro-continents drift from India plate or even Gondwana, and continents subduction seems to be accepted by many researchers (Müller 2010; Capitanio et al. 2010; Ingalls et al. 2016).

In this case, the tectonic setting of Linzizong Group volcanic rocks needs to be discussed again. According to Mo et al. (2008), the Linzizong Group volcanic rocks represent a magmatic response to the India-Asia continental collision beginning at ~70-65 Ma, which means the south margin of Gangdese arc is a collisional background. However, we have evidences indicating that Dianzhong formation is subduction-related, and this let us have confidence in prospect especially of epithermal deposits in Linzizong Group volcanic rocks.

5 Exploration Implications

Geology and mineralization characteristics of the Woruo gold deposit indicate that it belongs to the epithermal deposit too. So far, studies about the genesis and geodynamic setting of this deposit have not been reported, and the exploration also at a primary level. Its powerful vein system indicates the stronger hydrothermal activity in depth. The exploration of Sinongduo and Woruo enable us to make conclusion that Linzizong Group volcanic rocks especially the Dianzhong formation show great potential for exploration of Au, Ag, Pb and Zn. We hope it can be a breakthrough of epithermal gold deposit prediction and exploration in Gangdese Metallogenic Belt.

Acknowledgements

This study was jointly supported by the National Key Research and Development Project of China (2018YFC0604101, 2018YFC0604105) and the National Science Foundation of China (No. 41772075).
References


Mineralogy and mineral chemistry of ore minerals in the Erdaohe skarn Pb-Zn-Ag deposit: implication for system evolution

Jun-Sheng Yang • Xin-Biao Lü
Geological Survey Institute, China University of Geosciences, China

Abstract. The Erdaohe Pb-Zn-Ag deposit is located in the central Great Xing’an Range, the eastern segment of the Central Asian Orogenic Belt. The Triassic monzodiorite is regarded the causative intrusion for the skarn formation and major mineralization in the deposit. The predominant calcic skarn and subordinate manganoan skarn are developed and contain the majority of the ore body. Based on mineral composition and occurrence, five types of sphalerite and four types of galena are identified. Within the calcic skarn, sphalerite evolves from dark to red then yellow in color, combined with decrease of both Mn and Fe contents. Sphalerite in manganoan skarn is characteristic of low molar Fe/Mn ratio (<10). Galena and associated exsolution proves a sequential consumption of Bi, Te, Ag and Sb in the system. Estimated fugacity of S\textsubscript{2} (g) and Te\textsubscript{2} (g) in the main sulfide stage went through an increase ahead of the later overall decrease.

1 Introduction

The Great Xing’an Range has witnessed amalgamations of micro-blocks (Erguna Block, Xing’an Block, Songliao – Xilinhot Block, etc.) and a prolonged magmatic activity throughout the Phanerozoic (Jahn et al. 2011; Li et al. 2013; Liu et al. 2017; Wu et al. 2011). This region is also famous for its immensity in metal resource and diversity in ore types (Ouyang et al. 2015; Wu et al. 2014). Somehow the central part of the Great Xing’an Range is sparse in deposits.

1.1 Erdaohe Pb-Zn-Ag deposit

Exposed strata in the deposit are the Middle-Upper Permian Luohe Formation meta-siltstone, slate and carbonate rocks and the Middle Jurassic Tamulangou Formation to a lesser extent. A thrust fault strikes NE with a dip of 50° to 60°, controlling the distribution of strata and most intrusions. The monzodiorite is of the largest scale which intruded in Triassic. The other major intrusive rock is granite porphyry of Cretaceous age.

At present, mining as well as our study are merely carried out in the ore block I, which holds the majority of ore bodies, which are usually lenticular, banded or vein-like, along NE striking faults. Most ore bodies are hosted in skarn (Figure 1a and 1b), with a small proportion in the form of veins within distal strata. Both calcic skarn and manganoan skarn developed. The massive calcic skarn displays well spatial relationship with the monzodiorite in a sequence of altered monzodiorite-garnet dominated skarn-pyroxene dominated skarn-altered marble. The manganoan skarn always displays as rhodonite dominant veins cutting calcic skarn or carbonate strata, somehow limited at the northern verge of the contact.

Andradite-grossular garnet, pyroxene, apatite, local wollastonite and minor titanite are representative of prograde skarn. Retrograde skarn is dominated by an assemblage of epidote, amphibole, chlorite and minor quartz, hematite and magnetite. The relatively isolated manganoan skarn minerals are considered posterior to retrograde stage due to lower temperature (unpublished data of fluid inclusion homogenization temperature from rhodonite). The following sulfide stage can be further divided into three stages. During the sulfide stage, mineral assemblage is complicated in form of different types of major sulfides, such as sphalerite and galena.

3 Mineralogy and mineral chemistry

3.1 Sphalerite

Sphalerite is a major ore mineral widely formed in the whole sulfide stage. In early sulfide stage, sphalerite is dark to almost opaque in association with pyrrhotite and chalcopyrite (Figure 1c). Red sphalerite starts to emerge in abundance later in sulfide stage, frequently accompanied by galena and pyrite (Figure 1d and 1e).
Sphalerite in the late stage is yellow, also coexisting with pyrite and galena (Figure 1g). Chalcopyrite is not always emulsion in sphalerite, instead, sometimes replacing sphalerite along grain boundary or cleavages as crystal growth or simply in an uneven pattern. Apart from the earliest opaque sphalerite, transparency of the mineral is mostly controlled by density of chalcopyrite.

Major composition variations in sphalerite are Fe and Mn contents (Figure 2). Earliest opaque sphalerite (Sp-1) is only observed in calcic skarn and contains significant amount of Fe (average 11.93 wt. %) and moderate amount of Mn (average 1.32 wt. %). Fe and Mn contents in sphalerite in later stages are influenced by different occurrence. Within calcic skarn, red sphalerite (Sp-2a) carries moderate Fe content (average 6.29 wt. %) and low Mn content (average 0.20 wt. %). In manganoan skarn, red sphalerite (Sp-2b, Figure 1h) is mainly seen replacing rhodonite or as interstitial mineral, which is the lowest in Fe content (average 1.05 wt. %) but relatively high in Mn content (average 3.42 wt. %). Yellow sphalerite (Sp-3a, Figure 1i) occurs in veins cutting carbonate strata, with the lowest Mn content (average 0.17 wt. %) and low Fe content (average 3.95 wt. %).

Another type of yellow sphalerite (Sp-3b), which occurs with alabandite in manganoan skarn, exhibit the highest Mn content (average 4.05 wt. %) with low Fe content (average 1.87 wt. %). A faint correlation between color and cadmium content may exist: yellow sphalerite contains higher Cd content compared to red and opaque variants (average 0.46 over 0.37 wt. %). The Fe/Mn molar ratio works well in recognizing sphalerite from different occurrence. Earliest sphalerite yield moderate Fe/Mn ratio of around 10. Later sphalerite has Fe/Mn molar ratios significantly deviate from 10 (Figure 2b).

### 3.2 Galena and associated exsolution

Galena is the most important mineral accommodating silver in the deposit, commonly found later in sulfide stage. Optically, no difference is observed in galena variants. Mineral assemblage and exsolution texture are considered to identify different types. Earliest galena (Gn-1, Figure 1d) occurs with Sp-B1 in proximal calcic skarn, replacing or enclosing magnetite. Anisotropic acicular minerals (josèite-B) are observed exclusively in galena, therefore considered as a result of exsolution.
The second type (Gn-2, Figure 1e) also has analogous exsolution mineral (tetradymite), but collected further away from the proximal skarn with no magnetite observed. At the manganoan skarn-marble contact zone, the third type (Gn-3, Figure 1f) is observed with tiny gray (hessite) and pale yellow (silver-bearing tetrahedrite) exsolution minerals. The last type (Gn-4, Figure 1g) is associated with yellow sphalerite (Sp-3a) with no exsolution at all. Major compositional variations are observed in Bi, Ag, Cd, Te and Sb contents (Figure 3).

Gn-2 contains the highest Ag (average 1.49 wt. %) and Bi (average 3.71 wt. %) contents among all types. Gn-1 has comparable Bi (average 2.96 with 2.99 wt. %) but slightly lower Ag (average 1.12 with 1.29 wt. %) contents with Gn-3. Gn-4 displays the lowest Bi (average 0.13 wt. %) contents with nearly no Ag concentration. Calculated molar percentage of Bi forms a distinct linear correlation with the one of Ag. Cd content in galena varies little. Only late type (Gn-4) carries slightly more Cd (Figure 3c). Sb concentration in galena is similar to Cd, yet lower overall concentration and more obvious trend (Figure 3d). Early tetradymite group minerals in galena carry little Ag (no more than 0.2 wt. %) but more Sb (average 0.2 wt. %) than their host. Their highly variable Pb contents are likely resulted from sub-micrometric galena inclusions instead of some Pb-rich variants (see dashed trends in figure 4). Ag-bearing tetrahedrite in Gn-3 contains average 18.47 wt. % Ag and only average 0.76 wt. % As, with average Ag/ (Ag+Cu) molar ratio of 0.31 and Sb/ (Sb+As) molar ratio of 0.96.

4 Implication for system evolution

For Sp-1, Sp-2a and Sp-3a, decrease of both Mn and Fe concentration seems concordant with those in the hydrothermal system. Somehow, exceptionally high Mn concentrations of sphalerite in manganoan skarn display a reversed trend. As early Mn-rich minerals of rhodonite crystallize, accumulation of Mn in the hydrothermal is unlikely to be achieved. One possible explanation is that sphalerite obtains high Mn concentration via replacing Mn-rich minerals as rhodonite and alabandite.

Exsolution of joséite-B and tetradymite in early galena are indicative of the enrichment of Bi and Te. The Bi: Te (+S) ratio decrease from 1.27 (average of joséite-B, >1) to 0.64 (average of tetradymite, <1). According to the empirical redox indicator raised by Ciobanu et al. (2010),...
the environment changes from a relatively reduced one to a relatively oxidized one, in accordance with the disappearance of magnetite inclusion in later galena. Compositional changes of galena and associated mineral assemblages indicate a sequential consumption of Bi-Te-Ag-Sb in the system.

**Figure 4.** Schematic diagram comparing actual compositions to the ideal compositions of minerals in the system Bi (+Pb)-Te-S (modified after Cook et al. (2007)). Note the dashed lines indicative of possible mix of sub-micrometric galena inclusion.

Temperature of the sulfide stage is constrained to 270~310°C by homogenization temperature of fluid inclusion of quartz, calcite and white fluorite (unpublished data). Combining with major ore mineral assemblages, a log\(\text{f}_{\text{Te}_2} \cdot \text{log}_{\text{S}_2}\) diagram is presented (Figure 5). The inferred trend suggest a fugacity increase of both sulfur and tellurium due to early precipitation of silicate and oxide over sulfide, then followed by gradual fugacity decrease of both attributed to crystallization of both sulfide and Te-bearing minerals.

**Figure 5.** Log\(\text{f}_{\text{Te}_2}(g)\)-log\(\text{f}_{\text{S}_2}(g)\) diagram showing relative stability of tellurides and sulfides at 300°C (modified after Affi et al. (1988)). The shaded areas represents the estimated fugacity ranges of \(\text{Te}_2\) (g) and \(\text{S}_2\) (g) for different mineral assemblages in the deposit. \(\text{Fa}\) fayalite, \(\text{Po}\) pyrrhotite, \(\text{Sp}\) sphalerite, \(\text{Gn}\) galena, \(\text{Py}\) pyrite, \(\text{CcP}\) chalcopyrite, \(\text{Bn}\) bornite.

Temperature of the sulfide stage is constrained to 270~310°C by homogenization temperature of fluid inclusion of quartz, calcite and white fluorite (unpublished data). Combining with major ore mineral assemblages, a log\(\text{f}_{\text{Te}_2}(g)\)-log\(\text{f}_{\text{S}_2}(g)\) diagram is presented (Figure 5). The inferred trend suggest a fugacity increase of both sulfur and tellurium due to early precipitation of silicate and oxide over sulfide, then followed by gradual fugacity decrease of both attributed to crystallization of both sulfide and Te-bearing minerals.

**Acknowledgements**

This contribution is financially supported by the Inner Mongolia Autonomous Region Geological Prospecting Fund Management Center (Grand NO. NMKD2014-23). We appreciated Tongliaoxinyuan Mining Co., Ltd. and Meijun Yang for assistance in the field work and electron microprobe analyses, respectively.

**References**


Complicated copper sulfides of the Zijinshan high sulfidation epithermal Cu-Au deposit in Fujian, China

Mei Lu, Rong Ye*, Yongkang Wang
China University of Geosciences (Beijing)

Abstract. Zijinshan high sulfidation epithermal Cu-Au deposit has attracted a number of studies due to its complicated mineral compositions, especially copper sulfides. Among copper-sulfur system, digenite, djurleite, covellite, anilite and chalcocite have been observed at Zijinshan ore deposit. Relationship of blaubleibender covellite and other Cu-S sulfides is reported at this deposit for the first time. Blaubleibender covellite is exsolved from anilite, indicating they experience very low temperature. The Zijinshan ore forming system experienced at least three possible stages: pyrite + enargite, digenite + bornite + covellite, fine grained covellite + anilite + djurleite + blaubleibender covellite. Key words: Zijinshan epithermal deposit; copper sulfide; blaubleibender covellite

1 Introduction

The Zijinshan Orefield was discovered in the late 1970s in southeastern Fujian Province, China, including the Zijinshan high-sulfidation epithermal Cu-Au deposit, the Yueyang low-sulfidation epithermal Ag-polymetallic deposit, the Luoboling and Jingmei porphyry Cu-Mo deposits, the Wuziqi Longjiangting, and Ermiagou Cu deposits, and several prospects. According to Zhang 2013, the proven reserves in the Zijinshan Orefield were 399.82 t Au, 6339 t Ag, 4.14 Mt Cu, and 110,000 t Mo. There are various types of mineralization in the giant Zijinshan Orefield, making it worthy of detailed studies. Zijinshan world-class high sulfidation epithermal Cu-Au deposit has attracted a number of studies since it was recognized the first high sulfidation epithermal deposit in mainland China, as well as the hypothesis of close spatial and temporal association between high sulfidation Cu-Au deposit and Luoboling or deep potential porphyry copper mineralization (Huang et al. 2018; Li and Jiang 2017; So et al. 1998; Zhong et al. 2018).

2 Zijinshan Cu-Au deposit

Zijinshan Cu-Au deposit is located near the center of the Zijinshan Orefield, hosted by Middle-Late Jurassic middle-fine grained granite (169-150Ma, Xu et al.,2017), Early Cretaceous dactite-porphyrite, and cryptoexplosive breccia (Figure 1).

The gold veins were concealed in the upper silicification zones. The lower copper ore bodies were mainly in the alunite-quartz alteration zone in various morphology of vein, capsule, and lenticule. The copper ore bodies usually contained economic concentrations of Au and Ag. It has been proven to have Cu reserve of over five million tons (an average copper grade of 0.36 %) and Au reserve of 300 tons. In the year of 2017, Zijinshan deposit produced 3.875t gold and 75,850 t copper (from Zijin Mining).

Figure 1. Generalized geology and deposits of the Zijinshan Orefield.

3 Mineral paragenesis

The uppermost deposit was oxidized intensely, and hematite was formed in this stage intergrown with the remaining quartz, containing the gold enrichment. Digenite is not commonly found as primary phase in ores (Vaughan and Craig 1997). However, the primary Cu-bearing minerals are digenite, covellite and bornite, making Zijinshan very special as a world-class high sulfidation epithermal Cu-Au deposit. Other Cu-bearing minerals have been identified, including pyrite, anilite, djurleite, enargite, chalcopyrite and some W or Sn bearing minerals (Liu 2015). The mineral assemblage of Zijinshan are indicative of an enrichment zone but massive and disseminated ores do not fit the nature of classic enrichment zone. With increasing depth, the main Cu-mineral assemblage varies from bornite-rich to digenite-rich to covellite-rich, representing higher sulfur and oxygen fugacity (Liu 2015).
Blaubleibender (a German word means blue remaining) covellite differs from normal covellite in their copper content and are easily distinguished optically because they keep blue in color of ordinary vibration.

**Figure 2.** Copper sulfides at Zijinshan high sulfidation epithermal Cu-Au deposit. A. cracked bornite and striped covellite were surrounded by blaubleibender covellite and very fine covellite. B. blaubleibender covellite exsolution from anilite.

Immersion oil. Natural blaubleibender covellite is usually intergrown with digenite, and their formation is due to low temperature oxidation of more copper rich phases (Putnis et al. 1977). Blaubleibender covellite are subdivided into yarrowite Cu$_{9}$S$_{8}$ (equal to Cu$_{1.125}$S) and spionkopite Cu$_{39}$S$_{28}$ (equal to Cu$_{1.4}$S). The formation of metastable phases such as blaubleibender covellites produced by the low-temperature replacement of other copper sulfides (Vaughan and Craig 1997). Paragenesis of Blaubleibender covellite and other copper sulfides is reported here in this ore deposit for the first time, indicating Zijinshan ore deposit experienced a very low temperature when forming primary sulfides.

### 4 Conclusion

At Zijinshan high sulfidation epithermal deposit, there are digenite, enargite, djurnite, covellite, anilite, bornite, pyrite, and blaubleibender covellite in ores. The Zijinshan ore forming system experienced at least three possible stages: pyrite + enargite, digenite + bornite + covellite, fine grained covellite + anilite + djurleite + blaubleibender covellite. Complicated copper sulfides of this deposit are perhaps caused by the constant mixing of hydrothermal fluids and meteoric water.

### Acknowledgements

Authors want to express their sincere appreciation for reviewers and the NSF of China (grant number: 41573037, 41273063).

### References


The Ryabinovoe Cu-Au-porphyry deposit (Southern Yakutia, Russia): geology, wallrock alteration, noble gases isotope systematics and isotopic dating of ore-forming processes

Shatova N.V., Shatov V.V., Molchanov A.V., Terekhov A.V., Sergeev S.A., Prasolov E.M.
A.P. Karpinsky All Russian Geological Research Institute (VSEGEI), St. Petersburg, Russia

Dvornik G.P.
Institute Geology and Geochemistry (IGG UB RAS), Yekaterinburg, Russia.

Leontev V.I.
St. Petersburg Mining University (SPbMU), St. Petersburg, Russia.

Abstract. In the Ryabinovoe Cu-Au-porphyry deposit, the ore mineralization is localized within multi-stage metasomatism fields, which were formed in two stages. In the first, pre-ore stage, high-temperature potassium-sodium metasomatites – aegirine feldspathites – were appeared whereas gumbelites of carbonate-sericite-muscovite-orthoclase composition - in the second, low/medium-temperature stage. The results of isotopic (U-Pb, Rb-Sr, Re-Os, 40Ar/36Ar, 3He/4He, 20Ne) investigations of the above-mentioned metasomatites and ore mineralization are discussed in the paper.

1 The Ryabinovoe Ore Field

The Ryabinovoe ore field is associated with Mesozoic alkaline igneous rocks of the Ryabinovy stock and is situated in the Central Aldan Ore Region of South Yakutia. In the geological structure of the Ryabinovy stock, material and structural-textural features and the results of isotope geochronological studies using two independent U-Pb and Rb-Sr geochronometers, give two different groups of high potassium igneous rocks.

The early group, predominantly leucocratic rocks, is represented by aegirine-augite alkaline-feldspathic syenites, syenite-porphries and quartz syenites (nordmarkites) belonging to the Aldan Suite; the radiological age of magmatic crystallization of rocks is estimated to be 142-144 Ma. Syenite porphyry of the dyke series of the Aldan Suite showed a radiological age of 133±5 Ma (Shatov et al. 2012).

The late group, melanocratic rocks of subordinate importance manifested in the form of small stock-shaped bodies and dykes intersecting the Aldan Suite syenites, is represented by alkaline gabbroids, monzonitoids, melanocratic aegirine-augite syenites, phlogopite-pyroxene lamprophyres (minette) and eruptive breccias with lamproitic cement, which belong to a later Tobuk Suite with a radiological age of 130-141 Ma (Shatova et al. 2017).

Figure 1. Geological map of the Ryabinovoe ore field. The frame shows location of Figure 2.

1 – Quaternary alluvial deposits; 2 – Tobuk Suite – Lower Cretaceous (gabbro-monzonite, monzodiorite, melanocratic syenite, alkaline phlogopite-pyroxene lamprophyre and eruptive breccias with lamproitic cement); 3-4 - Aldan Suite – Lower Cretaceous (3 – porphyritic alkali-feldspathic aegirine-augite syenite and nordmarkite, the 1st phase, 4 - alkali-feldspathic aegirine-augite syenite, nordmarkite and syenite-porphry, the 2nd phase); 5 – Yukhtin Formation – Lower Jurassic (sandstone, siltstone, mudstone, conglomerate); 6-7 – Yudom Group – Middle Vendian-Lower Cambrian (6 – arenite, siltstone, dolomite, mudstone, conglomerate, 7 – dolomite, clay dolomite); 8 – Lower Proterozoic metamorphic rocks (amphibole, biotite and biotite-garnet granite-gneiss, gneissic granite, crystalline schist); 9 - faults (a - main, b - secondary).
1074 Life with Ore Deposits on Earth – 15th SGA Biennial Meeting 2019, Volume 2

2 The Ryabinovoe Cu-Au-Porphyry Deposit

The Ryabinovoe deposit is confined to the northeast endocontact part of the Ryabinovy stock (Fig. 1). Ore mineralization of the deposit is localized within two ore sites, Muskovitovy and Novy, among the hydrothermally altered syenites of the Aldan Suite, containing vein-impregnated sulphide (to 3-5%) mineralization (Fig. 2-3).

In ores of the deposit, the main ore mineral is pyrite, the minor minerals are chalcopyrite, sphalerite, galena, molybdenite, and arsenopyrite. Native gold, electrum, native silver, acanthite, tellurides of silver and gold (hessite, petzite, calaverite), fahlores, enargite, digenite, djurleite, stannite, carrollite, moncheite, erlichmanite, etc. are rare (Kochetkov et al. 1989; Vetluzhskikh et al. 2002; Dvornik 2014).

As of June 1, 2011, the total Au reserves at the Ryabinovoe deposit with cut-off grade of 0.8 g/t are estimated at 26 t (with an average grade of 2.05 g/t), and silver, at 56 tons (with an average grade of 4.4 g/t). The above Au and Ag reserves are concentrated in six
orebodies, five of which (Central, Western, Southern, Eastern, and Northern) are found within the Muskovitovy ore site, and the sixth, within the Novy ore site (Kisly et al. 2011).

3 Alteration Control

A mineralogical and petrographic study and mapping of halos of hydrothermally altered rocks, conducted by the authors of the paper, made it possible to establish that the emplacement and long-term development of the Ryabinovy syenite stock was accompanied by the mineral alteration zonation of granite-related type.

Close to the syenite stock, near-contact halos of skarnification, fenitization, and alkaline-amphibole propylitization are widespread with a concentric-zonal structure, inherited largely from the ellipsoid shape of the Ryabinovy stock (Ugryumov and Dvornik 1984; Kochetkov et al. 1989).

In the inner parts of the stock, the zonation of mineral alteration is represented by halos of high-temperature aegirine-feldspathic alteration types - feldspathites and replacing them in time halos of medium-low-temperature wallrock gumbeites or carbonate-sericite-muscovite-orthoclase hydrothermally altered rocks.

Among the gumbeites, two facies varieties are distinguished: carbonate-sericite-muscovite-orthoclase (G1 facies), developed mainly among syenites of the Ryabinovy stock from 550 to 750 m, and quartz-carbonate-barite-adularia (facies G2), accentuated in rocks of the ore field at hypsometric marks from 750 to 1100 m and above.

Thus, the lateral row of hydrothermally altered rocks identified at the present level of erosion, in essence, reflects the vertical zonation of mineral alteration, manifested in the Ryabinovoe ore field.

Fig. 4 shows a model-reconstruction of the vertical zonation of mineral alteration, constructed by interpolating all the mineralogical and petrographic data obtained from the line intersecting the Novy and Muskovitovy ore sites of the Ryabinovoe deposit.

The established modern pattern in the distribution of the above-considered zones of hydrothermal alterations within the Muskovitovy and Novy sites is, on the one hand, a reflection of material and structural-tectonic heterogeneities in the structure of the Ryabinovy stock itself and its morphology, and on the other hand, under the conditions of a heavily dissected topography (600-1150 m), is a reflection of an uneven cut by the modern erosion surface of three subparallel zones of the “cover” type, replacing each other in the intra-intrusive space bottom-up (in the direction of the vector of maximum variability): feldspathites → gumbeites of the carbonate-sericite-muscovite-orthoclase facies (G1) → gumbeites of the quartz-carbonate-barite-adularia facies (G2).

That is, in this series of hydrothermally altered rocks, gumbeites of the G2 facies occupy the uppermost link of the vertical column of mineral alteration (Terekhov et al. 2014).

4 Results of Isotopic Dating of Wallrock Mineral Alterations

In order to date isotopically (U-Pb, Rb-Sr and Re-Os) hydrothermally altered formations associated with the emplacement of the Ryabinovy syenite stock, five representative samples of hydrothermally altered rocks were studied, of which two belong to the “pre-gumbeite” aegirine feldspathites and three samples of wallrock gumbeites, replacing the Aldan Suite syenites.

Based on the use of three independent isotope geochronometers (U-Pb, Rb-Sr and Re-Os), it was found that the intra-intrusive altered rocks, aegirine feldspathites and wallrock gumbeites, were slightly separated in time from the final magmatic crystallization of the Aldan and Tobuk suites. High-temperature aegirine feldspathites formed in the interval of 132-143 Ma, and wallrock gumbeites ranging from 125-139 Ma (Fig. 5).

5 Geochemistry of Noble Gas Isotopes

This study used $^{40}\text{Ar}/^{36}\text{Ar}$, $^{3}{\text{He}}/^{4}\text{He}$, and $^{20}\text{Ne}$ in gas-liquid inclusions from altered rocks of the Muskovitovy and Novy ore sites and was carried out at VSEGEI Centre of Isotopic Research according to the method developed by Prasolov (1990).

Using the example of studying two samples of feldspathites and six samples of gumbeites of G1 and G2 facies, it was shown (Fig. 5) that the proportion of airborne argon in the vertical column of hydrothermally altered rocks from the Ryabinovoe deposit naturally increases from 70% in the sub-ore feldspathites (at hypsometric marks 600-650 m) to 87% in gumbeites of carbonate-sericite-muscovite-orthoclase facies G1 (at marks 700-800 m), reaching a maximum of 96% in gumbeites of quartz-carbonate-barite-adularia facies G2 (at marks above 950 m) within the Novy ore site (Fig. 5).

At the same time, the share of mantle helium in alteration types and ores remains extremely low ($\leq 2-3\%$) over the entire depth range of the vertical column of
mineral alteration, which indicates active participation in the final stages of the ore formation in the Ryabinovo deposit of predominantly vadose waters of the host rocks, altered in the thermogradient field of the Ryabinovy stock into hydrothermal solutions. Whereas the formation of pre-ore high-temperature feldspathites was most likely due to the effect on the host syenites of magmatogenic hydrothermal fluids of predominantly juvenile origin.

References


Geological position and structural control of ore mineralization of the Manukuyu-Varchatinsky ore cluster (the Polar Urals, Russia)

Julia N. Ivanova, Roman I. Vyhristenko, Ilya V. Vikentyev
Russian Academy of Sciences

Abstract. The Malouralsk volcano-plutonic belt (VPB) of the Polar Urals hosts the Toupugol-Khanmeyshorsky ore district and the Manukuyu-Varchatinsky ore cluster. The recent discoveries of the Novogodnee-Monto Au-Magnetite-skarn and the Petropavlovsk Au-porphyry deposits indicate that the belt is prospective for porphyry-style mineral systems. The comparative morphistructural and paleo-facial (paleovolcanic) analysis of Landsat 8 multispectral images demonstrates the relationship of annular and radial structures to gold mineralization. The identification of these structures in underexplored parts of the belt can be used as an aid to mineral exploration in this remote region.

1 Introduction

The Malouralsk VPB is located in the Polar Urals, to the East of the Main Uralian Fault zone and consists of a sequence of middle Silurian to lower Devonian volcanic rocks (Fig. 1a, b). The discovery of the Novogodnee-Monto gold-skarn-magnetite deposit, the Petropavlovsk gold-porphyry deposit and a number of other Au occurrences led to the identification of the Toupugol-Khanmeyshorsky ore district in the northern part of the Malouralsk VBP (Fig. 1b) (Soloviev et al. 2013; Ivanova et al. 2017; Vikentyev et al. 2017). These discoveries indicated the high perspectivity of the Malouralsk VPB. Further exploration work during the period 2010-2012 by Polyarnaya Partiya of Institute of mineralogy, geochemistry and crystal chemistry of rare elements (IMGRE) led to the discovery of the Polyarnaya Nadezhda, the Geokhimicheskoe, and the Blagodatnoye occurrences further to the South (Fig.1b). These discoveries were made through the multidisciplinary interpretation of geological, geochemical and geophysical data and the delineation of what became known as the Manukuyu-Varchatsinsky ore cluster.

The Polyarnaya Nadezhda ore occurrence has an estimated resource of 20 tons contained gold (P2 category) (Kremenetsky, 2012). Multispectral images from the Landsat 8 program from the area surrounding Polyarnaya Nadezhda were processed and analyzed to identify key geological features and structures associated with the gold mineralization. A key focus of this analysis and interpretation was the identification of linear and concentric structures.

2 Geological setting

The geology of the Manukuyu-Varchatinsky ore cluster is composed of a sequence volcanogenic and volcanogenic-sedimentary rocks of the Malouralskaya suite (middle Silurian – lower Devonian). In this sequence volcanic facies are dominant over the volcanogenic-sedimentary ones constituting and 60-80% of the total volume.

Figure 1. a Localization of the Manukuyu-Varchatinsky ore cluster and the Toupugol-Khanmeyshorsky ore district in within of the Russian Federation. b Position of the Manukuyu-Varchatinsky ore cluster in the Malouralskaya zone (structural basis was adopted after Chernyaev et al. 2005): 1 – gold deposit, 2 – gold occurrence, 3 – gold placer, 4 – V-Fe-Cu-(Au) occurrence, 5 – volcanogenic massive sulfide gold-bearing occurrence, 6 – the Central Uralian Megazone, 7 – basalt-andesite complex, 8 – ophiolites, 9 – the Malouralskaya zone, 10 – the Toupugol-Khanmeyshorsky ore district (1), the Manukuyu-Varchatinsky cluster (2).

Within the sedimentary facies present, bioherms are identified but rare and are composed of reef limestones. The Malouralskaya suite is subdivided into three series. The lower series is composed of subaerial agglomerates, bomb tuffs, tuff breccias, clastic flows, and lavas of andesitic composition. This series is interpreted as being...
representative of the relicts of the Silurian volcanic centres, e.g. the Manyukuyu massif, the Dzolyavarchati range. The middle series is restricted to the area of the Elkoshor stream, the Elkoshorskoe and the Tret'ya Rudnaya Gorka ore occurrences, and is located on the right bank of the Tanyu River. The upper series is localized on the right bank of the Tanyu River. This series is composed of pyroclastic and volcano-sedimentary rocks and lavas. These are characterized by a wide development of coarse pyroclastics (bomb tuffs, tuff conglomerates and tuff gravelstones). In general, the petrogeochemical composition and lithological characteristics of the igneous and tuffaceous rocks of the suite indicate that these rocks were formed as a result of eruptive-explosive activity of central-type volcanoes formed in a subduction-related setting. The alternation of packs of volcanic and sedimentary rocks indicates that periodic activation of volcanic activity took place during the accumulation period of rocks.

This Malouralskaya suite is intruded by the Devonian to Eifelian Sobsky and the late Devonian to early Carboniferous Kongorsky plutonic complexes. The Sobsky complex is formed of large intrusions of gabbro, diorite and tonalite. This complex frame a band of volcanic rocks to the west. Minor intrusions and dikes belong to the Kongorsky complex. This complex includes gabbro, gabbro-diorites, diorites, and monzodiorites (Shishkin et al. 2007; Kremenetsky 2012).

The hydrothermal and metasomatic alteration type observed in the area include: skarnification, epidotization, silification, albition, beresitization, and sulfidization. The skarns contain both magnetite dominated and magnetite-sulfide bodies with the magnetite skarns at the Pervaya Rudnaya Gorka, the Tret'ya Rudnaya Gorka, the Magnetitovoye, and others occurrence being associated with contacts of the intrusions. Metasomatitics and metamorphic rocks of the calcisilicate, sodium and magnesia series are genetically associated with gabbro-hyperbasite complexes.

Well-developed skarns are found near the contact of quartz diorites of the Sobsky complex with volcano-sedimentary rocks. An example of this type of mineralization is the ore body of the Novogodnee-Monto deposit (Soloviev et al. 2013). In the region, the skarn-type mineralization is considered as a highly prospective target for gold.

3 Methods

The data source for this study was NASA’s earth observation platform Landsat 8 with the Operational Land Imager (OLI) and Thermal InfraRed Sensor (TIR) sensors. The spectral bands used were 7, 3, 5 from the OLI sensor and the band 10 from the TIR sensor. The scenes used were (LC08_L1TP_165013_20180820_20180829_01_T1; LC08_L1TP_166013_20170707_20170716_01_T1; LC08_L1TP_166014_20180827_20180911_01_T1; LC08_L1TP_166013_20180726_20180731_01_T1) which were 35,000 m² in area and of a ground resolution ~30 m² per pixel. The bands were composited in to two RGB images, 7-5-3 and 10-7-3 for the purposes of analysis.

Hidden structures (arc, concentric, annular, and radial) were given out in the process of image analysis of multispectral satellite images. Lineaments are most clearly revealed in the regions adjacent to the border of the phototone and river drainage patterns.

The interpretation of the Landsat 8 was based on an integrated approach: paleo-facial and morphostructural analysis. Morphostructural analysis included the removal of informative structural indicators of the relief and hydrographic network from various images of the earth’s surface; identification of the main morphostructural elements, scale 1:200000; comparison with geological and geophysical maps, cartographic materials (Shishkin et al. 2012). Geophysical maps used include the maps of magnetic and gravitational fields, scale 1:200000 for the studied and surrounding areas. Maps of magnetic and gravitational fields were used to confirm and refine the contours of morphostructures.

4 Analysis of Landsat 8 Images

Image analysis of Landsat 8 Images and morphostructural analysis are widely used all the world for predictive perspective analysis for various types of minerals in different regions, including the Arctic (e.g., Pour 2012; Sarapää, Sarala 2013; Graham et al. 2017; Yousefi et al. 2018). Image analysis distinguished annular, arc, and radial lineaments within the ore cluster and adjacent territories. It should be noted that lineaments were less frequent in the southeastern part of the territory, than the adjacent area (Fig. 2). The structures are localized under a thick cover of Mesozoic sediments (about 1200 m) here, whereas the thickness is to 200 m in the southeastern part of the territory.

Two large oval structures are distinguished (Fig. 2b). Morphostructural № 1 has 54х44 km size. This morphostructural is complicated by smaller annular (about 10 km), arc, and radial lineaments. Most ore occurrences and mineralization points (Cu-Zn-pyre, Cu, Cu-Zn, Fe-Ti-V, Cu-Pb-Au – on periphery part, Pt, Fe-Cu-Au – on the center part) are localized in this morphostructural. The Polyarnaya Nadezhda, the Geokhimicheskoe, and the Blagodatnoye ore occurrences belong to morphostructural № 1. Morphostructural № 2 is smaller (48х38 km size) than the morphostructural № 1. Annular, arc, and radial lineaments complicate this morphostructural too. Ore occurrences and mineralization points (Cu-Mo, Fe-Ti-V, Cu – inside, Fe-Cu, Mo-Cu, Cu-Au – near) belong to morphostructural № 2.

Image analysis identified the radial zones. These have north east (up to 40) and northwest (up to 22 km) directions. These probably are more ancient activated structures. These lineaments correspond to weakened areas of the earth’s crust (decompression zones). These zones experienced periods of activation with the influx of mantle heat and focal crustal structures appeared. These controlled the placement of ore clusters. Thus, hydrothermal mineralization is localized in the
concentration points of the faults (the points of the intersection of lineaments near the center of large annular structures). Morphostructural № 1 and № 2 are volcano-plutonic heterogeneous structures of first order. They were probably formed under the influence of several geological processes and complicated by concentric structures of the second order (smaller diameter, morphostructural № 1). These structures with smaller diameters create feature of "telescoping" (Gorny et al. 2014).

The series of short closely parallel radial lineaments of the northeast directions were identified (Fig. 2b). These are concentrated in a strip to 25 km of wide and length to 105 km. This zone together forms structure of the northeast direction. Probably, this zone reflects the hidden structures and creates a complex block structure of the territory, and plays a controlling role in the placement of mineralization. This zone possibly has been formed later morphostructurals № 1 and № 2.

5 Comparative characteristics of the two territories

We compared morphostructural map with the more northern territory of the Toupugol-Khanneyshorsky ore district (Ivanova et al. 2017; Vikentyev et al. 2017) (Fig. 2a) to identify similar structure features and localization of gold mineralization, as well as to develop a prediction and predictive features for gold type of mineralization.

1. These territories contain the tectonic-magmatic structures of a complex nature.
2. Ore districts and clusters are localized on the territory of intersection of tectonic disturbances in regional long-lived zones with the NE and the NW-trending. These zones control ore mineralization.
3. Intrusive formations are represented by polyphase and uneven-age complexes. Skarn-magnetite and gold ore mineralization is associated with these intrusive formations.
4. The internal structure of annular morphostructural was complicated by the intersection of concentric and (or) arc faults, radial faults of the NE and the NW-trending of various ranks, as well as zones of concentration of small annular structures.
5. Ore deposits and ore occurrences are localized within large annular structures of complex formation history and long-term evolution.

Differences:
1. The Novogodny morphostructural is smaller than morphostructural № 1 and № 2 (6x10 km, 54x44 km and 48x38 km, respectively).
2. The annular and arc structures are accompanied by less extensive radial lineaments (up to 20 for the Novogodny morphostructural and up to 50 km for morphostructurals № 1 and № 2).
3. The Novogodny morphostructural is volcano-plutonic monogenic structure of the second rank. This
morphostructural was probably formed under the influence of one leading geological process.

6 Why on this territory have not yet discovered deposits

1. Large faults up to hundred km of long absent in this territory that would cross-favourable horizons and structures. Because of, absent of renovation of these faults and took place their further “blockage”.

2. The period of stretching followed intrusion phase. Compressive forces decreased. Such conditions contributed of the intrusion and “retract” the hydrothermal solutions. The condition of ore formation is intrusion of hydrothermal solutions into cracks in the zone of large faults (Cox et al. 2001).

3. Hydrothermal deposits are formed in conditions of differentiated tectonic movements of small amplitude. Weak uplifts enliven hydrothermal solutions and favour their penetration into raised wings of the folds. The amplitudes of vertical movements (from 1 to 5 km) in compression conditions impede the penetration of fluids in the zone as a whole and, thus, ore formation does not develop (Perelman 1989).

4. The factor of poor knowledge of the territory should not be excluded from consideration.

7 Conclusions

The Malouralsk VPB is characterized by a wide evolution of radial and annular structures. These structures are clearly detected on the multispectral Landsat 8 Images. In the result of analysis of Landsat 8 Images two large oval-shaped morphostructurals compounded by annular, arc, and radial lineaments of smaller rank were decoded. These complicated morphostructurals indicate that multi-stage development. Ore deposits and ore occurrences are mainly localized in the periphery of these morphostructurals.

The northeast direction zone wide up to 25 km and length about 105 km was allocated in the process of analysis of multispectral images. This zone possibly may control the ore mineralization.

The mineralization zones (gold deposits, ore manifestations, and mineralization points) of the Malouralskaya zone belong to complexly-constructed systems of annular and radial structures. Large annular morphostructurals have great importance in ore localization.

In general, the ore districts on the eastern slope of the Urals correspond to the zone of intersection of faults of regional significance. They marked by the form of extending lineaments with a predominantly north-western orientation and large annular structures. Gold hydrothermal mineralization within these ore districts should be localised in areas of thickening faults and in the intersections of radial lineaments near concentrations of large annular morphostructural.

Acknowledgements

The authors gratefully thank: the Russian Foundation for Basic Research (grant № 18-05-70041) for financial support; R.N. Armstrong for helpful comments leading to improvement in this manuscript.

References


Mineralisation in the K1 vein-system, Kencana Epithermal Deposit, Gosowong Goldfield

Thomas Tindell, Kotaro Yonezu
Kyushu University, Japan
Syafrazal
Institute of Technology Bandung, Indonesia

Abstract. The Gosowong goldfield encompasses one of the most extraordinarily rich gold provinces in Indonesia, or indeed the western Pacific region. The depositional area lies on Halmahera Island, straddling a zone roughly equidistant to Sulawesi Island to the west and Papua Island to the east. Volcano-magmatic activity is related to the closure of the Molucca Sea, with an arc-arc subduction forming the Sangihe Thrust and the parallel Halmahera Thrust. The subsequent Halmahera Arc lies along the north-western arm of Halmahera Island and the north-south aligned volcanic islands chain to the south. The geology of Halmahera may be separated into two major domains; the eastern domain composed of Mesozoic ophiolite complexes and overlying Oligocene clastic sediments, with the western domain composed of Neogene to recent volcanic and pyroclastic rocks. Discovered through the major finding of the Gosowong low-sulfidation deposit in 1994, two further extremely rich epithermal deposits (Togarachi and Kencana) were subsequently discovered amongst numerous prospects. The Kencana deposit is located in the southeastern area of the Gosowong goldfield, and lies within the Gosowong Formation, principally composed of a large-scale andesite package with numerous interlayered sandstone mudstone volcaniclastic deposits.

1 Introduction

Epithermal gold mineralization and their often associated magmatic-arc porphyry affiliations are well recognized throughout the Indonesian archipelago. Much focus, with regard to research, has been on the significant and economical deposits situated along the Sunda-Banda arc system. Precious metal epithermal-type mineralization in the Indonesian Archipelago is significant, and with much of the major discoveries found on the westward largest islands of Sumatra and Java. High-grade precious metal deposits (low-sulfidation-type) are distributed throughout Java Island, for example the Cibaliung, Pongok and Trenggalek deposits. Large world-class porphyry is well documented in the east, such as Batu Hijau on Sumbawa Island and the Grasberg deposit on Papua.

The Kencana deposit, located in the northern arm of Halmahera Island (Fig. 1), straddles a complicated grouping of plates, micro-plates, thrusts and subduction zones. Its north-eastern locality makes it far removed from the Sunda-Banda Arc and consequently a unique mineralization area. The deposit is a member of a group of epithermal deposits, prospects and porphyry systems, collectively referred to as the Gosowong Goldfield (Fig. 2). Within, there are three principle deposits; Gosowong, Toguraci and Kencana, all of which are classified as low-sulfidation epithermal-type and as yet encompass the richest precious metal deposits of Halmahera Island and indeed Indonesia. The Gosowong Goldfield was discovered in 1994, with mining commencing in the Gosowong deposit and subsequent discoveries at Toguraci and Kencana in 2000 and 2003 respectively. The Kencana deposit has the highest precious metal endowment of the Gosowong mining area, with an average grade in excess of 23g/t Au and a total resource of 4Mt. Here we provide a summary of the mineralization patterns in successive zones is presented, with discussions eluding to the mechanisms to which this mineralization is attributed.

2 Geology

2.1 Regional geology

The geology of Halmahera Island is relatively straightforward, though it is a member of a tectonically complicated mosaic of microplates (Hakim and Hall 1991). The island is situated in the northern portion of the Sorong Fault, siting between the almost equidistant islands of Sulawesi to the west and New Guinea to the east. The Molucca Sea separates Hamahera Island from the northern Minahassa Peninsula of Sulawesi. The eastern most tip of the Minahassa Peninsula forms the Sangihe Arc, whilst the western edge of Halmahera (and the north-south chain of volcanic islands) forms the Halmahera Arc, forming an arc-arc collisional zone. The eastern domain of the island hosts the oldest rock units, comprising a basement of Late Cretaceous ophiolites and volcanic rocks attributed to development of the forearc sequence, collectively referred to as the Ophiolitic Basement Complex (Hall 1987; Hall et al. 1988; Hakim and Hall 1991). These are unconformably overlying Miocene limestones. The Western domain is underlain by late Mesozoic volcanic rocks, which are unconformably covered by successive Paleogene-Quaternary volcanic and volcanoclastic rocks.

2.2 Local geology

The Gosowong Goldfield is situated in the lower neck of northern Halmahera Island, which is composed of Paleogene to Present volcanic-volcanoclastic and...
Figure 1. Geological boundaries of Halmahera Island and surrounding arc volcanism related islands. The southern and eastern limbs of the island host the Cretaceous ultramafic basement of obducted ophiolite sequences, whilst the northwestern limb is composed of the Paleogene to Present volcanogenic andesite packages. Inset (top right), Halmahera Island (red) in relation to wider Indonesian archipelago.

The Gosowong district is composed of four formations: Bacan Formation (Paleogene), the Gosowong Formation (Neogene), Kayasa Formation (Pliocene) and Quaternary Volcanic Formation.

The Gosowong Formation consists of volcanic and volcanioclastic rocks, called as Gosowong volcanioclastics. Gosowong volcanioclastics are composed of basaltic group and andesitic group. Andesitic group is overlain by Basaltic group. The basaltic group consists of volcanioclastic conglomerate, basalt andesite, intrusive andesite, basalt lava and volcanioclastic sandstone. Andesitic group is composed of; diorite, andesite fragmental lava, volcanioclastic conglomerate, volcanioclastic sandstone, volcanioclastic mudstone and andesite lava (Gemmell 2007). \(^{40}\text{Ar}/^{39}\text{Ar}\) ages of adularia from the epithermal mineralisation zone in Gosowong district ranged from 2.8Ma to 2.9Ma (Vansconcelos 1998) and from 2.4Ma to 2.9Ma (Olberg 2001). U-Pb isotopic age of host rock ranges from 3.1Ma to 3.7Ma (Steven and Daud 2011).

3 Mineralisation

3.1 Kencana veining

There are three principle veins at Kencana; K1, K2 and K-LINK. The K1 vein system is exposed on the surface, but the main ore zone is located approximately 90m below the surface and the main focus of this study. The upper portion is composed of quartz-calcite, and high-grade ores present in the crustiform-colloform banding at 100-150m depth, with Au grades in excess of 1000g/t. Moderate to high-grades are encountered in the quartz-hematitic mudstone/volcanioclastics breccia at 150-200m depth. The K2 vein system is composed of quartz-calcite veins, breccia and stockworks. The K-Link system is largely brecciated with gingoro banding recognised as dismembered vein material in the breccia. Au grades of the deposit are extremely high, ranging from 5 to >1000g/t in the highest-grade zones. Mineral resources of the deposit are more than 2.2 Moz Au and 2.2 Moz Ag.

3.2 Ore mineralization

The K1 breccia system contains an early (Stage I) microcrystalline quartz with chalcopyrite and electrum dissemination, with minor tellurides (hessite), this is followed by a later stage brecciation and resultant banded crustiform ore (Stage II), composed of; chalcopyrite, hessite, sylvanite, galena and sphalerite in order of abundance (Fig. 3). Analysis shows that there is a high Cd-composition in sphalerite and the extremely Cd- rich Zn sulfides recognised as zincian-greenockite.

3.3 Electrum

SEM-EDX measurements of electrum from Stages I and II show that broadly they have wide distribution from 15-44 At% Ag (Fig. 4). Stage-I electrum tends to exhibit higher Au compositions, with higher Ag compositions largely confined to Stage-II. The dominant trend for Ag composition from a suite of veins from K1, K2 and K-link ranges from 24 to 27 at%, indicative of extremely rich gold
This area hosts four subeconimic porphyries (Tabobo porphyry, Bora porphyry, Matat porphyry and Ngoali porphyry) and three main epithermal deposits (Gosowong deposit, Togurachi deposit and Kencana deposit).

![Figure 3](image.png)

**Figure 3.** Brecciated vein textures and ore minerals of the K1 Sub 12 and Sub 13 ore drives. Abbreviations: Qtz – quartz, Cpy – chalcopyrite, Ag-Te – hessite, Cpy-Au-Ag-Te – (electrum, hessite, sylvanite, petzite, stuzite), Gn – galena, Sph – sphalerite (zincian Greenockite).

![Figure 4](image.png)

**Figure 4.** Representative microphotograph from K1 Sub 13, Stage-II mineralization (Cpy-Au-Ag-Te). Abbreviations: ccp – chalcopyrite, ptz – petzite, hes – hessite, gn – galena, el – electrum.

![Figure 5](image.png)

**Figure 5.** Ag ratio in electrum from the K1 vein and representative samples from the K2 and K-link vein systems. Results indicate that the electrum from Sub-12 and 13 have the widest range, with higher Au compositions largely attributed to Stage I and higher Ag composition largely confined to Stage II.

### 4 Short considerations

Although detailed geochemical mechanisms are yet to be established, general trends can be discerned from the available data. Preliminary microthermometry of the quartz gangue associated with Stage-II suggests a precipitation temperature of 200 to 250°C. Coupled with the precious metal compositions and related Au-Ag-Te minerals present, a higher temperature for Stage-I mineralization may be considered.

### Acknowledgements

The authors thank all assistance from PT Nusa Halmahera mining for providing access and samples from the Gosowong goldfield.
References


Steven M, Daud S (2011) Transient kinematic changes in epithermal systems: Toguraci deposit, Halmahera, unpublished.

The new discovered Tasikmadu porphyry copper-gold prospect in Watulimo sub-district, Southern Trenggalek, Java Island, Indonesia: characteristics and exploration challenges

Arifudin Idrus¹, Trifatama Rahmalia², Kresna Kustrianugroho¹
¹Department of Geological Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia
²Department of Geological Engineering, ITNY Yogyakarta, Indonesia

Abstract. This is a frontier study dealing with geology and key characteristics including hydrothermal alteration, quartz vein/veinlet system and ore mineralization of the new discovered Tasikmadu porphyry copper-gold prospect in the southern part of Trenggalek district, East Java province, Indonesia. Regionally, the studied area is a moderate undulating volcaniclastic terrain occupied by Mandalika formation (Tomm) intruded by a series of acidic to intermediate plutonic rocks (Tomi), which is dominated by dioritic intrusion (di). At least three intrusive diorite types are identified, i.e. fine-, medium- and coarse-grained diorite porphyries. NE-SW- and W-E- trending strike-slip faults might play an important role controlling the formation of the porphyry copper-gold prospect. Four hydrothermal alteration zones developed throughout the prospect including central potassic, proximal phyllic, distal propylitic and superimposed argillic alteration. Ore mineralization is characterized by high-density mineralized stockwork of quartz vein/veinlet system. Early A, center-line AB/B, transitional chalcopyritic C and late pyritic D vein/veinlet of a typical porphyry system are obviously observed. Chalcopyrite and pyrite are observed. Bornite, a typical high temperature copper sulfide in porphyry systems, is found as a minor phase. The Tasikmadu porphyry copper-gold prospect shares some similarities and few discrepancies of its key characteristics in comparison to other porphyry copper-gold deposits worldwide.

1 Introduction

Indonesian archipelago is controlled by the tectonic setting of the region, which is manifested by magmatic arcs from various ages from Late Mesozoic through the Cenozoic. Most of the hydrothermal mineralisation is derived from six major Neogene magmatic arcs including the Sunda-Banda, Aceh, Central Kalimantan, Sulawesi-East Minandau, Halmahera and Central Papuan fold and thrust belt (Carlile and Mitchell, 1994). The Sunda-Banda arc is the longest of the magmatic arcs in Indonesia. It extends nearly 4,000 km from northern Sumatra through Sumbawa (Sunda arc) and onwards through Flores to its terminus in the Banda Islands (Banda arc). Several porphyry copper-gold prospects in Java Island (Fig.1) were discovered along Sunda-Banda magmatic arc, for instance, Batu Hijau in Sumbawa (Idrus, 2007), Tumpang Pitu in East Java (Hellman, 2010; Maryono et al., 2012), and Selogiri in Wonogiri (Imai et al., 2007). The study area, Tasikmadu is one of the porphyry copper-gold prospects situated in central segment of west-east trending Sunda Banda magmatic arc, which is administratively included East Java province of Indonesia. The prospect is a promising “new discovery” copper-gold mineralization in Java Island, which is proven by the occurrences of central potassic alteration in association with quartz vein/veinlet stockwork and an abundance of copper-bearing sulfides such as chalcopyrite, bornite, covellite, chalcocite and malachite. Detailed study of the prospect is still lacking. Therefore, this study is aimed to understand the deposit geology and some key characteristics of the deposit including hydrothermal alteration types and distribution, vein/veinlet system and ore mineralization. This would give a significant contribution for a better understanding of the deposit and future exploration strategy of the copper-gold mineralization in the region.

Figure 1. Research location (Tasikmadu prospect) plotted on the SRTM (Shuttle Radar Topography Mission) map of Java Island

2 Research methods

This study was conducted in four stages including literature, fieldwork, laboratory work, data processing and interpretation. Fieldwork includes mapping of surface geology, alteration and ore mineralization as well as sampling of representative rock types, altered rocks, quartz vein/veinlet stockwork and quartz vein in ore mineralization. Hydrothermal alteration mapping is focused on the type and distribution of the alteration halos from central potassic to proximal phyllic and distal propylitic types. Laboratory work includes vein textural and structural analysis, mineralogy (petrography, ore microscopy). A total of 22 samples were analysed at Department of Geological Engineering, Universitas Gadjah Mada.
3 Deposit geology

The studied area is categorized as a moderate undulating volcaniclastic terrain. The study area is underlain by a series of volcanic units, which from oldest to youngest are volcanic breccia, at least three phases of intrusive rocks mainly early fine-grained diorite, intermediate medium grained diorite and late coarse-grained diorite porphyries (Fig. 2). Those rock units are the members of Miocene Mandalika formation (Tomm). The youngest unit is a coastal deposit. The pre-mineralization rock unit i.e. volcanic breccia was intruded by the multiple series of diorite porphyries. The volcanic breccia is weakly altered to the distal propylitic domain. The causative mineralization intrusion is interpreted to be fine grained diorite porphyry, which is closely associated with quartz vein/veinlet stockwork occurrences. The fine grained diorite is spatially related to the distribution of central early potassic alteration, while the intermediate grained diorite is spatially associated with the occurrences of distal phyllitic and early proximal propylitic alterations. Several structure patterns are recognized in the study area including NE-SW, N-S, NNW-SSE- and W-E-trending strike-slip faults. However, NE-SW- and W-E- trending strike-slip faults are interpreted to be causative structure playing an important role controlling the formation of the porphyry copper-gold prospect.

4 Hydrothermal alteration

Four hydrothermal alteration zones developed throughout the prospect including central potassic, proximal phyllic, distal propylitic and superimposed argillic alteration (Fig. 3). Central potassic alteration is typified by fine-grained secondary biotite and magnetite. Phyllic alteration is typified by sericite-quartz-pyrite±chlore, whereas propylitic alteration is characterized by chlorite+epidote+smeectite+quartz. Arillic alteration is presented by illite-smectite-quartz-sericite-dickite±chlore. Ore mineralization is closely associated with potassic alteration and high-dense quartz vein/veinlet stockwork. The potassic alteration is spatially associated with high abundances of copper bearing sulfides such as chalcopyrite, bornite, covellite, azurite, chalcocite and malachite.

5 Vein/veinlet system and ore mineralization

Ore mineralization is characterized by high-density mineralized stockwork of quartz vein/veinlet system. Several typical quartz veins/veinlets in the porphyry systems such as early A, center-line AB/B, transitional chalcopyritic C and late pyritic D veins/veinlets are recognized and occurred throughout the prospect. The prospect area is centered on at least 1x1.5 km² of early potassic alteration, which is spatially (and potentially coeavally) associated with high-density mineralized vein/veinlet stockwork zone. Chalcopyrite and pyrite are ubiquitously observed. Bornite is present in the minor portion. Bornite is occasionally replaced by chalcopyrite in the rim and/or following cleavages forming lamellae texture. Microscopically Intergrown chalcocite and covellite replacing bornite are observed. Gold inclusion in copper-bearing sulphides. On the surface, the strongly mineralized host rock is clearly stained by colorful malachite, azurite and other supergene copper-bearing minerals.

6 Concluding remarks and implication for exploration

6.1 Concluding remarks

The Tasikmadu porphyry copper-gold prospect is centered on by multiple series of intrusive diorite porphyries. NE-SW- and W-E- trending strike-slip faults are interpreted to be causative structure playing an important role controlling the formation of the porphyry copper-gold prospect. Early fine-grained diorite porphyry is interpreted to be a causative mineralization intrusion. Early potassic, intermediate phyllic, early propylitic and late argillic alteration zones are well developed. Ore mineralization is closely associated with central potassic alteration and high-dense quartz vein/veinlet stockwork. The potassic alteration is spatially and temporally suffered the early fine-grained diorite porphyry, and associated with high abundances of copper bearing sulfides such as chalcopyrite, bornite, covellite, azurite, chalcocite and malachite.

6.2 Implication for exploration

Several porphyry copper-gold prospects were discovered along the mineralized Neogene Sunda-Banda magmatic arc, for instance, Batu Hijau in Sumbawa, Tumpang Pitu in East Java, and Selogiri in Wonogiri. The Tasikmadu is one of the best porphyry copper-gold prospects outcropping within central Java Island segment of the magmatic arc. The prospect is hosted by multiple series of intrusive diorite porphyries. Early fine-grained diorite porphyry is interpreted to be an intrusion that caused mineralisation. Early potassic, intermediate phyllic, early propylitic and late argillic alteration zones are centered on the fine-grained diorite porphyry stock. Thus, the Tasikmadu porpyry copper-gold meets the criteria of the Diorite porphyry model (after Hollister, 1978). The Tasikmadu prospect is a promising “new discovery” copper-gold mineralization in Java Island. Central early potassic alteration in association with quartz vein/veinlet stockwork and the abundances of copper bearing sulfides such as chalcopyrite, bornite, covellite, chalcocite and malachite is well exposed and preserved. The occurrence and discovery of the Tasikmadu porphyry copper-gold prospect may imply that other undiscovered porphyry copper-gold deposits along central to east segments of Java Island as a part of the mineralized Sunda-Banda magmatic arc may exist and could be discovered in the
**Figure 2** Geological map of the Tasikmadu porphyry copper-gold prospect, Trenggalek, Java Island.

**Figure 3** Hydrothermal alteration and mineralization map of the Tasikmadu porphyry copper-gold prospect, Trenggalek, Java Island.
future. Thus, it needs an effective and cost-benefit exploration model on the basis of the deposit genetic model.

Acknowledgements

Fieldwork and laboratory analyses funding was partly supported by PT. Erde Ressourcen and PT. Primata Batu Mulia. Therefore, we would like to express our sincere thanks and appreciation to the managements of both mining companies for their supports. We are also thankful to anonymous reviewer for the improvement of the manuscript.

References


Contributions to the mineralogical and geochemical characterization of Fe-Sn-Zn-Cu-In skarn-type mineralization in the Schwarzenberg mining district, Germany

Malte Stoltnow  
TU Bergakademie Freiberg, Institute of Mineralogy, Germany  
Deutsches GeoForschungsZentrum GFZ, Germany  
University of Potsdam, Inst. of Earth and Env. Science, Germany

Thomas Seifert, Tilman J. Jeske, Sabine Gilbricht  
TU Bergakademie Freiberg, Institute of Mineralogy, Germany

Joachim Krause  
Helmholtz Institute Freiberg for Resource Technology (HIF), Germany

Abstract. The Schwarzenberg mining district in the western Erzgebirge hosts numerous skarn-hosted tin-polymetallic deposits, such as Breitenbrunn. The St. Christoph mine is located in the Breitenbrunn deposit and is the locus typicus of christophite, an iron-rich sphalerite variety, which can be associated with indium enrichment. This study presents a revision of the paragenetic scheme, a contribution to the indium behavior and potential, and discussion on the origin of the sulfur. This was achieved through reflected light microscopy, SEM-based MLA, EPMA, and bulk mineral sulfur isotope analysis on 37 sulfide-rich skarn samples from a mineral collection. The paragenetic scheme includes: a pre-mineralization stage of anhydrous calc-silicates and hydrous minerals; an oxide stage, dominated by magnetite; a sulfide stage of predominantly sphalerite, minor pyrite, chalcopyrite, arsenopyrite, and galena. Some sphalerite samples present elevated indium contents of up to 0.44 wt%. Elevated iron contents (4-10 wt%) in sphalerite can be tentatively linked to increased indium incorporation, but further analyses are required. Analyzed sulfides exhibit homogeneous $\delta^{34}S$ values (-1 to +2 ‰ VCDT), assumed to be post-magmatic. They correlate with other Fe-Sn-Zn-Cu-In skarn deposits in the western Erzgebirge, and Permian vein-hosted associations throughout the Erzgebirge region.

1 Introduction

Situated in the western Erzgebirge, the Schwarzenberg mining district (Fig. 1) is well-known for both historic mining and being a target of active exploration of skarn-hosted Sn-polymetallic deposits. In addition to the promising Hämmerlein-Tellerhäuser and Pöhla-Globenstein deposits, the district also hosts the less investigated Breitenbrunn and Antonsthal deposits. The St. Christoph mine is located in the Breitenbrunn deposit and is the locus typicus of the iron-rich sphalerite variety christophite. Christophite has been shown to be associated with indium enrichment (Leutwein 1943). This study presents a revision of the paragenetic scheme, a contribution to the indium behavior and potential, and discussion on the origin of the sulfur.

2 Geological setting

The Schwarzenberg mining district is located east of the Eibenstock granite massif and along the Schwarzenberg gneiss cupola, which is situated in the central part of the Gera-Jáchymov Zone, a large-scale transregional deep reaching lineament (Fig. 1).

The Schwarzenberger augengneiss is surrounded by a concentric complex of Cambrian metasedimentary rocks which comprise gneisses, schists, metacarbonates, metagreywackes, quartzites, metavolcanics, and phyllites. These units are transgressed by major, ENE-WSE-trending (i.e. Weißer Hirsch and Arnoldshammer
faults) and minor, NW-SE-trending faults (Fig. 1).

Intrusions of the Schwarzenberg mining district comprise late-collisional granites and post-collisional porphyric and lamprophyric dikes (Fig. 1).

The district is host to numerous mineralized skarn bodies, which are arranged in a circle around the Schwarzenberg augen gneiss and hosted by the Cambrian metasediments (Fig. 1). Baumann et al. (2000) subdivided the skarn bodies according to the spatial distribution of their mineralization style, into northern and southern zones of the cupola. The northern zone of the cupola (north of the Weißer Hirsch fault) is dominated by sulfide ores, whereas the southern zone (south of the Weißer Hirsch fault) is dominated by oxidic ores, or mixed sulfidic-oxidic type ores (Fig. 1).

3 Methods

For this study, a total of 37 sulfide-rich skarn samples were taken from the ore deposit collection (Lagerstättensammlung - LaSa) at the Institute of Mineralogy, TU Bergakademie Freiberg. Preparation steps comprised 25 mm embeddings and sulfide mineral concentrates. Methods conducted on the samples include reflected light microscopy, secondary electron microscopy (SEM)-based mineral liberation analysis (MLA lab TUBAF), electron probe microanalysis (EPMA lab HIF), and analysis of the mineral sulfur isotopic composition (stable isotope lab WWU Münster) and bulk sphalerite geochemistry (n=5) by ICP-MS (Actlabs).

4 Results

4.1 Paragenetic scheme

The revised paragenetic scheme (Fig. 2) is predominantly based on observations from this study, with integration of the observations of Wolf (1995) and Hösel et al. (2003) from studies on the sub-district Pöhla-Globenstein. The classified stages include a pre-mineralization stage and a mineralization stage.

4.1.1 Pre-mineralization stage

Early skarn minerals comprise anhydrous (i.e. pyroxene and early garnet; Fig. 3-D), in addition to hydrous minerals (e.g. epidote). Pyroxene, early garnet, and epidote never replace ore minerals. This stage is barren of oxidic and sulfidic mineral phases.

4.1.2 Mineralization stage

The mineralization stage describes a timespan where oxidic and sulfidic mineralization occurs, accompanied by less abundant arsenides and native metals, and is subdivided into an oxide and a sulfide stage.

4.1.3 Oxide stage

Early subhedral amphibole (Fig. 3F) and magnetite (Fig. 3A, B, D) are the dominant mineral phases of the oxide stage. Both replace early skarn minerals and are replaced by oxide stage cassiterite (Fig. 3F) and later sulfides. Hematite occurs in form of martite in some cases, which is not replaced by later ore minerals.

4.1.4 Sulfide stage

Early pyrite, löllingite, sphalerite, chalcopyrite, and early arsenopyrite are roughly coincident. Chalcopyrite 1 (Fig. 3-C) is present as chalcopyrite disease in sphalerite. Patchy chalcopyrite 2 (Fig. 3-C, -E) can be differentiated from chalcopyrite 1 only by shape, as no age relationships are obvious. Pyrite 2, in most cases, forms laminated bird’s eye aggregates with marcassite.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Pre-mineralization</th>
<th>Mineralization</th>
<th>Oxidic</th>
<th>Sulfidic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gangue minerals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyroxene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Garnet</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epidote</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphibole</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcedony</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ludwigite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teutallite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galadrites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apaite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rutile/Titanite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phlogopite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Ore minerals | | | |
|--------------|--------------|--------|
| Oxides | | | |
| Magnetite | | | |
| Cassiterite | | | |
| Galena | | | |
| Sulfides, arsenides, native metals | | | |
| Pyrite | | | |
| Magnetite | | | |
| Sphalerite | | | |
| Lillingtonite | | | |
| Arsenopyrite | | | |
| Native bournonite | | | |
| Chalcopyrite | | | |
| Galena | | | |
| Faulinite | | | |
| Bi-Pb-Ag sulphide | | | |
| Ag-bearing minerals | | | |

Figure 2. Paragenetic scheme of the Schwarzenberg mining district. The sequences are predominantly based on petrographic observations carried out during this study. Literature data (grey bars) from: Wolf (1995) and Hösel et al. (2003).

The late phase of the sulfide stage is characterized by the emplacement of fibrous chlorite which transverses, fractures, and intensely marginally corrodes earlier mineral phases. Late pyrite 3 (coarse euhedral, sieve-like blasts) and galena are roughly coincident with the chlorite and replace earlier sphalerite. Late cassiterite can be found as round crystals, related to late veinlets, as well as in the form of thin fringes around patchy chalcopyrite 2. Subsequently, pyrite 3 is surrounded by thin fringes of the youngest arsenopyrite.
4.2 Sphalerite geochemistry

Indium is present in minor abundances (Fig. 4A), with three of twelve samples, 64782 (0.20-0.30 wt%, average = 0.27 wt%, n = 10), 65551 (0.02 wt%, n = 11), and 65600 (0.23-0.44 wt%, average = 0.36 wt%, n = 11) showing elevated indium contents.

Zn and Fe have a strong negative correlation (Fig. 4B). The overall range shows Zn values from 49.3 to 64.4 wt% with a mean value of 57.3 wt% (12 samples, n = 272 analyses) and Fe values from 1.5 to 15.6 wt%, with a mean value of 8 wt% (12 samples, n = 272 analyses). Bulk sphalerite ICP-MS analyses (n = 5) revealed concentrations of In 101-195 ppm, average 154 ppm, Cu with <0.05-1.55 wt%, average 0.66 wt%, and Fe 6.36-16.70 wt%, average 13.7 wt%.

According to the In content, samples can be divided into three groups. The first group comprises the samples with low Fe contents (0-4 wt%) and no detectable In, the second group with intermediate Fe contents (4-10 wt%) and partly detectable In, and the third group with high Fe contents (10-16 wt%) and no detectable In.

4.3 Sulfide sulfur isotopic compositions

Sulfur isotope compositions of sulfide minerals (sphalerite, chalcopyrite, and arsenopyrite) from 21 samples are shown in Fig. 5. They show δ34S values between -0.9 and 2.0 ‰ VCDT.

The δ34S VCDT median is 0.8 ‰ and the average is 0.7 ‰ (n = 21). First quartile plots at 0.4 ‰ and the third quartile at δ34S VCDT 1.1 ‰. Therefore, with no large overall variation, the average measured δ34S VCDT composition is 0.7 ‰.

5 Discussion

5.1 Indium behavior and potential

Three of twelve samples analyzed with EPMA confirmed the occurrence of elevated indium contents of the Breitenbrunn deposit, with up to 0.44 wt% In in sphalerite. However, the lack of detectable In in many samples
implies a heterogeneous In distribution in the ore bodies. Elevated Fe contents (>4 wt%) were tentatively linked with the incorporation of indium in sphalerite, but further analyses are required for confirmation. This also applies to the observation of indium concentrations below detection limit in samples with markedly high iron contents (>10 wt%).

5.2 Origin of the mineralizing fluids

Based on their petrographic observations, Wolf (1995) and Hösel (2003) distinguished several stages in the formation of mineralized ore bodies in this area, fitting to the genetic skarn formation model of Einaudi et al. (1981). This includes the early stage of sedimentation, a stage of regional metamorphic hornfels-skarnoid formation, a stage of contact metamorphic-prograde skarn mineral formation, a greisen stage, and a late stage related to a hydrothermal overprint of the skarns. Compared to observations made in this study, our identified stages include a pre-mineralization stage which is assumed to coincide with the prograde skarn-forming stages, and a mineralization stage. The latter presumably coincides with the greisen- and retrograde stages, or might represent a stage involving mineralizing fluids which are independent of the skarn development (Jeske and Seifert 2017). In the latter case, fertile fluids caused mineralization of the skarn bodies, which acted solely as geochemical barriers.

This is supported by the homogeneous sulfur isotopic composition (Fig. 6). The homogeneity of the values is confirmed by analyses of sulfides from the Hämmerlein Sn-Skarn deposit (Jeske and Seifert 2018) which is also situated in the study area. Late and postcollisional Li-F small intrusion granites and rhyolitic (Seifert and Kempe 1994) and lamprophyric dikes (Seifert 2008), could act as possible rare metal and sulfur sources.

Figure 6. Comparison of sulfur isotopic compositions of sulfides from different skarn deposit and vein mineralization types; 1: Rößler et al. (1966), Seifert et al. (1992), Seifert (1994), Herrmann et al. (1995), Seifert (1995), and Bauer et al. (2018); 2: Jeske and Seifert (2018); 3: This study.

Acknowledgements

For the sample selection and documentation in the LaSa project, we would like to thank the TU Bergakademie Freiberg and the Federal Ministry of Education and Research (BMBF) for promoting this thesis, through the “ResERVar” project, which is part of the “r4” funding program of Germany.

References


Leutwein F (1943) Vorkommen und Gewinnung von Indium. Forschungslaboratorium des Bergreviers Freiberg (Sächsisches Staatsarchiv, Bergarchiv Freiberg, 40030 Oberbergamt (neu) - staatliche Lagerstättenforschungsstelle, Nr. 1-0261), Freiberg, Germany


Seifert T, Baumann L, Jung D (1992) On the Problem of the Relationship Between Sn(-W) and Quartz-Polymetallic Mineralizations in the Marienberg Deposit District. ZGW 20:371


Transition from porphyry to epithermal Cu-Au environments in Sardinia – Italy

Sandro Fadda, Maddalena Fiori, Carlo Matzuzzi
National Research Council
Institute of Environmental Geology and Geoengineering, Italy

Abstract. In Sardinia acidic fluids form argillic alteration halos and/or silicic lithocaps over Tertiary porphyry systems which may host subsequent mineralization. The spatial, geochemical and geophysical evidence suggests that the two systems may be genetically related and may help to determine the transition of a magmatic hydrothermal system from porphyry to epithermal environments. Tetrahedrite-tennantite series minerals occur extensively in hydrothermal deposits although in minor quantity as compared with other sulfides. At Furtei Au deposit available chemical data of these minerals and of the telluride-rich parts of drillcore samples, indicate direct magmatic inputs to the mineralizing solutions thus a transition of this system from porphyry to epithermal environments is envisaged and the relationship between mineral assemblages and sulfidation states may be assessed as well as evolution of ore solutions outlined. The Tertiary bodies occurring in the Siliqua sector display alteration and mineralisation patterns which can be referred to as a porphyry copper system consistent with a diorite model with the presence of epithermal silicapyrite alteration. Field observations and time and space relationships seem to suggest development of porphyry-style veining followed by several epithermal stage mineralised breccias which may be related to the adjacently outcropping porphyry system or telescoped to the periphery of some other stocks still buried at depth.

1 Introduction

Epithermal precious metal deposits may be distinguished in high-, intermediate- and low-sulfidation deposits based on the sulfidation state of their primary sulfide assemblage. A link between porphyry and epithermal mineralization is inferred especially in high-sulfidation (HS) systems where a single hydrothermal system, evolving over space and time would be responsible for forming the porphyry and HS ore body. The porphyry fluid may be related directly to the mineralization of the spatially associated epithermal system at proximal to distal positions relative to the quartz diorite dikes, with a continuum of mineralization styles associated with an evolving and migrating hydrothermal fluid. In a vertically zoned system, the epithermal top may have been eroded and/or the porphyry intrusive source is too deep to access. Te-bearing minerals and sulfosalts, as well as their mutual relationships in epithermal precious metal systems, offer potential for deciphering changes in temperature and sulfidation state (Cook and Ciobanu 2002). Their deposition is traditionally restricted to one or two stages that always follows initial sulfide deposition. 

The Te-rich paragenetic assemblages may be examined to investigate the spatial variation in tetrahedrite chemistry (Wu and Peterson 1977) and sulfidation states in the evolving hydrothermal column from plutonic to epithermal zones.

2 The Furtei epithermal Au deposit

The Furtei Au deposit is the only example of HS mineralization in Sardinia (Fig.1). It is typically acid-sulfate in style (Fiori et al. 2001).

Figure 1. Geological map of Sardinia with the sites under study.

Under the surficial oxidized zone of supergene nature, the primary sulfide zone is largely hosted by diatreme breccia and characterized by a vertical zoning of the mineral assemblage, dominated by pyrite-enargite-luzonite-gold at higher levels, whereas in the deep zone tetrahedrite, minor base metal sulfides and Te-rich minerals are present, especially in the deeper parts of the orebodies. Gold mostly occurs as high-fineness native metal and within some tellurides. A quantitative approach
to the study of hydrothermal zoning was pursued by systematic, detailed microanalytical and high-magnification investigations of the telluride-rich samples and sulfosalts from different parts of the ore-bodies of the mine. Several samples were selected from drill cores from economic and non-economic parts of the mine to establish the continuity of the zones and the spatial association among the deposits. The lateral distribution of minerals allows for the exposure of a cross-section of the mineralised column, at the present level of erosion, from porphyry to peripheral veins having epithermal characteristics. Samples for analysis were selected from open pits and drill cores chosen to represent the stages of ore formation over the vertical and lateral extent of the mine.

Table 1 shows the three main ore mineral assemblages in the deposit.

<table>
<thead>
<tr>
<th>Mineral assemblages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidized surface (shallow)</strong></td>
</tr>
<tr>
<td>Jarosite (with native Au max 1-2% Ag), gypsum, Fe-Mn-hydroxides, digenite, covellite, scorodite.</td>
</tr>
<tr>
<td><strong>Sulfide (shallow)</strong></td>
</tr>
<tr>
<td>enargite-luzonite, pyrite,chalcopyrite, sphalerite, covellite, digenite, galena, arsenopyrite, native Au (max 1-2% Ag), bornite in enargite.</td>
</tr>
<tr>
<td><strong>Sulfide (deep)</strong></td>
</tr>
<tr>
<td>Tennantite-tetrahedrite, Te-bearing tetrahedrite up to goldfieldite, pyrite, calaverite, krennerite, coloradoite, native Te, enargite, aikinite, native Au (max. content 6% Ag), chalcopyrite, stannite and native tin in enargite-luzonite.</td>
</tr>
</tbody>
</table>

The As-sulfosalt assemblage grades into the telluride assemblage with increasing depth. In the deeper parts of the system the paragenesis evolves into a Te- and Sb-rich assemblage with the presence of increasing tetrahedrite and Te-rich tetrahedrite up to goldfieldite, calaverite and krennerite, sometimes associated with native Te. Native Au in drillcore samples always appears as blebs within enargite. It is ubiquitous and fairly pure, with a maximum Ag content around 6%. Minerals of the tetrahedrite series, ranging from tetrahedrite, Cu$_{12}$Sb$_2$S$_{13}$, to tennantite, Cu$_{12}$As$_4$S$_{13}$, occur in minor amounts in all ore types often including gold and tellurium phases such as native tellurium and tellurides. Other varieties are due to substitutions of Te for (Sb, As). However the most abundant and ubiquitous ore minerals are enargite and luzonite, pyrite, sphalerite and arsenopyrite are also of importance. Chalcopyrite can be fairly common in places, but is always present in the upper levels with covellite and sulfosalts. Tetrahedrite commonly appears as veinlets and swarms disseminated in chalcopyrite, or occurs as interstitial grains with the other sulfides or fills the interstices of pyrite and chalcopyrite; some tetrahedrite grains grew in the holes of porous vuggy silica.

Geophysical evidence for the presence of a relatively shallow intrusion at 1 to 1.5 km present depth is reported by Meloni (1994). Volumes of high temperature fluids may have been rapidly flushed upwards from the already emplaced porphyry into a ready network of fractures, breccias and channel ways. Fluid inclusion data (Ruggieri et al. 1997) are similar to those found in many porphyry Cu deposits, including Calabona (Fig. 1) where a minerographic study on ore samples included petrographic and fluid inclusion studies to characterize alteration, mineralization, and fluid phase circulation in the dacite porphyry system. The alteration pattern and assemblages at Calabona reflect the style shown by several studies on porphyry copper deposits and three major generations of mineralizations were distinguished: early, intermediate, and late (Frezzotti et al. 1992). Fluids associated with late stages of hydrothermal circulation have significantly lower salinities and are characterized by a progressive cooling (500°- 90°C) and dilution throughout the shallow and peripheral zones of the intrusions and with late quartz-pyrite veins. These fluids are interpreted to be responsible for the argillic alteration, which was possibly facilitated by the extensive fracturing and influx of meteoric water. The similarity of the fluid inclusion data from the Calabona deposit suggests that epithermal mineralization at Furtei may be associated with a porphyry system with a fluid of magmatic derivation circulating at deeper level followed by the mixing of the high-temperature magmatic hypersaline brine with cooler low-salinity meteoric water at shallow depth. The epithermal mineralization of Furtei can be divided into two stages postdating the silicic, and much of the advanced argillic alteration and was characterized by a distinct zoning with depth: the HS-state sulfosalts, enargite and luzonite are the principal Cu minerals in the orebody and occur at a shallow level, with abundant euhalic pyrite and gold. At depth tennantite-tetrahedrite, chalcopyrite, stannite, Au, Ag-tellurides including coloradoite, petzite, hessite are present. Ruggeri et al. (1997) estimated $f_{S2}$ and $Te_{2}$ for the formation of Is Concas sector deep mineral assemblages in the Furtei site. The construction of $f_{S2}$-$Te_{2}$ diagrams at 100°C and 300°C (Affifi et al. 1988b) has shown that the topologies of these diagrams are essentially constant with changing temperature making these diagrams useful for comparison of telluride assemblages in low-temperature (<350°C) hydrothermal deposits.

The commonly observed dominant telluride mineral assemblages stable at the deep levels of Furtei ore bodies allows a narrow domain to be constrained in $Te_{2}$-$f_{S2}$ space (Fig. 2). Deposition of sulfide-gold mineralization at shallow depth occurred under comparatively high $f_{S2}$, whereas deep assemblages where characterized by lower $f_{S2}$. Gold mineralization is associated with tennantite and chalcopyrite which partially replaces enargite; luzonite appearing paragenetically later. Because Te solubilities are predicted to be low in auriferous chloride waters (Cooke et al. 2001), deposition of tellurides and native tellurium in intermediate-/low-sulfidation (IS/LS) environments may result from condensation of magmatically-derived $H_2Te(g)$ and $Te_2(g)$ into deep-level chloride waters.
Such magmatic input into the hydrothermal system is later than the input of sulfur, since telluride deposition is always preceded by that of sulfides. The fugacity of Te₂ is very important and is controlled by the supply of this element from the source, and also locally controlled by reactions between the fluid and rock minerals or changes in fluid chemistry. Whether gold occurs in the native form, in petzite or in sylvanite is influenced by variations of this parameter. The relative stabilities of hessite and calaverite depend on the initial tellurium concentration and Ag:Au ratio in the water. However, minor amounts of Te can dissolve into chloride waters and could precipitate into lower temperature surficial acid sulfate waters by cooling or fluid mixing producing geochemical anomalies only or Te-rich mineralizations. Study of the mineral assemblages in the Furtei ore bodies demonstrates that introduction of gold in HS ores is related to IS assemblages, indicating an evolution from an IS towards HS environment. This implies that HS-style epithermal mineral assemblages may be precipitated from Au-bearing LS/IS waters with a distinct vertical zonation of electrum and Te-bearing species. In fact, the deeper part of the ore is characterized by tetrahedrites, Te-rich minerals, including precious metal tellurides, Te-tetrahedrite and native tellurium evolving in shallow level to enargite-luzonite, Cu-Fe-sulfides and native gold. The ore minerals also indicate that a part of gold introduction (in native form and in sulfosalts) has taken place contemporaneously with deposition of the HS assemblage, thus suggesting a genetic link between the two sulfidation states in the same ore deposition environment. There is a strong suggestion that the magmatic-hydrothermal system at Furtei underwent an evolution from an earlier IS porphyry-style mineralization, to IS-HS mineralizations in porphyry related, base-metal and epithermal precious-metal veins. Tellurium was introduced by both HS and IS solutions in a succession of phases of progressively lower Te content until the establishment of the observed paragenesis. The initial increase in fTe₂ from the magmatic source led to saturation, with the appearance of native Te and di-tellurides (sylvanite, calaverite, krennerite), followed in turn by altaite, coloradoite, hessite, petzite and finally gold with gradual decreasing fTe₂ values. Condensation of Te-bearing magmatic volatiles may be essential for the formation of Te-rich mineral assemblages at depth, thus consuming the major part of the initial available tellurium. For aqueous tellurium species, cooling and mixing of fluids are predicted to be an effective, temperature dependent depositional mechanism. During multistage boiling, sufficient tellurium may be transported in the gas phase through the epithermal environment up to the shallow zones where it could condense back into groundwater leading to the observed vertical zonation from goldfieldite at depth to Te-free tetrahedrites in the outer zones. This chemical zonation suggests a component of vertical migration for the mineralising fluids progressing away from the pluton which seems to have acted not only as a heat source but provided material input. The relationship between the proportion of Te and (Sb+As) in tetrahedrite-goldfieldite from deep to shallow level ore bodies of the Furtei mine verifies the substitution of (Sb+As) by tellurium until the end-member goldfieldite is reached (Fig. 3).

![Figure 2. Telluride-sulfide stability diagram at 300°C in fTe₂-fS₂ space, after Afifi et al. (1988b). The shaded domain corresponds to the mineral assemblages of Is Cacas sector, Furtei mine.](image)

However, mixing of different fluids at shallow levels seems to have been important in controlling the chemistry of tetrahedrite series, and late stage fluids may have been oxidized as indicated by the presence of barite in the epithermal assemblage. In the ore assemblage, the presence of arsenopyrite indicates that the mineralising fluids had a generally low sulfidation state. For tetrahedrite and chalcopyrite to have followed this mineral in the paragenetic sequence, a slight increase in fS₂ and/or decrease in temperature would have been necessary (Fig. 4). In conclusion, the chemical composition of tetrahedrite can record some of the chemical variables of the hydrothermal fluids at the time of mineralisation. The correlation of compositional variations of this mineral series through the Furtei deposit can delineate a zoning pattern in which Te decreases away from a presumable, porphyry-style center of the hydrothermal system.

![Figure 3. Relationship between Te and (Sb+As) in goldfieldite-tetrahedrite from Furtei mine.](image)
3 A Porphyry-copper in the Siliqua volcanic complex

The andesitic and dioritic bodies occurring in the Siliqua sector (Fig.1), formed during the Tertiary calc-alkaline magmatic cycle, display alteration and mineralisation patterns which can be referred to as a porphyry copper system consistent with a diorite model. In the northern part of this sector an exploration drilling campaign showed high gold contents, strong silicification and the presence of epithermal silica-pyrite alteration. The field observations and time and space relationships between the porphyry and epithermal styles of mineralisation and host rocks seem to suggest successive development of alternating porphyry-style veining and igneous and/or hydrothermal breccias, followed by several epithermal stage mineralised breccias within previously advanced argillic-altered subvolcanic and volcanic rocks (Fiori et al. 1999). The epithermal occurrences may be considered to be related to the adjacent outcropping porphyry system or telescoped to the periphery of some other stocks still buried at depth. Detailed petrographic studies for the reconstruction of such a complex scenario are in progress. Perhaps the best geotectonic conditions for the formation of porphyry ore systems, i. e. such as to permit a rapid and easy access of magmas to the shallow crust, were limited in time and space. Excellent exposures provide good opportunity to study spatial, temporal, and possibly genetic links between porphyry and epithermal stages of the continuous development of a complex magmatic-hydrothermal-epithermal activity. The epithermal occurrences in the study area may be considered to represent the upper parts of porphyry bodies still buried at depth. But the existence of such a magmatic contribution, genetically connected, may be only speculated as yet. Alternatively, the close space and time relationships between possibly multiple intrusion phases and different epithermal fluids along the same or different plumbing systems, may support a genetic connection if erosion and tectonism in the province are taken into account. Systematic exploration will provide further data for a correct interpretation of previous detailed field and petrographic studies; this interpretation may form the basis for reconstructing the chemical, spatial and temporal evolution of the events. Chemical analyses of fluid inclusions from both the porphyry and the epithermal parts of the system, combined with electron microprobe analyses of magmatic phenocrysts and hydrothermal minerals, are currently in progress and will be of primary interest in understanding magmatic factors controlling the mineralisation. Microthermometry, isotopic geochemistry and tracing, as well as high-precision (U-Pb and Ar-Ar) dating of the different magmatic and hydrothermal regimes will also be of help to study the connection between these two mineralisation styles and possibly to trace the porphyry to epithermal transition, if present.

Acknowledgments: The research has been supported by the CNR - IGAG, Cagliari, Italy.

References

Cook NJ, Ciobanu CL, (2002). Tellurides: more than mineralogical curiosities, but also markers of fS2-fO2 evolution in zoned hydrothermal systems. IMA, 18th General Meeting, Edimburg, Programme with Abstracts: 283
Fiori M, Granizio F, Grillo SM 1999, Hydrothermal breccias in the southern sector of the Tertiary volcanogenic Cu-Au-Ag province of Sardinia, Italy. Proceeding of the fifth biennal SGA meeting and the tenth quadrennial IAGD meeting: Mineral deposits: Processes to processing, 491-494.

Figure 4. Transition between paragenesis of arsenopyrite evolving to tetrahedrite-bearing assemblage. Thermodynamic data are taken from Craig and Barton (1973).
Geological setting and lithological controls of breccia-hosted Cu-Au ore at the Late Cretaceous Kvemo Bolnisi prospect, Bolnisi, Lesser Caucasus, Georgia

Nino Popkhadze
A. Janelidze Institute of Geology of Iv.Javakhishvili Tbilisi State University, Georgia

Greg Corbett
Corbett Geological Services Pty. Ltd., Australia

Jason Cunliffe
International Mineral Exploration Consultants LTD., UK

James Royall, Simon Cleghorn, Mikheil Chokhonelidze, Jack Davies, Ryan Hampton, John Newman, Leqso Gelashvili, Koba Khmaladze, Tariel Tedliashvili
Georgian Mining Corporation (GCG mining); GCG Mining, Bolnisi, Georgia

Abstract. Detailed field mapping and drill core description was undertaken at the Kvemo Bolnisi prospect located in the Bolnisi ore district, of the Lesser Caucasus, in Southern Georgia. This study facilitated the distinction between the main host rock facies units and understanding of the lithological control to copper-gold mineralization. The base of the oxidation zone controls the distribution of supergene gold and underlying copper mineralization in upper non-welded permeable ignimbrite, while the lower welded rhyolite ignimbrite hosts mostly copper ore mostly within the cross cutting the polymictic breccia pipe. The columnar jointed, post-ore dacite body represents the final volcanic event in this area.

1 Introduction

The Bolnisi ore district belongs to the renowned 10,000 km-long Tethyan Eurasian Metallogenic Belt (TEMB; Fig. 1; Jankovic 1997). The Kvemo Bolnisi Cu-Au mineral deposit is part of the Artvin-Bolnisi unit of the TEMB located in the northern part of the Lesser Caucasus. The Bolnisi district hosts numerous producing Late Cretaceous ore deposits, including the Madneuli, Sakdrisi, Beqtakari Cu-Au and polymetallic deposits. Kvemo Bolnisi breccia-hosted Cu-Au deposit is located at a distance of 6 km from the Madneuli deposit, which produced approximately 85 Mt of copper and gold bearing ore, at a reported grade of 1.0 g/t Au and 1.0% Cu, over a period of 30 years. At Kvemo Bolnisi, the resources have been estimated as 947,000 tones at an average grade of 0.93 Cu and 0.15 g/t Au. (Rich Metals Group) company, including Bnelikhevi, David Gareji, and Mushevan. The Kvemo Bolnisi prospect represents the highest priority target for exploration by the Georgian Mining Corporation, which also has the Dambludi, Tsiteli Sopeli, Tamarisi and Balichi prospects under investigation. The main aims of our work are to understand the lithological and structural controls for the development of the main ore zones in order to understand the distribution and anatomy of the Cu-Au mineralization.

2 Regional geology and stratigraphy

The Kvemo Bolnisi prospect is located in Artvin-Bolnisi zone, which belongs to the Lesser Caucasus. The Lesser Caucasus extends over the territories of Armenia, Azerbaijan and Georgia. It consists of three
tectonic zones (Sosson et al. 2010), which are from SW to NE: (1) the South Armenian Block (SAB), (2) the Amasia-Sevan-Akera suture zone (ASASZ) and (3) the southern Eurasian plate margin consisting of the Somkheto-Karabagh belt (SKB) and the Kapan block (KB) (Fig. 1). The Somkheto-Karabagh belt is known in Georgia as the Artvin-Bolnisi zone (Yilmaz et al. 2000). The host rocks for the ore deposits and prospects in the Bolnisi district are composed of Late Cretaceous volcanic and volcano-sedimentary rocks emplaced into a depression between the basement rocks of the Khrami and Loki massifs (Zakariadze et al 2007). Predominant Late Cretaceous volcanic and pyroclastic rocks are in this region include rhyodacitic ignimbrite, ash fall and density current deposits with a phreatomagmatic origin (Popkhadze et al 2017). The distribution of rhyodacitic to basaltic lava domes has led to speculation that a central caldera may have played a role in the localization of the Cu-Au exploration prospects in the vicinity of Kvemo Bolnisi. Based on lithological and paleontological data, Late Cretaceous volcanic and volcano-sedimentary rocks in this region are subdivided into six volcanogenic suites, and are Cenomanian to Campanian and Maastrichtian in age (Gambashidze 1984). Ore deposits in this region are associated with Late Cretaceous explosive volcanic events in different stratigraphic levels. According to Gugushvili (2004), deposits/prospects from the eastern part of the district, including: Madneuli, Kvemo Bolnisi, Tsiteli Sopeli, Mushevani and David-Gareji are hosted by stratigraphically older rocks of the late Turonian to early Santonian Mashavera suite. A second group of ore deposits/prospects, including: Saktresi, Darbazi, Imedi, Beqtakari, Bnelikhevi and Samgereti are hosted by stratigraphically younger rocks of the Campanian Gasandami suite.

3 Geology of Kvemo Bolnisi

3.1 Host rock facies architecture of the Kvemo Bolnisi prospect

This study has focused upon the physical volcanology and facies analyses during a mapping program, together with detailed drill core logging and interpretations. The complete data set including correlation of outcrop and drill core samples allows us to distinguish the following facies types in Kvemo Bolnisi area: lithic/pumice-rich tuff or non-welded ignimbrite, fine-grained tuff, columnar-jointed dacite dome, polymictic breccia, a bedded volcano-sedimentary sequence and welded ignimbrite. The detailed description and interpretation of the Kvemo Bolnisi east polymictic breccia pipe, allow us to constrain the stratigraphy of the host rocks of this area (Fig.2). The stratigraphically upper lithic/pumice tuff is strongly oxidized, fractured and in some areas silicified. The highly porous, permeable and glassy pumice/lithic tuff was affected by pervasive argillic (illite) alteration (Fig 3a). During the petrographic investigation, it was difficult to recognize pumice or lithic clasts in the tuff, as they are affected by argillic alteration. In some places, remnants
of pumice clasts were identified. The lower stratigraphic unit consists of welded (fiamme) ignimbrite (Fig.3b). In some cases, this fiamme might be considered as a fiamme in secondary welded pumice-rich facies, produced by secondary welding of pumice-rich clastic facies. The formation of such fiammes is possible in contact with hot lava or an intrusion. Sometimes, fiamme produced by secondary welding of fiamme-rich clastic facies are virtually indistinguishable from fiamme in conventional primary welded pyroclastic facies (McPhie and Hunns, 1995).

Figure 3. The host rock architecture from KB area: a - lithic/pumice-rich tuff; b - welded (fiamme) ignimbrite; c - fine and medium-grained, bedded volcano-sedimentary tuff, with classical slide-slump units; d - mineralized polymictic breccia; e - margin of breccia pipe showing the mixture of wall rock - with breccia clasts.

The fine- and medium-grained, bedded volcano-sedimentary tuff, with classical slide-slump unit crop out at the contact with non-welded ingimbrite and might me interpreted as an older stratigraphically unit in this sequence (Fig.3c). The mineralized polymictic breccia pipe is cross-cutting all previously mentioned host rock sequences, including felsic dikes (Fig.3d). While a columnar-jointed post-ore dacite dome represents the last volcanic event in the Kvemo Bolnisi area (Fig.3e). The polymictic breccia pipe crops out in the western part of the Kvemo Bolnisi prospect, as a matrix-rich to clast-supported breccia of well rounded, milled clasts of fine tuff, less silicified ignimbrite, and also clasts of felsic dikes and other silicified clasts. In the Kvemo Bolnisi the polymictic breccia pipe margin is discernible in outcrop and drill hole intercepts as a mixture of wall rock – lithic/pumice tuff (ignimbrite) with breccia clasts (Fig.3f).

3.2 Ore zones and lithological controls at Kvemo Bolnisi

The Kvemo Bolnisi project includes different ore zones, including (Fig.4): Kvemo Bolnisi west, which is the gold zone 3 characterized by polymetallic-gold-silver mineralization; Kvemo Bolnisi south, which includes the copper zone 1, where the breccia pipe and other structures are identified. Gold zones 1 and 2 represent the gold oxide ore, developed from the surface to the base of the oxidation zone, between a depth of 40 and 70m (https://www.georgianmining.com/projects/).

Figure 4. Model of the Kvemo Bolnisi prospect, including different copper and gold mineralized zones (Source: Georgian Mining corporation).

The gold zones 1 and 2 represent the upper stratigraphic level, consist of strongly oxidized lithic/pumice tuff (non-welded ignimbrite) with shallow supergene Au mineralization (Fig. 5a, b).

Figure 5. Characteristic features of ore at the Kvemo Bolnisi copper-gold prospect: a,b strongly silicified, crackle fractured lithic/pumice tuff cross cut by quartz-iron oxide veinlets; c – iron oxide veinlet above the redox boundary zone with chalcocite in the transition zone; d – clast-supported open space polymictic breccia filled with quartz-pyrite-chalcopyrite; e – clast-supported subrounded to rounded breccia. Pyrite and chalcopyrite are in the matrix.

This zone extends down to the base of the oxidation zone, which is clearly identified in nearly all drill holes. Chalcocite is present coating pre-existing sulphides and
The transitional breccia is less silicified and more affected by argillic alteration, and it contains a juvenile clast.

4 Conclusions

The permeability of host rock units in the Bolnisi district, including: non-welded ignimbrite, lithic/pumice tuff and different types of breccia, provides a favorable environment for fluid migration and ore formation. The existence of mineralized polymictic breccia in the Kvemo Bolnisi area provides an attractive exploration target. Different stages of ore formation and fluid migration are overprinted in polymictic breccia. Most of the clasts in this breccia are mineralized, which indicates there has been an early stage of ore formation which is overprinted by a later breccia infill mineralization. The breccia pipe is interpreted to have evolved from a magmatic hydrothermal to a more phreatomagmatic nature with an associated change in mainly breccia matrix-hosted mineralization low sulphidation Cu-rich quartz-sulphide Au+Cu style to Au rich carbonate-base metal Au mineralization, as typical of these types of breccia deposits. The key controls on the mineralization is the breccia pipes, which are mineralized with hypogene auriferous pyrite and chalcopyrite. In the supergene environment the sulphides are oxidized giving rise to a classic sequence of oxidized and enriched gold mineralization where copper mineralization is mobilized and redeposited at the base of oxidation giving rise to strongly enriched chalcocite mineralization overprinting primary sulphides.

Acknowledgements

The authors would like to thank: the members of staff of the Georgian Mining Corporation and Rich Metals Group (RMG) company for the collaboration and sharing the information; SGA, SEG, and IAVCEI organizations and the Shota Rustaveli National Science Foundation in Georgia for attending many international conferences, where the work and results from the Bolnisi district were presented. The Swiss National Science Foundation (grant 200020_168996) is also thanked for support.

References


Popkhadze N, Moritz R, Natsvlishvili M, Bitsadze N (2017) First evidence of phreatomagmatic breccia at the Madneuli Polymetallic Deposit, Bolnisi district, Lesser Caucasus, Georgia. In: proceedings of the 14th SGA Biennial Meeting: Mineral resources to discovery, 1:323-326; 20-23 August Quebec City, Canada


Regional-scale mapping of mineral potential for porphyry Cu-Au deposits in southeastern Europe

Felix Camenzuli and Hartwig E. Frimmel
University of Würzburg, Germany

Adam Wooldridge
Vardar Minerals

Abstract. The Balkan Peninsula is probably Europe’s most famous region for porphyry Cu(-Au) deposits thanks to the collision between Eurasia and Gondwana and preceding subduction of the Tethyan oceanic lithosphere. A complex plate tectonic history left behind magmatic arcs which are known for porphyry and related epithermal deposits. To better assess the potential for discovering new such deposits, especially in areas covered by younger strata, we followed a GIS-based mineral potential mapping approach using exclusively ESRI ArcMap. For this purpose, geological data from eight Balkan countries were combined. The results revealed a particularly high probability of porphyry Cu(-Au) mineralization in arc-related rocks of Tertiary age and not only in Cretaceous arc rocks, which have been the centre of past mining activities.

1 Introduction

Porphyry Cu deposits account for some 80% of the global Cu resources and can contain also several other metals at economic grades (Sillitoe 2014). Europe’s largest porphyry Cu deposits are located on the Balkan Peninsula – a region that has seen mining of ores since antiquity. Extraction of gold and copper there is thought to have had a major influence on the cultural and economic development of early Europe (Kaiser Rohrmeier et al. 2013).

Today’s exploration faces the problem that most of the bigger deposits that have a surface expression have been found and mined already (Hronsky and Groves 2008; Huston et al. 2016). The challenge is to discover new deposits under cover. The Balkan Peninsula is no exception in this regard. Prior to cost-intensive local geological mapping as well as geophysical and geochemical surveying and eventually drilling, identifying prospective target areas on a larger scale based on available geological, geochemical and geophysical information and a solid genetic model has become standard practice. This is readily achieved by GIS, in which a number of different kinds of data can be combined and spatially overlain resulting in mineral potential maps (Bonham-Carter 1994). Such a modelling approach can be data-driven or knowledge-driven. The latter is preferred when the amount of input data, such as known mineral deposits/occurrences, geochemical anomalies, etc., is limited. In that case, existing empirical models for the genesis of the deposit type of interest form the base of the modelling as they determine the weight of each layer of information, that is, each layer represents a major factor controlling the formation and spatial distribution of ore (Bonham-Carter 1994). The combination of all these factors has become known as mineral system approach, first used by Wyborn et al. (1994) for hydrothermal deposits. Modelling is scale-dependent. If scale increases, number of relevant factors, and thus complexity of the system decreases (Hronsky and Groves 2008).

Similar to the work by Billa et al. (2004), who examined the porphyry and epithermal deposits of the central Andes on a continental scale, this study aims at conducting large-scale predictive modelling of the exploration potential for porphyry and related epithermal Cu-Au deposits in the Balkan Peninsula using fuzzy logic and a knowledge-driven model. The studied area of interest (AOI) covers ~1*10^6 km^2 as illustrated in Figure 1.

Figure 1. Map of the studied area showing the extent of data coverage.
2 Geological background

The AOI forms part of the Tethyan Eurasian metallogenic belt and extends L-shaped from Romania to Bulgaria. The subduction and collision events that shaped the convergent margin of Eurasia in the Balkan Peninsula are a consequence of closure of the Paleotethys and from the Cretaceous to the Neo-tethys (Stampfli and Borel 2004). As a result, magmatism and mineralization occurred in different parts of the AOI during three major periods: a Cretaceous, a Paleocene to Oligocene, and a Miocene magmatic arc can be distinguished (Marton et al. 2013).

The Cretaceous arc, referred to as Banatitic Magmatic and Metallogenic Belt (BMMB; Ciobanu et al. 2002), was formed due to the subduction of the Vardar oceanic lithosphere beneath the Serbo-Macedonian continent, which started in the late Jurassic. The Vardar Ocean filled one of the back-arc basins that were closed between the Jurassic and the Cretaceous in the region of the Balkans and Carpathians. This was followed by the accretion of microcontinents and island-arcs, resulting in syn-collisional calc-alkaline magmatism around the Cretaceous-Tertiary boundary (Richards 2015; Ciobanu et al. 2002). Porphyry Cu and high-sulfidation Cu-Au mineralization affected mainly andesitic-dacitic rocks and was limited to belt-parallel basins.

The BMMB hosts the famous deposits Majdanpek, Veliki Krivulj and Bor located in the Serbian Timok ore district (Timok Magmatic Complex), as well as Elatsite and Assarel of the Bulgarian Panagyurishte ore district. The timing of mineralization in these districts varied as the position of the subduction zone shifted. Whereas mineralization in the Panagyurishte ore district took place between 92 and 86 Ma, it was around 86-84 Ma in the Timok ore district (Fig. 2; Quadt et al. 2007, Richards 2015).

Historical mining activity has focused on the Cretaceous arc. Active subduction was long believed to be indispensable for fertile magmatism and porphyry mineralization and indeed, the Cretaceous deposits of the Balkan Peninsula can be explained by subduction-related mineralization processes. There are, however, some major deposits that have been formed later, e.g. the Buchim and Skouries deposits (Fig. 2).

As summarized by Richards (2015), porphyry Cu deposits occur scattered in both space and time within the Tethyan Belt, reflecting different settings of formation. When the subduction zone shifted in the Paleogene to the Hellenic Trench, porphyry and epithermal mineralization took place again in the Balkans and the eastern Rhodopes. This has been explained by Richards (2015) who suggested that the formation of the younger porphyry Cu-Au and epithermal Au deposits was initiated by remelting of subduction-metasomatized subcontinental lithospheric mantle or lower crustal hydrous cumulate zones. Thus, the bulk of Cenozoic deposits of the Tethyan Belt can be considered to be of either back-arc, post-subduction or collisional origin. In the case of the Balkan Peninsula, the formation of these deposits was related to the closure of Vardar Ocean. Consequently, collisional orogens can be regarded as being as attractive for porphyry mineralization as subduction settings (Richards 2015).

3 Methodology

The genetic model underlying this study assumed four critical factors that have to be satisfied in order to form a porphyry/epithermal Cu-Au system: (i) mineralization is primarily tectonically controlled; (ii) it is spatially and genetically related to felsic to intermediate porphyry intrusive bodies; (iii) these intrusions occurred in root zones of volcanoes in subduction-related, continental ridge/arcs and/or island arc settings; and (iv) they are limited in age to Cretaceous and Eocene-Miocene times. Geological data was used as primary data source. That data was originally taken from 1:200000 to 1:500000 geological maps. Prior to modelling, that data was unified due to strong country-specific differences in extent and quality of data. Lithological and age data were simplified in a classification scheme, respectively. From the processed data three predictor maps or layers were prepared: a "lithology" layer, representing lithology suitable for hosting porphyry Cu mineralization, that is, intrusive and extrusive magmatic rocks of felsic to intermediate composition.

The second layer, "subvolcanic level", reflects the assumption that porphyry Cu deposits are located in volcanic root zones and was obtained from mapped contacts of extrusive and intrusive igneous rocks. Those areas were ascertained from the distance of both intrusive and extrusive rocks to points of a grid, having a cell length of 1 km. The smaller the distance the higher the value of representing the contact. Both the "lithology" and "subvolcanic level" layers were prepared for each time window known to be critical for mineralization. Due to data inconsistencies and lack of necessary age resolution on many of the available geological maps, only two periods could be distinguished: Cretaceous and Tertiary.

The third layer, "Cu-anomalies", is based on point data of locations from which anomalously high Cu concentrations have been reported. Only those anomalies were considered further, which occur within or nearby areas of rock types typical of porphyry/epithermal environments in order to exclude genetically unrelated mineralization. The proximity of those anomaly point data was implemented by circled polygons of different radii representing the decrease of Cu enrichment with distance. Smallest radii were 250 m and 500 m, which are the expected size of porphyry stocks (Sillitoe 2014). The probability values were set to decrease away from the anomalies. This layer was used for modelling mineral potential maps for both Cretaceous and Tertiary times. Tectonic control was not considered in a separate layer because it is effectively represented by the lithology layer as the magmatic rocks of interest tend to be emplaced along the same large-scale structures (crustal-scale lineaments) as the associated mineralization.

Mineral potential mapping of this study was carried out with a knowledge-driven model and the usage of Fuzzy logic, using a Fuzzy gamma operator with a value of 0.98.
following a recommendation by An et al. (1991). For each period, a separate mineral potential map was modelled. Highest probability of porphyry Cu mineralization is expressed by a value of ~1, and no probability by a value of ~0. The results obtained for both the Cretaceous and Tertiary time slices were validated by 72 locations of known Cu deposits or occurrences as given in the USGS database “Global assessment of undiscovered copper resources” (Dicken et al. 2016), by comparing modelled probability values and the location of the deposits/occurrences as point data. In a second step, the vicinity (5 km radius) of the point data was included and the highest value was taken from this circular surrounding. For better comparison, the probability values were classified as low (0.25 ≥ x), medium (0.25 ≤ x ≤ 0.75) and high (x ≥ 0.75).

4 Results

The modelled mineral potential maps for the Cretaceous and Tertiary periods (Fig. 2) show several differences regarding the spatial distribution of areas with high and medium probability for porphyry Cu mineralization. In comparison to the Cretaceous, the potential map for Tertiary deposits reveal a number of differences: (i) high and medium probability areas are more abundant, (ii) they are bigger in extent, (iii) more widely distributed, and (iv) they are spatially separated from the potentially mineralized Cretaceous areas. The areas of Cretaceous age are arranged in an arc-shaped zone extending from central-eastern Serbia via central- and southwestern Bulgaria to central, southeastern Bulgaria. The zone has its smallest extent in the north, and becomes wider to the south and southeast, where it continues as two small separated bands. In contrast, areas of Tertiary age are mostly located further to the south and west, appear as a funnel-shaped zone extending from the northwestern to the southwestern parts of the AOI. The zone broadens in extent from the area of Macedonia onwards. In regard to (iv) it is necessary to note that there are parts of the AOI where areas of high a medium probability of both periods exist. These are mainly central-eastern Serbia and central and southern Bulgaria. The areas of highest probability values for the Cretaceous and Tertiary differ, however, in geographic position.

The results show that the areas with the highest probability values are restricted to small domains in central-eastern Serbia in the case of Cretaceous age, whereas those of Tertiary age are somewhat further north. The other centers of highest probability of Tertiary deposits are arranged linearly from eastern and southern Serbia to western and southwestern Bulgaria.

The validation of the mineral potential maps showed that 36 % of the known deposits/occurrences lie directly in areas of high probability, 7 % in areas of medium probability. If the surroundings of the known locations are included in the validation, 67 % of the locations lie within, or in ≤5 km proximity of, an area of high probability. Using the same method on areas of medium probability, 1% of the locations lie within or in proximity of those areas. Combining areas of high and medium probability, the mineral potential map based on known deposits/occurrences as point data, explains 43 % of the existing locations. If one includes the vicinity around known deposits/occurrences, this percentage increases to 68%.

Figure 2. Mineral potential maps showing suitable areas for copper mineralization of Cretaceous (A) and Tertiary (B) age. Both maps were produced by using a Fuzzy Gamma operator with a value of 0.98. Additionally, the existing mining locations and their status after USGS database - Dicken et al. (2016) are shown as well as the names and age data of selected deposits (after Richards 2105).

5 Interpretation and discussion

Modelled mineral potential maps are typically validated with known deposits. Previous studies illustrate a strong dependence of the model’s accuracy on the spatial scale, as proposed by e.g. Hronskey and Groves (2008). Mutele et al. (2017) did prospectivity mapping of granite-related polymetallic mineralization of an area on the scale of 10⁵ km² area in the Bushveld Igneous Complex. The validation of their study showed that all known mineral occurrences are within areas of modelled high and medium probability. In contrast, the study by Billa et al.
(2004) on predicting epithermal and porphyry systems in the Andes at a continental-scale of $10^6 \text{ km}^2$ found only $\sim 64$% of known deposits lying within areas of modelled high and medium probability (excluding the vicinity of known deposits). Similarly, our results (68%, including vicinity of known deposits), referring to an AOI on the scale of $10^6 \text{ km}^2$, fall short of a 100% coverage and illustrate the importance of scale for the accuracy of mineral potential maps. Without doubt, applying a more complex model should lead to a mineral potential map that can explain a higher number of deposits/occurrences.

Furthermore, our results, being strongly dictated by the spatial distribution of the different magmatic arcs (Marton et al. 2013), provide information on the relative fertility of these arcs. While historic mining activities focused on the Cretaceous arc, this study attests to a considerable potential also in the Tertiary arc. The latter area shows a higher number and greater extent of areas with high and medium probability.

6 Conclusions

Regional-scale mineral potential mapping has shown its ability to delineate regions of elevated probability for hosting porphyry Cu (and related epithermal Au) deposits as exemplified here for the Balkan Peninsula. The usefulness of the model is supported by its ability to predict known deposits in spite of simple input data. Overall the results show a much higher probability for porphyry Cu mineralization in the Tertiary arc than in the Cretaceous one. Thus, the Tertiary arc could become an even more important target for future exploration as the Cretaceous arc has been already.

Acknowledgements

We thank Vardar Minerals Ltd. for providing the regional databases.

References


Mineralogical characterization of Te-Au porphyry-epithermal California prospect in Tolima, Colombia

Iván Mateo Espinel Pachón, Juan Carlos Molano Mendoza, Juan David Alarcón Rodriguez, Mónica Ágreda López
Universidad Nacional de Colombia

Andrés Felipe González Durán
CDTEC Gemlab

Abstract. The California prospect is located 200 km west from Bogotá, Colombia and only 8 km SE from La Colosa Au-rich porphyry. The mineralization is associated with two porphyritic dacites that intruded muscovite-quartz-graphite schists of Palaeozoic age. The ore minerals are accompanied by a strong phyllic alteration which affects both the host rock and the hypabyssal bodies. Using clay minerals and Ga, Ge, In, Mn and Fe concentrations in sphalerite (GGIMFis) geothermometer, it was possible to differentiate two areas. In the hottest area, tetradymite was reported for the first time and it is related to structural gold concentration in pyrites.

1 Introduction

A gold-rich porphyry deposit was defined as a porphyry copper deposit that contains more than 0.4 g/t Au (Sillitoe 1979). Few Au-rich porphyry deposits have been found worldwide; there are some examples in the Maricunga Belt in Chile (Vila and Sillitoe 1991), Cajamarca in Perú (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 intrusions. 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 470 Mtonnes with an Au content of 0.9 g/t (Gil-Rodriguez 2010).

The California prospect is located about 8 km southeast from La Colosa (Fig. 1). In 1960's there was gold exploitation but, a couple of years later the mine closed due to Colombian armed conflict. Gold was extract from quartz veins and loads, using mercury amalgamation.

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 volcanites (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 and Spikings (2013) proposed a synchronous exhumation process occur during 117-107 Ma for Arquía Complex.

Villagomez et al. (2011) reported an age on zircons from a metatuff in Quebradagrande Complex, Arquía Complex and Mesozoic oceanic volcanites (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 age 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).

3 Methodology

Thirty rock samples were collected during several field trips through series of outcrops on “Las Hormas” creek. Respective macroscopic descriptions were done, characterizing the hydrothermal alteration and the types of veinlets. Ten significant samples were selected for petrographic and metallographic studies using polished thin sections. Raman spectroscopy was used to verify metallographic and petrographic observations.

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 softwares SpecMin-Pro-3.1. Version and The Espectral Geologist (TSG). In order to verify and complement the previous data, X-ray Diffraction was done in all samples using a Brucker D2 phaser Diffractometer, the data was analyzed with the software DIFFRAC.EVA.

Finally, WDS points were measured over sphalerites, pyrites and tellurides using an electronic microprobe JEOL JXA-8230.

4 Results

In the creek three different rocks were identified. The hypabyssal bodies were classified using the QAPF triangle for volcanic rocks of Streckeisen (1980):

-Dacite 1: Dacite with a green matrix product of chloritization. (Fig. 2).

-Dacite 2: Dacite with a whitish color, with quartz, sericite and disseminate pyrite, hints for a phyllic alteration (Lowell 1970). Also, some sulphide veinlets were observed (Fig. 3).

Field observations show that Dacite 1 cuts Dacite 2 and that both have different grain size. In muscovite-quartz schists with graphite, a phyllic alteration was recognized by the presence of quartz and sericite. Additionally, some veinlets of sulphides clearly cut the foliation planes of the rock (Fig. 4).

The last event identified in the area was quartz-veins with disseminated sulphides, cutting the foliation of the schists.

Figure 2. Outcrop of Dacite 1 composed mainly by quartz and plagioclase. The green color of the rock is related with the chloritic alteration.

Figure 3. Outcrop of Dacite 2. Whitish color due to phyllic alteration, presence of a sulphide veinlet.

Figure 4. Muscovite-quartz schists with graphite. Phyllic alteration in different areas. Veinlets of sulphides are clearly observed.

4.1 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 due to the interactions of Ibague and Palestina faults, considering that Cauca-Romeral faults system, Ibague fault and Palestina fault is a conjugate dextral-fault set.

4.2 Mineralization

The mineralization was divided in two zones, according to alteration and mineral assemblage:

Zone 1: Lithologies with phyllic alteration, sulphides veinlets, tetradyomite and structural gold.

Zone 2: Quartz veins with disseminated sulphides cutting the foliation of the schists.

In the first zone, the mineral assemblage is: Quartz+Pyrite+Chalcopyrite+Arsenopyrite+Sphalerite+Galena+Marcasite+Pyrrhotite+Tetradyomite+High
crystallinity illite+Jarosite (Fig 5 and 6).

Figure 5. Reflected light photomicrograph with crossed nicols of Dacite 1. Note chalcopyrite disease in sphalerite. Pyrite (Py), Chalcopyrite (Ccp), Sphalerite (Sp) and Galena (Gn).

Figure 6. Reflected light photomicrograph with crossed nicols of a veinlet in a muscovite-quartz schist with graphite. Pyrite (Py), Pyrrhotite (Po).

According to Table 1, the high crystallinity illite was determined using X-ray diffraction and the relation (ALOH/H2O)>1 (Pontual 1997). Steiner (1968) and Reyes (1990) established that when illite has a high crystallinity the temperatures should be over 300 °C. This information fits with the presence of >250 °C minerals like pyrrhotite and arsenopyrite.

Table 1. Data and relations obtained using The Spectral Geology (TSG).

<table>
<thead>
<tr>
<th>Sample</th>
<th>ALOH</th>
<th>H2O</th>
<th>ALOH/H2O</th>
<th>Mineral</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFG003 (schist)</td>
<td>0.147</td>
<td>0.051</td>
<td></td>
<td>4.73 MUSCOVITE</td>
<td>&lt;300°C</td>
</tr>
<tr>
<td>AFG004 (schist)</td>
<td>0.23</td>
<td>0.058</td>
<td></td>
<td>3.97 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG004 (schist)</td>
<td>0.147</td>
<td>0.068</td>
<td></td>
<td>2.047 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG005 (schist)</td>
<td>0.279</td>
<td>0.134</td>
<td></td>
<td>2.008 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.429</td>
<td>0.23</td>
<td></td>
<td>1.066 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.388</td>
<td>0.182</td>
<td></td>
<td>1.861 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG005 (schist)</td>
<td>0.295</td>
<td>0.165</td>
<td></td>
<td>1.787 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.333</td>
<td>0.153</td>
<td></td>
<td>1.703 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.333</td>
<td>0.153</td>
<td></td>
<td>1.874 Smectite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG004 (schist)</td>
<td>0.333</td>
<td>0.153</td>
<td></td>
<td>1.862 Smectite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.321</td>
<td>0.227</td>
<td></td>
<td>1.422 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.321</td>
<td>0.227</td>
<td></td>
<td>1.422 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.445</td>
<td>0.219</td>
<td></td>
<td>1.794 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.445</td>
<td>0.219</td>
<td></td>
<td>1.794 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG001 (schist)</td>
<td>0.188</td>
<td>0.149</td>
<td></td>
<td>1.334 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.174</td>
<td>0.131</td>
<td></td>
<td>1.333 Phengite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.298</td>
<td>0.233</td>
<td></td>
<td>1.279 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG006 (schist)</td>
<td>0.123</td>
<td>0.099</td>
<td></td>
<td>1.125 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG005 (schist)</td>
<td>0.187</td>
<td>0.234</td>
<td></td>
<td>0.796 Illite</td>
<td>220°C-300°C</td>
</tr>
<tr>
<td>AFG004_Superior</td>
<td>0.185</td>
<td>0.248</td>
<td></td>
<td>0.667 Smectite</td>
<td>220°C-300°C</td>
</tr>
</tbody>
</table>

In the second zone, the mineral assemblage is: Pyrite+Sphalerite+Galena+Chalcopyrite+Carbonates+Quartz (Fig 7 and 8).

Figure 7. Reflected light photomicrograph with crossed nicols of a quartz vein. Pyrite (Py), Chalcopyrite (Ccp), Sphalerite (Sp) and Galena (Ga).

Figure 8. Reflected light photomicrograph with crossed nicols of a quartz vein. Quartz Qz), Carbonates (Calc) and Sphalerite (Sp).

The temperatures in this area using the GGIMFis geothermometer are ~ 174 °C which are consistent with...
the mineral assemblage. Note that the sphalerite crystals are bigger and euhedral in this area.

5 Conclusions

The mineral occurrence is divided in two main zones. The first one shows phyllic alteration with temperatures ~253 °C and the mineral assemblage of pyrite, marcasite, pyrrhotite, sphalerite, chalcopyrite, galena, tetradymite, high crystallinity illite and jarosite. The second zone presents a simple mineralogy of quartz, sphalerite, chalcopyrite, galena and carbonates with temperatures of ~174 °C.

The occurrence of structural gold in pyrite is associated with the presence of tellurium in the area.

The disseminated mineralization accompanied by phyllic alteration produced by the intrusion of hypabyssal bodies, may suggest the existence of an unroofed porphyry system with an epithermal overprint. However, more field, geochemical and isotopic evidence is needed to confirm this supposition.

Tetradymite is a good pathfinder, due to its relation with gold mineralization within the area. In Colombia, there are only few articles and investigations where tellurides systems are reported and studied. California is a good prospect for gold greenfield exploration due to the structural setting, mineralogy, temperatures and gold mining history.

Acknowledgements


References


Sillitoe RH (2008) Special paper: Major Gold Deposits and belts of the North and South American Cordillera: Distribution, Tectonomagmatic Settings, and Metallogenic Considerations. Econ Geol 103:663–887


Geology setting and metallogenesis of the Alta Floresta Province, southern Amazon Craton (Brazil)

Veronica Trevisan, Roberto Xavier
Institute of Geosciences, University of Campinas, Brazil

Steffen Hagemann, Anthony Kemp, Robert Loucks
Centre for Exploration Targeting, The University of Western Australia, Australia

Jian-Feng Gao
State Key Laboratory of Ore Deposit Geochemistry, Chinese Academy of Sciences, Guiyang, China

Abstract. The Alta Floresta Province consists of Paleoproterozoic plutonic-volcanic sequences (2.01-1.75 Ga) originated from a series of successive magmatic arcs that accreted to the southwestern margin of the Central Amazon Province. The geologic framework of the eastern sector of the province is organized into: 2.8-1.97 Ga deformed metamorphic and metamorphosed granitic basement; 1.97-1.78 Ga I-type plutonic-volcanic and volcano-sedimentary sequences; 1.78-1.77 Ga post-orogenic and anorogenic plutonic-volcanic units; and Mesoprotroozoic (~1.3 Ga) to Quaternary sedimentary sequences. The ore deposits are clustered into four main groups: (i) disseminated Au-Cu-Mo; (ii) structurally-controlled vein-type Au-Cu-Mo; (iii) disseminated Cu-Mo; and (iv) structurally-controlled vein-type Au-Zn-Pb-Cu. Groups (i) to (iii) are characterized by pyrite-chalcopyrite-molybdenite, whereas group (iv) consists of pyrite-sphalerite-galena-chalcopyrite-digenite. In most deposits, mineralization is contained within muscovite-chorite-quartz-rich or silica-rich zones. The fluid regime of groups (i) and (ii) is mainly represented by CO2-rich fluids, whereas group (iv) by two-phase aqueous fluids with heterogeneous degree of filling. Re-Os on pyrite and molybdenite and Pb-Pb on pyrite geochronology systems constrain the mineralization age between 1.84 - 1.77 Ga. This overlaps with the ages of porphyritic granitoids, and in a regional scale with ages of the Colider and Teles Pires suites. These deposits represent magmatic-hydrothermal systems and are considered to share broad similarities with porphyry-epithermal deposits.

1 Introduction

The Alta Floresta Province (AFP) is located in the southern sector of the Amazon Craton, between the Tapajós-Parima (2.03 - 1.88 Ga) and Rondônia-Juruena (1.82 - 1.54 Ga) tectonic provinces (Santos et al. 2006) in the Mato Grosso state, Brazil. The province outlines a NW-SE to E-W-striking belt of 500 km extent and 30 km wide containing plutonic-volcanic sequences generated in continental arc to post-collisional settings during the Paleoproterozoic (2.01 – 1.75 Ga; Souza et al. 2005; Paes de Barros 2007, Assis 2015) (Fig. 1). This province has historically been an important gold-producing region in Brazil (~4 Moz from 1990 and 1999), especially its eastern segment, where the number of mining sites totals over a hundred placer and medium to high-grade and low-tonnage (< 5t) “hard rock” gold deposits, mainly exploited by local artisanal prospectors (garimpeiros; Paes de Barros 2007). However, since the 1980’s, junior companies, and more recently (2015 to today) major companies, have been exploring and discovering large-scale “hard rock” polymetallic deposits. The scarcity of outcrops, the Mesoprotroozoic to Quaternary sedimentary cover over the plutonic-volcanic sequences, and poor understanding of geological controls for the mineralization have made exploration challenging in this region.

Based on the metallic association and mineralization style, the deposits are clustered into four main groups (Xavier et al. 2011; Trevisan et al. 2017): (i) disseminated Au-Cu-Mo; (ii) structurally-controlled vein-type Au-Cu-Mo; (iii) disseminated Cu-Mo; and (iv) structurally-controlled vein-type Au-Zn-Pb-Cu mineralization (e.g. Francisco, Bigode, Carrapato and Luiz deposits).

This work provides an overview of the regional geology and main characteristics of these deposits based on host rocks, structures and vein textures, hydrothermal alteration, ore associations, fluid regime, and U-Pb, Pb-Pb and Re-Os geochronology. These deposits have been considered (Moura et al. 2006; Xavier et al. 2011; Trevisan et al. 2017; Assis et al. 2017; Xavier et al. 2011; Trevisan et al. 2017; Assis et al. 2017) to represent magmatic-hydrothermal systems that display broad similarities to Au-Cu-Mo, Cu-Mo porphyry and Au-Zn-Pb-Cu epithermal systems.

2 Regional geology

In the eastern sector of the AFP, basement rocks of Orosirian age (2.8 – 1.97 Ga) rarely crop out and include tonalitic-to-granitic gneiss and migmatite intruded by calc-alkaline foliated and nondeformed monzogranite to tonalite (Paes de Barros 2007; Assis et al. 2017). The previous units are crosscut by Orosirian non-deformed I-type granitoids including the Aragão granite (1.99 – 1.93 Ga; Miguel-Jr 2011), Novo Mundo granite
that varies from monzogranite (1.97 Ga) to syenogranite (1.96 Ga), Pé Quente Intrusive Suite composed of monzonite (1.97 Ga; Miguel-Jr 2011) and biotite tonalite (1.9 Ga; Assis 2015), Nhando granite (1.88 – 1.84 Ga; Silva and Abram 2008), Matupá Intrusive Suite (1.87 – 1.86 Ga; Moura et al. 2006), Flor da Mata granite (1.87 Ga; unpublished data), União do Norte granodiorite (1.85 Ga; Miguel-Jr 2011); undifferentiated granite (1.8 Ga; unpublished data), and Peixoto granite (1.79 – 1.78 Ga; Paes de Barros 2007; Silva et al. 2014). Except for the Flor da Mata, undifferentiated and Peixoto granites, all other units host mineralization. Collectively, these plutonic-volcanic sequences show affinities to oxidized I-type, calc-alkaline, medium to high-K, metaluminous to slightly peraluminous granites originated in continental arc settings. Also, volcaniclastic sediments represented by immature feldspathic-sandstone, feldspathic-wacke, lithic-sandstone, and conglomerate rocks from the Serra Formosa Formation overlies an unknown basement (~2.0 Ga; Miguel-Jr 2011). These units are often crosscut by dikes and rocks that vary in composition from basalt-diorite-gabbro to andesite-dacite. According to Duarte (2015), this ~1.82 – 1.77 Ga mafic-intermediate magmatism episode may belong to the Colider suite, which also hosts mineralization.

Units listed above are intruded by post-orogenic and anorogenic felsic plutonic-volcanic units represented by the Teles Pires Intrusive suite (1.78 – 1.75 Ga; Silva and Abram 2008), which includes the União do Norte porphyry (1.77 Ga; Miguel-Jr 2011) and the Braço Sul tuffs (unknown age; Paes de Barros 2007).

Overlying all the units listed above are Mesoproterozoic rocks of the Caiabis group (Dardanelo Formation), composed of sandstone, arkose, siltstone, mudstone, volcanic greywackes and basal conglomerate (maximum ages ~1.3 Ga; Leite and Saes 2003). The Mesozoic and Cenozoic are represented by detritus-lateritic covers, whereas the Quaternary by alluvial deposits (Souza et al. 2005) (Fig. 2).

Despite the lack of consensus regarding the regional tectonic framework of the AFP, Assis (2015) correlates the units to three tectono-magmatic events: (stage 1) 2.1 to 1.95 Ga, coeval with the Cuíú-Cuíú magmatic arc defined by the Tapajós-Parima tectonic province; (stage 2) 1.88 to 1.82 Ga, Juruena magmatic arc evolved within the Rondônia-Juruena tectonic province; and (stage 3) 1.78 to 1.75 Ga, the post-orogenic and anorogenic felsic magmatism of the Juruena magmatic arc.

3 Features of the deposits

3.1 Host rocks

The deposits in the AFP are mainly hosted by tonalitic to syeno-monzogranitic intrusions (1.98, 1.90 and 1.87 Ga), quartz-feldspar porphyries (1.98, 1.97 and 1.77 Ga), and, to a lesser degree, basement rocks (2.0 to 1.98 Ga) and volcanic/volcaniclastic sequences (2.0 Ga) (Moura et al. 2006, Paes de Barros 2007, Silva and Abram 2008, Assis et al. 2017). In some deposits, aplitic and mafic to intermediate rocks of unknown ages frequently contain mineralization (e.g. Luiz and Pé Quente deposits).

3.2 Structures and vein textures

The vein-type deposits are controlled by NNW, NW and E-W-striking shear zones or faults. The veins commonly display massive to banded, open-space filling (e.g. comb, crustiform, zonal, colloform, cockade, mini geodes), recrystallization (e.g. flamboyant or feathery), platy (e.g. bladed calcite and quartz), and vuggy textures. Stockwork veins and hydrothermal breccias are also found in these deposits (Trevisan 2015).

3.3 Hydrothermal alteration and mineralization

In all deposits, the mineralization occurs within and/or enveloped by pervasive muscovite-quartz-sulfides-carbonate-magnetite (phyllic alteration), orthoclase-quartz-hematite-sulfides-microcline or biotite-quartz-magnetite-carbonate-sulfides (potassic alteration) halos or silification represented by fronts of replacement or aggregates and quartz infill alteration (e.g. quartz veins, stockwork zones, fracture-fill, and hydrothermal breccias). However, disseminated gold mineralization associated with early pervasive albite-quartz-coarse-grained pyrite (sodic alteration) is also recognized at Pé Quente deposit. Outwards from the ore zones, carbonatization, silification, potassic (K-feldspar),
3.4 Fluid characteristics

Fluid inclusion studies in quartz from the ore zones of the deposits belonging to groups (i) and (ii) reveal the presence of three types of fluids: (i) two-phase aqueous with variable salinity (2.1 – 26.1 wt.% eq. NaCl) and homogenization temperature between 126.5°C and 268.4°C; (ii) aqueous-carbonic fluids of low salinity (6.1 to 8.9 wt.% eq. NaCl) and homogenization temperatures between 251.6°C and 334.6°C; and, more subordinately, (iii) high saline (33.6 to 37 wt.% eq. NaCl) aqueous fluid represented by halite-bearing fluid inclusions with homogenization temperatures between 98.9 and 211.9°C and dissolution temperature of halite between 200.2 and 280.3°C (Assis et al. 2015). There is no fluid inclusions or stable isotopes data available in the literature for group (iii) so far.

3.5 Timing of mineralization

The Re-Os ages obtained in pyrite and molybdenite from groups (i) and (ii) deposits yielded weighted average model ages at 1786.7 ± 3.2 Ma (MSWD = 0.96; molybdenite, X1 deposit; Assis et al. 2017), 1787 ± 6.2 Ma (MSWD = 2.2; pyrite, Luizão deposit; Assis et al. 2017), 1787 ± 5.5 Ma (MSWD = 0.99; pyrite, Pé Quente deposit; Assis et al. 2017), and 1787 ± 17 Ma (molybdenite, Paraíba deposit; unpublished data). Conventional Pb-Pb geochronometry yielded an age of 1841 ± 22 Ma (MSWD = 1.6; Santos 2011) in pyrite from the Paraíba deposit. The Re-Os analyses in sulfides from group (iii) deposits are still under progress.

Sericite 40Ar-39Ar plateau ages from the phyllic alteration halo of the Francisco deposit (group iv) yielded ages between 1779 ± 6.3 and 1777 ± 6.3 Ma (Assis 2015), very similar to the Re-Os ages obtained for groups (i) and (ii).

4 Conclusions and future work

The continental arc setting attributed to the AFP plutonic-volcanic units, the close spatial relationship between the mineralization and granitic plutons, structures and vein textures, types and distribution of the hydrothermal alteration and ore paragenesis, collectively suggest that the Au-Cu-Mo, Cu-Mo and Au-Zn-Pb-Cu deposits may be genetically linked to the emplacement of magmatic-hydrothermal systems. This is further corroborated by the
pyrite and molybdenite Re-Os and sericite ⁴⁰Ar-³⁹Ar ages described above that closely overlap the crystallization ages of the quartz-feldspar porphyries at the X1 (1.78 Ga; Assis 2015) and Paraiba (1.79 Ga). A similar age interval has also been obtained for other intrusion-hosted deposits in the province: Re-Os model ages of pyrite of ~1.78 Ga for the Luizão and Pé Quente deposits; Re-Os model age of 1.8 Ga in ore-related molybdenite at the Juruena gold district (Paranalta suite) in the northern sector of the province (Serrato 2014). Nevertheless, quartz-feldspar porphyry outcrops or interception by drill cores have not been reported so far in these cases. Hence, the interval of 1.77 to 1.84 Ga seems to mark an important regional metallogeny episode in the Alta Floresta Province. The regional felsic magmatism in the province that displays a broad temporal association with this 1.77 – 1.84 Ga event includes volcanics and granitic intrusions that belong to the Colider (1.82 – 1.77 Ga), Paranalta (1.81 – 1.79 Ga) and Teles Pires (1.78 – 1.75 Ga) intrusive suites.

At the deposit scale, exsolution of aqueous-carbonic fluids from crystallizing quartz-feldspar porphyries in the deposits belonging to groups (i) and (ii) may have triggered the magmatic-hydrothermal system. The CO₂-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). Heterogeneous entrapment by fluid phase separation (immiscibility processes) accompanied by progressive mixing with externally-derived fluids (meteoric) causing CO₂ dilution and cooling may have caused the lowering of the solubility of gold and other metals. In contrast, in the case of group (iv), boiling process may have driven precipitation of metals in a shallower crustal level.

Based on the geotectonic setting, combined with the geological characteristics of the mineralization and their temporal relationship with the porphyritic rocks, we argue that ore-forming processes at the deposits from the eastern sector of the Alta Floresta Province were similar to those observed in Mesozoic-Cenozoic Au-Cu-Mo and related Au ± Cu (± Mo) systems in the Alta Floresta Gold Province. However, the magmatic-hydrothermal systems associated with these deposits appear to be controlled dominantly by pressure (Lowenstern 2001). Hence, the interval of 1.77 to 1.84 Ga seems to mark an important regional metallogeny episode in the Alta Floresta Province. The regional felsic magmatism in the province that displays a broad temporal association with this 1.77 – 1.84 Ga event includes volcanics and granitic intrusions that belong to the Colider (1.82 – 1.77 Ga), Paranalta (1.81 – 1.79 Ga) and Teles Pires (1.78 – 1.75 Ga) intrusive suites.

At the deposit scale, exsolution of aqueous-carbonic fluids from crystallizing quartz-feldspar porphyries in the deposits belonging to groups (i) and (ii) may have triggered the magmatic-hydrothermal system. The CO₂-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). Heterogeneous entrapment by fluid phase separation (immiscibility processes) accompanied by progressive mixing with externally-derived fluids (meteoric) causing CO₂ dilution and cooling may have caused the lowering of the solubility of gold and other metals. In contrast, in the case of group (iv), boiling process may have driven precipitation of metals in a shallower crustal level.

Based on the geotectonic setting, combined with the geological characteristics of the mineralization and their temporal relationship with the porphyritic rocks, we argue that ore-forming processes at the deposits from the eastern sector of the Alta Floresta Province were similar to those observed in Mesozoic-Cenozoic Au-Cu-Mo and Cu-Mo-Au porphyry systems, but emplaced at deeper crustal levels, and Au-Zn-Pb-Cu epithermal systems.

Future work will include dating of granitoids via SHRIMP U-Pb on zircon, which will potentially provide crystallization ages than can help to better constrain the magmatic framework of the eastern sector of the province. Whole-rock geochemical analyses, and Lu-Hf, trace elements and O isotopes analyses on the same zircons will be applied in order to constrain the chemistry, source/contamination, evolution and fertility potential of the magmas.

Acknowledgements

This research was funded by CNPq/Brazil (grant 142061/2016-6) and SKL/OG/Chinese Academy of Sciences (project number 201507).

References


Trace element variation in ore minerals from the Iron Cap deposit (KSM), British Columbia, Canada: Implications for fluid evolution in porphyry-epithermal gold systems

Hugh Graham, Daniel Morgan, Robert Chapman, and David Banks
University of Leeds, UK

Abstract. Trace amounts of elements such as As, Sb, Se, Te, Pd, Hg and Au are commonly identified in porphyry and epithermal mineral deposits. Investigating variations in the concentration, distribution and hosting of these elements in an ore mineral suite has the potential to enable elucidation of the specific characteristics of discrete fluids throughout the evolution of a mineralizing magmatic-hydrothermal system. The Iron Cap deposit in the Kerr-Sulphurets-Mitchell (KSM) district, British Columbia, Canada, provides an opportunity to interpret the characteristics of hydrothermal fluids from an early porphyry stage, through transition, to a late epithermal stage. A suite of 60 core samples are characterized by petrographic methods to constrain the sequence of vein formation at Iron Cap, and identify deposit mineralogy. The results of initial trace element analysis of ore minerals by SEM-EDX analysis has shown that pyrite growth zones are Cu- or As-bearing, and arsenopyrite growth zones have a variable Fe:As:S ratio. Galena commonly contains Se, ranging in concentration from ~2 wt.% to clausthalite (PbSe). Additionally, gold in the deposit contains between 2-42 wt. % Ag. These initial discoveries will allow a methodology to be developed to interpret fluid conditions with trace element variations.

1 Introduction

Trace element studies are now increasingly applied to a range of mineral deposits, including porphyry, epithermal, volcanogenic massive sulphide, and orogenic gold (e.g., Huston et al. 1995; Reich et al. 2013; Zhang et al. 2018; Augustin and Gaboury 2019). Sulphides such as pyrite may be analyzed by electron microprobe (EMP) or laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to measure the concentration and distribution of elements within a single crystal (e.g., Large et al. 2009). The trace element composition of a crystal can be used to assist the understanding of mineral paragenesis, identify relative element abundances in mineralizing fluids throughout ore formation, enable speculation of fluid conditions (e.g., temperature), and improve mineralization vectoring (e.g., Sykora et al. 2018). However, few studies use trace element data to consider the wide range of factors that could be influential in enrichment or depletion of an element at a given site, such as fluid chemistry (e.g., pH, phase, salinity, $R_{O_2}$, $R_{S_2}$, ligand availability), trace element mineral incorporation mechanisms (lattice substitution vs. inclusion), fluid-mineral partition coefficients, and the effect of post-deposition remobilization, recrystallization or diffusion (e.g., Grant et al. 2018). Furthermore, there remains a paucity of research investigating trace elements in an ore mineral suite, where sulphides (e.g., galena, sphalerite, molybdenite, arsenopyrite), sulphosalts (e.g., tetrahedrite-tennantite), tellurides (e.g., hessite, altaite), selenides (e.g., clausthalite, naumannite) and metal alloys may together exhibit a trace element partitioning signature that might better constrain the nature of mineralizing fluids at certain points in time and space, taking into account the above factors.

Porphyry- and epithermal-style mineral deposits are often spatially, temporally and genetically linked as they form from magmatic-hydrothermal systems at convergent tectonic margins (Sillitoe 2010). These magmatic-hydrothermal systems are complex, and comprise multiple stages. As such, there is significant variability in mineralizing fluid characteristics throughout their evolution, with the transitional period from porphyry to epithermal conditions remaining a key topic of discussion (e.g., Gammons and Williams-Jones 1997; Hedenquist et al. 1998; Heinrich 2005; Pudack et al. 2009; Maydagán et al. 2015). The application of a comprehensive trace element study to a porphyry-epithermal system has the potential to elucidate the sequential transitions in physico-chemical conditions of hydrothermal fluids at different stages of deposit formation.

The Iron Cap deposit, in the Kerr-Sulphurets-Mitchell (KSM) district, British Columbia, Canada, exhibits features of both porphyry and epithermal mineralization, and is being investigated as a case study for this research. To date, a suite of 60 core samples have been collected from the deposit, encompassing deep porphyry through to shallow epithermal environments. Here, we present the initial results of petrographic and trace element analyses, and suggest potential methods for interpreting the characteristics of hydrothermal fluids at Iron Cap.

2 Geological setting

The KSM district hosts four Cu-Au, predominantly porphyry-style deposits: Kerr, Sulphurets, Mitchell and Iron Cap. Together, they host proven and probable reserves of 38.8 Moz Au, 4.63 Mt of Cu, 0.09 Mt of Mo and 183 Moz of Ag, at grades of 0.55 g/t Au, 0.21% Cu, 42.6 g/t Mo and 2.6 g/t Ag, making KSM one of the...
largest undeveloped Cu-Au districts in the world and particularly one of the most gold-rich in terms of total contained metal (Seabridge Gold 2018). KSM is situated in the porphyry-endowed Stikine arc terrane of the Canadian Cordillera, with most deposits in the region having formed during a prolific ~15 m.y. period of mineralization at the Triassic-Jurassic boundary (Fig. 1; Febbo et al. 2015).

A series of Early Jurassic diorite to syenite intrusions are the magmatic source for the KSM deposits, with adjacent wall rocks comprising volcaniclastic and sedimentary units. Mineralization at Iron Cap is predominantly hosted within porphyritic monzonite and unclassified quartz vein-rich intrusions. The plunging orebody exhibits potassic alteration at depth, zoning outward to peripheral propylitic in the wall rocks, and phyllitic alteration that is largely restricted to shallower parts of the deposit (Campbell and Dilles 2017). Deposit margins partially outcrop at surface, with the remainder buried beneath the barren hanging wall of a thrust fault. Post-mineralization deformation occurred in the Middle Cretaceous, with metamorphism reaching lower greenschist facies (Aldrick 1993).

3 Vein generations

Ongoing petrographic analysis of core samples has so far discriminated at least 8 vein stages at Iron Cap (Table 1, Fig. 2). Further work is required to fully characterize all vein generations, ascertain variation in vein mineralogy and confidently determine the relative timing of veins. Additional generations may also be characterized with further petrography.

Table 1. Initial assessment of vein types and order of emplacement in the Iron Cap deposit. Note that not all veins have been analyzed by scanning electron microscopy (SEM) to identify minor phases.

<table>
<thead>
<tr>
<th>Vein generation</th>
<th>Mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Magnetite-quartz-chalcopyrite ± galena</td>
</tr>
<tr>
<td>2</td>
<td>Quartz-pyrite-chalcopyrite-molybdenite ± galena</td>
</tr>
<tr>
<td>3</td>
<td>Pyrite-quartz ± chalcopyrite ± galena</td>
</tr>
<tr>
<td>4</td>
<td>Chlorite-quartz-chalcopyrite ± galena ± gold</td>
</tr>
<tr>
<td>5</td>
<td>Quartz-tennantite/tetrahedrite-chalcopyrite ± galena ± altaite ± Ag-Hg alloy ± hessite ± petzite</td>
</tr>
<tr>
<td>6</td>
<td>Quartz-pyrite-chalcopyrite-sphalerite-chlorite-carbonate</td>
</tr>
<tr>
<td>7</td>
<td>Quartz-pyrite-arsenopyrite-sphalerite-carbonate ± gold</td>
</tr>
<tr>
<td>8</td>
<td>Carbonate</td>
</tr>
</tbody>
</table>

Figure 2. Type occurrences of vein generations 3, 4 and 8, as outlined in Table 1.
Initial results and discussion

4.1 Sulphide zonations

Scanning electron microscopy (SEM) has identified a number of trace element variations within pyrite and in arsenopyrite growth zones. Different pyrite generations observed in type 3 vein show variance in Cu, with an increased abundance of galena inclusions in the Cu-bearing pyrite (Fig. 3). This may indicate that boiling was influential in the formation of the Cu-bearing pyrite, owing to the chemistry and inclusion abundance (Román et al. 2018). The chalcopyrite rim grown around the first pyrite generation (Py1) may have sourced the Cu for incorporation into the adjacent Cu-rich pyrite; possibly with recrystallization of chalcopyrite into pyrite, and excess Cu distributed elsewhere. Diffusion of Cu from the chalcopyrite into Py2 may have also occurred, before growth of Py3, as the euhedral crystal shape is preserved, which would likely not be the case if diffusion occurred post-Py3.

4.2 Galena-clausthalite series

A solid solution series exists between galena (PbS) and clausthalite (PbSe; Shiga and Urashima 1989). Core samples from different depths and alteration zones in the Iron Cap deposit host galena as a minor phase (including vein types 1-5), and often show the presence of Se in SEM-energy dispersive X-ray (EDX) analysis. When quantitatively measured, variance in the Se content of galena crystals is evident, with some samples having galena of comparable S:Se ratios throughout, and others having variable ratios relating to different vein types or alteration. Rare clausthalite grains also occur. Both Se-bearing galena and clausthalite are commonly found with, or included in chalcopyrite and/or tennantite/tetrahedrite, suggesting similar solubility, transport and deposition controls between Cu and Se. Understanding the controls on the Se:S ratio of the galena-clausthalite series may allow changes in the physico-chemical characteristics of the fluid to be tracked over time and through space. For example, temperature is often proposed to be a key control on the abundance of Se in mineral deposits and, if a similar control exists when incorporating Se into galena, then the temperature evolution of a fluid phase could be constrained by measuring the Se:S ratio of galena crystals throughout the paragenesis (e.g., Auclair et al. 1987; Keith 2016).

4.3 Metal alloys

Gold at Iron Cap is present as inclusions in chalcopyrite, pyrite, arsenopyrite, and also found within cracks in pyrite and rarely free in altered groundmass or vein carbonate. Differences in the Au:Ag ratio of grains between samples, veins and host site have been recognized by SEM-EDX. The range in measured Ag content of gold grains across all the analyzed samples is 2-42 weight % Ag. One sample hosting vein type 5 also contains multiple occurrences of a Ag-Hg alloy, indicating that this vein-forming fluid may have been relatively Au-poor;
additionally suggested by the rare presence of petzite (Ag₃AuTe₂) instead of native gold. Differences in the physico-chemical conditions of the fluids are likely to be a key control on the Au:Ag ratio of native gold (e.g., Gammons & Williams-Jones 1995), and thus investigating metal alloy compositions along with the trace element composition of the ore mineral suite at Iron Cap may provide further constraints on fluid conditions.

5 Conclusions and future work

Initial petrography and SEM has characterized at least 8 vein generations at Iron Cap, knowledge of which are essential to investigate the change in hydrothermal fluid conditions over time, as each vein type relates to a separate or transitioning fluid. Trace element variations have been recognized, with pyrite exhibiting Cu- or As-bearing growth zones, and arsenopyrite showing variable Fe:As:S ratios between zones, with specific zones hosting gold. Galena contains variable amounts of Se, with clausenthalite rarely present, and gold exhibits changes in Au:Ag ratio, with a Ag-Hg alloy observed instead of gold in one vein phase. Further analytical work, chiefly EMP and LA-ICP-MS, will quantitatively measure the concentration of trace elements in each vein type, while additional petrography and SEM will fully characterize vein mineralogy and paragenesis, and highlight differences in trace element distribution that can be investigated further. Modelling of fluid conditions using the acquired data will follow, providing insight to the transition from porphyry to epithermal conditions at Iron Cap.

Acknowledgements

This project is funded by the NERC. The lead author thanks Geoscience BC for funds provided through the scholarship program, and the Society of Economic Geologists is acknowledged for financial support provided through a Graduate Student Fellowship. Seabridge Gold Inc. is grateful for access to the KSM project, and for logistical support and accommodation provided during sample collection.

References


An integrated accessory mineral approach to understanding post-subduction magmatism and mineralisation

Jessica Berry, Andrew J. Miles, David A. Holwell
School of Geography, Geology, and the Environment, University of Leicester, UK

Shaun Graham
Carl Zeiss Ltd., UK

C. Johan Lissenberg
School of Earth and Ocean Sciences, Cardiff University, UK

Chiara M. Petrone
Natural History Museum, UK

Abstract. Post-subduction and predominantly alkaline magmas are commonly associated with gold (Au) and tellurium (Te) mineralisation. By contrast, calc-alkaline subduction-related magmas are more often associated with copper mineralisation. Amphibole and sulfide-bearing cumulates formed in the lower crust during active subduction are an important repository for water and gold during the passage of calc-alkaline magmas through the crust. However, these cumulates also have the potential to act as a fertile source of Au and Te during later episodes of post-subduction magmatism when remobilized. A suite of accessory minerals have been analyzed from variably mineralized syn- and post-subduction plutons associated with the Laramide Orogeny in the Colorado Mineral Belt. The common occurrence of inherited zircons in plutonic rocks means they provide a potentially valuable opportunity to assess the role of lower crustal cumulates in the formation of mineralized post-subduction magmas. Spatial and temporal characteristics of syn- and post-subduction intrusions in Colorado are considered. Gold mineralisation is closely associated with post-subduction magmas. Further analysis of barren and fertile syn- and post-subduction suites using Zeiss’ Automated Mineralogic system has shown that zircon, apatite, titanite, and magnetite are present in all samples. Apatite hosted within zircon, and sulfides (pyrite, chalcopyrite) hosted within titanite are also present.

1 Introduction

During subduction, the break-down of hydrous minerals in the down-going slab liberate water and metals, and cause partial melting of the overlying mantle wedge. Magma differentiation occurs during intrusion of these partial melts into the lower crust.

Arc magmas commonly exhibit cryptic evidence for significant amphibole fractionation despite the common absence of amphibole phenocrysts in erupted magmas (Davidson et al. 2007). This is thought to reflect the formation of amphibole-rich cumulates in the lower crust via basaltic underplating. These cumulates behave as a “sponge” and filter for water. Further evidence also suggests that these cumulates contain significant amounts of metal-enriched sulfides that may act as effective filters for highly chalcophile elements such as Cu, Au and Te during magmatic differentiation (Richards 2011).

Sulfide saturation in the lower crust during subduction may limit the formation of Au-Cu porphyry deposits. However, these sulfides may act as fertile sources of Au and Te if they become remobilized during later magmatic events, resulting in the formation of younger Au-bearing porphyry-epithermal systems (Richards 2009). Post-subduction, or post-collisional tectonic settings commonly enable remelting and remobilization of lower crustal cumulates due to slab roll-back or breakoff (Richards 2009).

In many cases, these Au-Te porphyry-epithermal systems are accompanied by completely barren systems that are apparently part of the same magmatic events. The cause of this is unknown. Understanding the gateways that magma must pass through to become either fertile (able to generate mineral deposits) or barren (unable to generate mineral deposits) is critical for exploration.

2 The use of accessory minerals in tracing ore forming processes

Whole-rock data is often limited in its use; rocks are susceptible to alteration and represent homogenised compositions that reflect the cumulative effect of multiple magmatic processes (Miles et al. 2013; Bruand et al. 2016). It is therefore difficult to isolate individual magmatic events that are critical for reconstructing mineralisation processes using whole-rock data alone.

Accessory minerals, such as zircon, titanite, and magnetite, by contrast, are generally robust and often host inclusions of otherwise less-robust minerals (Miles et al. 2013; Wilkinson et al. 2017), which may include sulfides (Simpson 2014).
Zircon chemistry and isotopic signatures, when coupled with high precision U-Pb geochronology, can be useful when assessing successive stages of magmatic history. An increasing number of studies are showing that many zircons are antecrysts; they may contain cores that crystallised during earlier stages of magmatism, and were inherited from different parts of the magmatic system (Miller et al. 2007; Barboni et al. 2013; Miles et al. 2013). The inheritance of zircons from deeper parts of the crust is a critical method for accessing the role of cumulates, and may record protracted magmatic histories (Jackson et al. 2018).

Apatite, titanite (sphene), and magnetite can also be useful fertility indicators. Apatite has an affinity for REE and can be used to determine fluid and volatile exsolution and composition (Boyce and Hervig 2009; Bruand et al. 2016). Apatite geochemistry compared to whole-rock may also be used to determine magmatic histories over different lengths of time (Miles et al. 2013).

3 The Colorado Mineral Belt

The Colorado Mineral Belt spans an area more than 500 km in length, and 20 – 40 km in width in central – western Colorado, USA. Many igneous centres are associated with extensive and predominantly epithermal Au and Te mineralisation with occasional porphyry gold deposits. Most importantly, the region hosts both subduction-related, and post-subduction-related magmas, with both barren and fertile intrusive complexes.

Subduction-related magmatism in the region began during the Laramide Orogeny, when the Farallon plate was subducted beneath the North American plate. Arc-type magmatism occurred from 75 Ma to 45 Ma, during which time subduction of the Farallon slab was shallow. Magmatism at this time was predominantly calc-alkaline, silica oversaturated and silica saturated (Cunningham et al. 1994; Chapin 2012).

The cessation of subduction at 45 Ma was rapid, and post-subduction magmas, predominantly calc-alkaline to alkaline, were generated between 45 Ma and 25 Ma, during steepening and westward roll-back of the Farallon slab (Cunningham et al. 1994; English et al. 2003; Chapin 2012).

The world class Cripple Creek Au-Te deposit formed at ~ 30 Ma (Kelley and Ludington 2002) on the margin of the northward propagating Rio Grande Rift and during continued slab roll-back. The deposit is associated with a phonolite and alkali basalt diatreme complex and hosts an estimated 1,000 t of Au-Te as native gold, gold-tellurides in quartz veins, and disseminated gold (Saunders 1986; Jensen and Barton 2007).

3.1 Spatial and temporal characteristics

Spatial and temporal characteristics of syn- and post-subduction intrusions in Colorado are evidence of significant influence from previous magmatic events. Proterozoic intrusions (1.8 Ga, 1.4 Ga, 1.1 Ga; Whitmeyer and Karlstrom 2007) show controls on the spatial dynamics of successive magmatism, and are found to define pathways for successive magmatism, blocking pathways in areas where Proterozoic intrusions are present. Gold occurrences are occasionally associated with these Precambrian granite intrusions, suggesting some metallogenic potential for them.

Laramide-age, subduction-related intrusions are poorly exposed at the surface (~ 700 km²). These are shown as the black intrusions in Figure 1. Post-Laramide, post-subduction intrusions show a larger surface area (~ 3,500 km²) compared to subduction-related intrusions. This may suggest a higher volume of intrusion during post-subduction magmatism. Spatially, these post-subduction intrusions fill voids where no subduction-related magmas have intruded.

Subduction-related plutons comprise 17% of the total syn- and post-subduction intrusions in the Colorado Mineral Belt (based on area). 83% are post-subduction intrusions (blue outcrops on Figure 1), 33% of gold occurrences are associated with syn-subduction intrusions. 67% of the gold occurrences are associated with post-subduction intrusions. Red ovals in Figure 1 represents an area with a high density of gold occurrences.

Post-subduction intrusions are associated with approximately twice as many gold occurrences than with syn-subduction intrusions. This is suggestive of a concentration of gold in a post-subduction setting. Whilst gold is found in occurrence with subduction-related intrusions, it is more commonly found in post-subduction settings. This is perhaps a function of the volumes of magma that are present for both syn- and post-subduction.
3.2 Automated Mineralogy

Four suites of rocks from the Colorado Mineral Belt have been assessed, covering a selection of barren and fertile samples from both subduction-related and post-subduction intrusions.

Two barren subduction-related samples and three barren post-subduction samples were collected from Twin Lakes (granite, granodiorite), and Gothic Mountain, Kebler Pass, and Chalk Mountain (dacite, rhyolite), respectively. One fertile subduction-related sample and two fertile post-subduction samples were collected from Breckenridge (granite), and Montezuma and Bon Ton (granites), respectively.

These samples were mapped using Zeiss’ Automated Mineralogic Element Mapping instrument. A bright phase search (BPS) was set to capture zircon, apatite, titanite, and magnetite, and any sulfide phases, and a dilute threshold was applied to provide textural and contextual information for each accessory phase. Samples were mapped at a resolution of 5 μm.

By gathering automated mineralogy information from these samples we can texturally constrain the associations and paragenesis of accessory minerals, in order to give spatial context for any subsequent isotopic work. Already, this mapping has shown that zircon, apatite, titanite, and magnetite are present in each sample from barren and fertile, syn- and post-subduction systems. The uniform presence of these minerals across all samples means a direct comparison can be made of each accessory phase.

Acknowledgements

This PhD is funded by NERC, with additional funding from Carl Zeiss Ltd as CASE partner. Thanks to Carl Zeiss Ltd. for access to facilities, and training with Automated Mineralogic software. Additional thanks to Tom Knott at the University of Leicester.

References


Saunders JA (1986) Petrology, Mineralogy, and Geochemistry of Representative Gold Tellurium Ores from Colorado. PhD, Colorado School of Mines

Simpson R (2014) Sulfide inclusions in zircon and their significance to understanding the evolution of copper porphyries in the Macquarie Arc, New South Wales, Bachelor of Science (Hons.). School of Earth and Environmental Sciences, University of Wollongong


Magmatic hydrothermal systems: from Porphyry to Epithermal 1119
Trace element chemistry, polytypes, isotopic composition and Re-Os dates of molybdenite from the Bingham Canyon Cu-Au-Mo porphyry deposit, Utah

Simon Kocher 1, 2, Jamie J. Wilkinson 1, 2, Robin N. Armstrong 1, Iain McDonald 3, Mark Rehkaemper 2, Robert A. Creaser 4, Jens Najorka 5
1LODE, Department of Earth Sciences, Natural History Museum, London, United Kingdom; 2Department of Earth Sciences & Engineering, Imperial College London, London, United Kingdom; 3School of Earth and Ocean Sciences, Cardiff University, Cardiff, United Kingdom; 4Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB; 5Core Research Laboratories, Natural History Museum, London, United Kingdom

Abstract. The controls on the formation of Mo-rich porphyry mineralization remain poorly constrained. By characterizing molybdenite from well constrained samples with Re-Os dating it is possible to trace the processes controlling Mo mineralization at one of the world’s most prolific Cu-Au-Mo porphyry deposits at Bingham Canyon. Petrographic observations indicate three major modes of occurrence of molybdenite, two different types of quartz veins and molybdenite disseminated in porphyritic matrix. Molybdenite trace element compositions are a function of their respective magmatic sources and are capable of recording hydrothermal overprints. In deeper parts of the deposits, Mo isotopes correlate with depth, and are interpreted to be the result of Rayleigh distillation during molybdenite precipitation from a hydrothermal fluid. Polytype compositions show no systematic variations across the deposit. High precision Re-Os dates indicate that molybdenum mineralization formed between 37.62 - 38.22 Ma during a late hydrothermal event coinciding with the emplacement of the youngest porphyry phase. The decoupled deposition of Mo and Cu at Bingham is attributed to the preferential early extraction of Cu from the underlying, less evolved magma chamber, followed by Mo extraction from a more evolved magma.

1 Introduction

99% of molybdenum is recovered from porphyry deposits (Sillitoe 2010) where it is concentrated by 2-3 orders of magnitude relative to the magmatic source, making it the metal with the single strongest affinity to a single deposit type. Due to the economic significance of porphyry-type deposits, considerable research has been undertaken to constrain the behavior of Cu and Au from the generation of a hydrous magma through the precipitation of ore minerals from a hydrothermal fluid (e.g. Williams-Jones and Heinrich 2005). Molybdenum, generally being a co- or by-product, has received less attention even though it has important uses in metallurgy.

To better understand the controls on and timing of Mo mineralization in porphyry deposits, molybdenite samples from Bingham Canyon were analyzed for trace elements, polytypes and isotopic compositions and Re-Os dates.

2 Deposit geology and mineralization

The Bingham Canyon deposit is located 45 km southwest of Salt Lake City, Utah. It is related to Eocene, I-type, shallow-level intrusions emplaced into a thick sequence of shallow marine sedimentary rocks, including quartzite and limestone (Fig. 1).

Mineralization is present as spatially separated Cu and Mo ore bodies hosted by a series of felsic-intermediate intrusions, comprising equigranular monzonite, quartz monzonite porphyry, latite porphyry, and quartz latite porphyry (Fig. 1; e.g. Redmond and Einaudi 2010). Molybdenite occurs as disseminated aggregates in quartz latite porphyry and predominantly in two different
types of quartz veins as fine or coarse-grained flakes (Fig. 2). Molybdenite-bearing quartz veins are generally late-stage and cross cut all porphyry intrusions and Cu mineralization.

Figure 2. Types of molybdenite mineralization at Bingham Canyon. (A) BSE image of disseminated molybdenite in K-spar, biotite and quartz-rich groundmass; (B) Typical example of type 1 vein with multiple bands of fine-grained molybdenite; (C) Type 2 quartz-molybdenite with abundant coarse-grained molybdenite along vein margins.

3 Trace element chemistry

Laser ablation inductively-coupled-plasma mass spectrometry was used to analyze concentrations of major and trace elements in 25 polished molybdenite samples. All measurements were carried out on a New Wave Research UP213 UV laser system attached to a Thermo X Series ICPMS at Cardiff University. Quantitative calibration was achieved using a set of synthetic Ni-Fe-S quenched sulfide standards, natural molybdenite and galena.

Within individual samples most trace element concentrations are mostly homogeneous. Rhenium concentrations in Molybdenite records large variations ranging from <10 to >1000 ppm sometimes even within individual mineral grains. Some elements, including Te, Pb, and Au are concentrated in discrete mineral inclusions, mainly galena and tellurides with a metal/Te ratio of 2/1.

In a ternary Re-(Zn+Pb+As)-(Bi+Te+Au) plot (Fig. 3) data from various deposits plot in discrete fields, suggesting that molybdenite has the potential to record important information on mineralizing processes. In a Re-Se diagram, data from most deposits show no systematic variation on a deposit-scale, thus suggesting that the Re-Se concentrations in molybdenite are controlled by their magma sources. This is consistent with elevated Se concentrations in molybdenites at Bingham, Hilltop and Boddington, which display a stronger mantle component as indicated by higher Re content.

4 Molybdenite polytypes

Molybdenite naturally occurs as two different polytypes, most commonly as hexagonal (2H) and less abundantly as rhombohedral (3R) polytype. The controls on polytype formation are poorly constrained, but likely the result of trace element concentrations (mainly Re) and formation temperatures (e.g. Newberry 1979).

Twenty-six molybdenite-bearing vein samples were selected for polytype analysis (Fig. 1). Samples were crushed, hand-picked and the pure molybdenite concentrates ground into a fine powder prior to analysis. To counteract the effects of preferred orientation, measurements were carried out in transmitted mode on a Panalytical X-Pert Pro MPD X-ray scanning diffractometer equipped with an X-Celerator position...
sensitive detector. Relative abundances of polytypes were quantified following the Rietveld method using the GSAS program (Larson and Von Dreede, 2005).

Results indicate that the majority of molybdenite at Bingham crystallized as the 2H polytype and contains no detectable 3R polytype component. Only three samples were found to contain the 3R polytype in varying proportions from 5% to a maximum of 23%. 3R abundance appears to be unrelated to host rock lithology, vein type and mineral association; however, the 3R-bearing samples tend to be located the furthest from the unmineralized center of the deposit. No obvious correlations were found between trace element concentration and polytype abundance, however, the sample with the highest proportion of 3R polytype contains the highest Re concentrations.

5 Isotopic composition

Molybdenum has seven stable isotopes and in order to assess isotope fractionation under hydrothermal conditions, molybdenite from 20 different hand specimens (Fig. 1) were analyzed for inter-sample δ98Mo variations. The measurements were performed on a Nu Instruments Nu Plasma HR MC-ICP-MS at the Imperial College MAGIC Laboratory.

δ98Mo values of molybdenite range from -0.82‰ to +1.14‰ with a median of -0.23‰ ± 0.02 (Table 1). Disseminated molybdenite measured from two samples range from -0.11‰ to -0.01‰. Isotopic composition of vein-hosted molybdenite follows a trend towards lighter values (Fig. 4). No correlation is seen between Re concentration and isotopic composition.

Table 1. Mo isotopic compositions of Bingham molybdenite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lith.</th>
<th>Type</th>
<th>δ98Mo (%)</th>
<th>±2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC13SK007</td>
<td>QLP</td>
<td>diss.</td>
<td>-0.11</td>
<td>0.02</td>
</tr>
<tr>
<td>BC13SK023</td>
<td>QLP</td>
<td>2a</td>
<td>-0.19</td>
<td>0.03</td>
</tr>
<tr>
<td>BC13SK047</td>
<td>EN</td>
<td>1</td>
<td>1.14</td>
<td>0.03</td>
</tr>
<tr>
<td>BC13SK049</td>
<td>MZ</td>
<td>2b</td>
<td>-0.82</td>
<td>0.02</td>
</tr>
<tr>
<td>BC13SK065</td>
<td>MZ</td>
<td>2b</td>
<td>-0.61</td>
<td>0.03</td>
</tr>
<tr>
<td>BC13SK070</td>
<td>SK</td>
<td>1</td>
<td>-0.45</td>
<td>0.01</td>
</tr>
<tr>
<td>BC13SK075</td>
<td>EN</td>
<td>1</td>
<td>0.38</td>
<td>0.03</td>
</tr>
<tr>
<td>BC13SK084</td>
<td>QMP</td>
<td>2a</td>
<td>-0.69</td>
<td>0.05</td>
</tr>
<tr>
<td>BC13SK106</td>
<td>MZ</td>
<td>2a</td>
<td>-0.22</td>
<td>0.03</td>
</tr>
<tr>
<td>BC13SK110</td>
<td>QZ</td>
<td>1</td>
<td>0.22</td>
<td>0.03</td>
</tr>
<tr>
<td>BC13SK119</td>
<td>QMP</td>
<td>2b</td>
<td>-0.40</td>
<td>0.02</td>
</tr>
<tr>
<td>BC13SK128</td>
<td>LP</td>
<td>2b</td>
<td>-0.68</td>
<td>0.02</td>
</tr>
<tr>
<td>BC13SK143</td>
<td>MZ</td>
<td>1</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>BC14SK008</td>
<td>QLP</td>
<td>diss.</td>
<td>-0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>BC14SK018</td>
<td>MZ</td>
<td>2a</td>
<td>0.16</td>
<td>0.02</td>
</tr>
<tr>
<td>BC14SK029</td>
<td>QMP</td>
<td>2b</td>
<td>-0.16</td>
<td>0.03</td>
</tr>
<tr>
<td>BC14SK039</td>
<td>QMP</td>
<td>1</td>
<td>-0.25</td>
<td>0.02</td>
</tr>
<tr>
<td>BC14SK045</td>
<td>SK</td>
<td>2b</td>
<td>-0.35</td>
<td>0.02</td>
</tr>
<tr>
<td>BC14SK049</td>
<td>MZ</td>
<td>2b</td>
<td>-0.46</td>
<td>0.02</td>
</tr>
<tr>
<td>BC11JW1</td>
<td>QMP</td>
<td>2a</td>
<td>-0.45</td>
<td>0.03</td>
</tr>
</tbody>
</table>

On a plot showing sample elevation versus δ98Mo, two populations are observed (Fig. 4). Deeper samples follow a trend from heavier δ98Mo values in Type 1 veins at greater depth to lighter values in slightly shallower Type 2 veins. This is interpreted to be the result of Rayleigh distillation. The shallow population shows no clear trend.

Samples analyzed in this study record the widest range of δ98Mo to date (Mathur et al. 2009; Greber et al. 2014; Shafiei et al. 2014; Wang et al. 2015; Yao et al. 2016), casting doubt on the suitability of Mo isotopes as tracer for magma origin (Wang et al. 2015).

Figure 4. (A) Average molybdenum isotope compositions show a trend towards lighter values from disseminated to Type 2b molybdenite. (B) No correlation exists between Re content of molybdenite and δ98Mo. (C) Sample elevation vs. δ98Mo plot illustrating two different groups. Deeper samples follow a trend towards lighter values with increasing elevation. Shallower molybdenite samples show no clear trend.

6 Re-Os dates

Ten samples were selected for Re-Os dating (Fig. 1) and were prepared and analyzed at the University of Alberta Radiogenic Isotope Facility, Canada, using the method of Selby and Creaser (2001). Prior to processing, samples were examined microscopically to identify molybdenite of interest and to make sure only one generation of molybdenite was selected for analysis. Isotope dilution and negative thermal ion mass spectrometry (ID-NTIMS) isotope measurements were performed on N-TIMS using a Thermo Triton mass spectrometer fitted with Faraday Collectors.

Ten samples from molybdenite-bearing veins were analyzed and the main population yield dates that range from 37.97 ± 0.17 and 37.62 ± 0.17 Ma (Fig. 5). One sample, BC14SK018 yielded an older date of 38.22 ± 0.17 Ma and is considered to represent an earlier molybdenite generation. The main population records crystallization over 350 ka and is consistent with U-Pb zircon dates (38.10 – 37.78 Ma) obtained from porphyritic intrusions (von Quadt et al. 2011). No clear trends are observed between Re-Os molybdenite dates and vein type, elevation, distance to unmineralized center of the deposit or host rock.
Mineralization at Bingham formed within (2011) for porphyry intrusions, suggesting that Cu-Au-Mo at Bingham, Re concentrations range from 1-100 ppm. Molybdenites from different deposit types vary in their importance as a potential tracer for mineralizing trace element chemistry, thus highlighting their nano-scale mineral inclusions.

- Molybdenite at Bingham occurs in two different types of hydrothermal veins and is disseminated in a magmatic-hydrothermal breccia. Selenium, W and Re are incorporated into the molybdenite structure. Pb, Pd and Te are present in polytype. Mixed 2H-3R molybdenite were found distal to assimilation. These relatively low values might be attributed to crustal generation.
- At Bingham, Re concentrations range from 1-1000 ppm. These relatively low values might be attributed to crustal assimilation.
- Analyzed molybdenite is predominantly of the 2H polytype. Mixed 2H-3R molybdenite were found distal to the barren core of the deposit. Hydrothermal molybdenite yields δ⁸⁷⁹⁸Mo δ⁸⁷⁹⁸Mo values correlate with vein-type and depth which is interpreted to be caused by Rayleigh distillation. Ten new high-precision Re-Os ages indicate that the main population crystallized over 350 ka.
- Re-Os ages overlap with U-Pb ages (von Quadt et al. 2011) for porphyry intrusions, suggesting that Cu-Au-Mo mineralization at Bingham formed within -480 ka.
- Sample BC14SK18 is Re-rich, contains abundant 3R polytypes and yielded the oldest Re-Os date, and is therefore thought to represent an early molybdenite generation.

7 Conclusions

- Molybdenite at Bingham occurs in two different types of hydrothermal veins and is disseminated in a magmatic-hydrothermal breccia.
- Selenium, W and Re are incorporated into the molybdenite structure. Pb, Pd and Te are present in nano-scale mineral inclusions.
- Molybdenites from different deposit types vary in their trace element chemistry, thus highlighting their importance as a potential tracer for mineralizing processes.
- At Bingham, Re concentrations range from 1-1000 ppm. These relatively low values might be attributed to crustal assimilation.
- Analyzed molybdenite is predominantly of the 2H polytype. Mixed 2H-3R molybdenite were found distal to the barren core of the deposit.
- Hydrothermal molybdenite yields δ⁸⁷⁹⁸Mo between -0.82‰ and 1.14‰, recording the widest range in any porphyry deposit to date.
- Magmatic molybdenite yields an average δ⁸⁷⁹⁸Mo of -0.06, which is in the range of values reported for the mantle.
- δ⁸⁷⁹⁸Mo values correlate with vein-type and depth which is interpreted to be caused by Rayleigh distillation.
- Ten new high-precision Re-Os ages indicate that the main population crystallized over 350 ka.
- Re-Os ages overlap with U-Pb ages (von Quadt et al. 2011) for porphyry intrusions, suggesting that Cu-Au-Mo mineralization at Bingham formed within -480 ka.
- Sample BC14SK18 is Re-rich, contains abundant 3R polytypes and yielded the oldest Re-Os date, and is therefore thought to represent an early molybdenite generation.

Acknowledgements

I would like to thank Imperial College London, Department of Earth Science and Engineering, for a Janet Watson Ph.D. scholarship. Fieldwork and laboratory analyses were made possible through the financial support of Rio Tinto, The Institute of Materials, Minerals and Mining bursary scheme (2013-2014), the Society of Economic Geologists Hugh E. McKinstry Fund (2014-2015), and the Society of Economic Geologists travel bursary scheme (2014).

At Bingham, I would like to thank Kim Schroeder and other members of the geology team, in particular Rudy Ganske, Nate Bishop, Jenny Lutz, Jeff Hoggan and Greg Sayer for sharing their expert knowledge.

References


Larson AC and Von Dreele RB (2005), General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748.


Williams-Jones AE and Heinrich CA (2005) 100th Anniversary special paper: vapor transport of metals and the formation of magmatic-hydrothermal ore deposits. Econ. Geol., 100(7):1287-1312.


Figure 5. Re-Os ages of 10 molybdenite samples from Bingham Canyon.
Salinity of magmatic fluid: experiments, phase equilibrium models, and implications for ore formation

David Dolejš
Institute of Earth and Environmental Sciences, University of Freiburg, Germany

Abstract. Chlorine concentration, often determined as the salinity of a hydrothermal fluid, is the most important control on the solubility and transport efficiency of metals during ore-forming processes. We provide new experimental data and design a comprehensive phase-equilibrium model of magmatic crystallization and fluid exsolution that predicts variations in fluid salinity and alkali ratio as a function of magma composition, temperature and pressure throughout the magmatic-hydrothermal transition. In isothermally decompressing systems, granitic or rhyolitic, near-eutectic melt exsolves vapor with negligible changes in salinity; exsolution of a brine is only encountered at the solidus. In isobarically cooling systems, fluid exsolution is often suppressed until significant crystallization occurs, then continues by simultaneous exsolution of vapor and brine. In non-eutectic melt compositions, which progressively crystallize upon cooling, the nature, salinity and the amount of fluid phase are strongly pressure-dependent. At 100 MPa, the magma exsolves vapor first, rapidly followed by vapor-and-brine saturation. At 200 MPa, the magma exsolves brine first, with its salinity decreasing and nearly continuously evolving to low-salinity vapor. These scenarios elucidate fundamental control mechanisms on the relative timing of brine or vapor saturation and their production rates, thus delineating intervals of efficient metal sequestration into hydrothermal fluids.

1 Introduction

The salinity of magmatic-hydrothermal fluid, or more specifically the total Cl and HCl concentrations, are the most important controls on partitioning of elements from silicate magmas and subsequent metal transport in hydrothermal systems (e.g., Audétat et al. 2008; Harlov and Aranovich 2018). Concentrations of elements, particularly the chalcophile and transition metals in aqueous fluids, directly correlate with the fluid chlorinity, and subsequent breakdown of metal-chloride complexes dictates efficiency of ore precipitation (e.g., Wood & Samson 1998; Heinrich & Candela 2014). From intrusive to shallow epithermal settings, salinity and composition of hydrothermal fluids change dramatically and this is only partly due to subcritical phase separation in the H2O-NaCl system. It is still unclear: (1) what controls the salinity of magmatic fluids; (2) whether one or two fluid phases can simultaneously separate from magmas; and (3) how analytical data from melt inclusions can be linked to fluid chemistry or be used to monitor the course of the magmatic-hydrothermal transition.

From a theoretical viewpoint, the chlorine concentration in aqueous fluid exsolving from a silicate melt is a complex function of the chlorine solubility in the parental silicate melt, temperature and pressure. Previous experimental studies have addressed these dependencies in a variety of simple or multicomponent systems (e.g., Webster 2004; Dalou et al. 2015; Webster et al. 2015; see Dolejš & Zajacz 2018 for review). Phase-equilibrium and spectroscopic approaches indicate that chlorine in silicate melts is preferentially complexed by alkalies (e.g., Sandland et al. 2004; Baesner et al. 2014; Grousset et al. 2015), thus these components and their variation (e.g., melt aluminosity or alkalinity) should exert first-order control on chlorine behavior. This observation has motivated our new experimental work in the system Na2O-Al2O3-SiO2-NaCl.

As hydrous magmas evolve through the magmatic-hydrothermal transition by decompression or cooling, fluid salinity is not only a function of instantaneous values of chlorine partition coefficients but is also subject to mass balance and mass conservation between crystals, residual melt and hydrothermal fluid. This restrictive principle has led us to develop a comprehensive phase-equilibrium model for predicting crystallization and fluid exsolution quantitatively, as a function of magma composition and under any ambient gradients in temperature and/or pressure.

2 Chlorine solubility in peraluminous to peralkaline silicic melts

We have experimentally determined chlorine solubility in five anhydrous Na2O-Al2O3-SiO2 melts at 1100–1600 °C and up to 2.0 GPa. The starting compositions were albite-quartz eutectic (Ab95Qz4.5 = NaAlSiO4), albite (NaAlSi3O8), and their peralkaline and peraluminous derivatives with nominal alumina saturation index, ASI = 0.6, 0.8 and 1.2, respectively. Experiments were performed in quenching furnaces (1100–1575 °C and 1 atm) and piston cylinder apparatus (1400 °C and 0.5–2.0 GPa). All starting glasses were doped with 5 wt% NaCl as a chlorine source and were found to saturate with molten NaCl which formed an immiscible phase.

In all compositions, chlorine solubility in the melt is independent of temperature but it significantly increases with pressure. Therefore, the dissolution of NaCl into the silicate network is purely entropic and it implies that NaCl remains associated as passive molecular species in the melt network. At 1400 °C the chlorine solubility in the NaAlO2-SiO2 system increases with decreasing SiO2 concentration as a result of competition of chloride species for free volume in the silicate tetrahedral
framework. In the quartz-albite eutectic melts ranging from peralkaline to peraluminous composition the chlorine solubility exhibits a minimum near the subaluminous composition where molar Al/(Na-Cl) ~ 1. The chlorine solubility increases in both peralkaline and peraluminous melts, in a ratio of 2.8–2.9 that is comparable to a charge ratio of Al<sup>3+</sup>/Na = 3.

3 Phase equilibrium model for crystallization and fluid exsolation from granitic and rhyolitic melts

We use experimental data on chlorine solubility in granitic melts at 800–1060 °C and 50–200 MPa to devise and calibrate a thermodynamic model for silicate melt in the system Qz-Or-Ab-H<sub>2</sub>O-Cl<sub>2</sub>O-1. Properties of H<sub>2</sub>O-NaCl-KCl fluids are described by the Kosinski-Anderko-Pitzer equation of state, and phase equilibria in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-K<sub>2</sub>O-H<sub>2</sub>O-Cl<sub>2</sub>O<sub>1</sub> system were calculated by Gibbs energy minimization. This setup enables predictions of fluid saturation during equilibrium or fractional crystallization or decomposition and instantaneously calculates proportions and compositions of coexisting solid, melt and fluid phases.

We have modelled fractional devolatilization during isothermal decompression and isobaric crystallization of a minimum haplogranitic melt (Qz<sub>38</sub>Ab<sub>49</sub>Or<sub>15</sub>) with Cl/H<sub>2</sub>O = 0.02 (3.7 wt% H<sub>2</sub>O, 740 ppm Cl) from 800 °C and 100 MPa (Fig. 1a) in which a melt isothermally rises to lower pressures. Fluid release is continuous and the fluid composition corresponds to low-salinity vapor (1.4 to 0.7 wt% NaCl + KCl). This process is solely driven by decompression (first boiling), and significant crystallization only occurs 5 MPa above the solidus. Nearly invariant crystallization implies loss of all volatiles (H<sub>2</sub>O and Cl) from the magma, which is accommodated by formation of brine, in addition to the vapor, at the solidus. The vapor-brine composition is dictated by the solvus in the H<sub>2</sub>O-NaCl-KCl system (0.9 vs. 83.8 wt% NaCl + KCl, respectively) but is expected to further change as the fluids migrate towards lower pressure.

In Fig. 1b, an identical initial melt evolves by isobaric cooling. In this case, a positive dependence of H<sub>2</sub>O solubility with temperature leads to fluid undersaturation, hence inducing discontinuous devolatilization events. The magma remains fluid-undersaturated until significant crystallization occurs near the solidus (~740 °C). Here, fluid saturation is related to second boiling and the vapor and brine exsolve simultaneously. As in the previous scenario, their composition is invariantly dictated by the solvus in the H<sub>2</sub>O-NaCl-KCl system (0.3 vs. 70.6 wt% NaCl + KCl). When the fluids are retained at their formation level (P = 100 MPa) and cool, the solvus shape is negligibly sensitive to temperature and the vapor and brine salinities remain essentially constant. These scenarios are applicable to behavior of near-eutectic or minimum melts in highly evolved plutons. The saturation with brine at the solidus allows for incompatible enrichment of ore and other minor elements in late stage, residual melt, and these elements are then efficiently sequestered by the high-salinity brine at the solidus.

In order to explore the consequences of continuous magmatic crystallization on fluid exsolution, we have performed additional cooling and crystallization simulations starting with feldspar-saturated haplogranitic melt (Qz<sub>15</sub>Ab<sub>49</sub>Or<sub>36</sub>) with Cl/H<sub>2</sub>O = 0.02 at fluid saturation. In Fig. 2a, a feldspar-saturated melt cools isobarically at 100 MPa. This path is analogous to that in Fig. 1b, where the melt composition is a minimum one. However, in this case, cooling leads to continuous feldspar crystallization (~10 % solids per 10 °C) and induces continuous fluid saturation. The separating fluid is a vapor (~1.7 wt% NaCl + KCl) until the increasing Cl/H<sub>2</sub>O ratio in the residual melt reaches simultaneous saturation with a brine. Brine (~71 wt% NaCl + KCl) and vapor exsolve simultaneously above and at the solidus. The fluid production increases rapidly (approximately doubles) at the solidus, as a consequence of magma composition.

In Fig. 2b, a feldspar-saturated melt has been emplaced at 200 MPa and allowed to isobarically cool. This approach illustrates the effect of depth on hydrothermal systems, which significantly affects the size of the vapor-brine solvus in the H<sub>2</sub>O-NaCl-KCl system. Upon cooling, an initial melt with Cl/H<sub>2</sub>O = 0.02 saturates first with a brine, with rapidly decreasing salinity (from 57.2 to 46.1 wt% NaCl + KCl). At 770 °C, the fluid composition reaches the vapor-brine solvus and invariantly switches to the vapor (19.4 wt% NaCl + KCl). Upon further crystallization, the vapor remains the only exsolving fluid and its salinity decreases to 0.3 wt% NaCl + KCl.

These simulations are applicable to crystallizing plutons after final emplacement. When the magma is already crystal-saturated, accumulation of volatiles in the residual melt generally promotes earlier or exclusive saturation with a high-salinity brine. Such systems will experience early sequestration of metals into hydrothermal fluids, possibly predating incompatible enrichment of metals in residual melt. Systems that are emplaced at shallow level (~100 MPa) will eventually exsolve two fluids – vapor and brine – simultaneously, and their composition is only dictated by the extent of the fluid solvus in the H<sub>2</sub>O-NaCl-KCl system. The amounts of vapor and brine, and the Cl/H<sub>2</sub>O ratio in the melt are buffered by the vapor-brine coexistence and remain invariant. Therefore, the composition of melt inclusions at this stage cannot be a useful monitor of the devolatilization process. Systems that are emplaced at deep level (~200 MPa) exsolve one fluid only because the extent of fluid miscibility is large or even complete. The initial fluid is a highly saline brine, which evolves rapidly and continuously decreases in salinity towards lower salinity vapor. The early fluids will rapidly exhaust the metal budget of their parental magma. The lack of a wide vapor-brine solvus, together with the mass balance effect, causes large changes (dramatic decrease) in the Cl/H<sub>2</sub>O ratio of the residual melt. Therefore, melt inclusions in deep-seated devolatilizing intrusions are likely to capture the progress of devolatilization and mirror the concomitant changes in fluid salinity.
Figure 1. Crystallization and fluid exsolution from minimum haplogranitic melt (Qz38Ab33Or29) with Cl/H2O = 0.02 at fluid saturation: (a) isothermal decompression at $T = 800$ °C; (b) isobaric cooling at $P = 100$ MPa.

Figure 2. Isobaric crystallization and fluid exsolution from feldspar-saturated haplogranitic melt (Qz15Ab49Or36) with Cl/H2O at fluid saturation: (a) isobaric cooling at $P = 100$ MPa; (b) isobaric cooling at $P = 200$ MPa.
4 Implications for ore-forming processes

We have devised solubility experiments and phase equilibrium models that allow us to calculate chlorine solubility in peraluminous to peralkaline silicic magmas and to quantitatively predict and assess exsolution and composition of hydrothermal fluids during magma cooling, crystallization and/or decompression.

Our experimental results indicate that chlorine solubility in silicate melts strongly decreases with decreasing pressure. This leads to increasing chloride activity and general promotion of halide saturation during magma ascent. By contrast, temperature has no significant effect on chlorine solubility in silicate melts.

Variations in the alumina saturation index, that is, the peralkaline or peraluminous nature of the melt, have a substantial effect on chlorine solubility. The chlorine solubility rises proportionally with excess alkalies or aluminum in the melt. Consequently, the activity of the chloride species, the partition coefficient of chlorine between fluid and melt, and fluid salinity are predicted to increase in subaluminous systems. Since chlorine is preferentially associated with alkalies in the silicate melt structure, variations in melt alkalinity or aluminosity are likely to affect the onset of fluid saturation and fluid salinity in compositionally heterogeneous or evolving magmatic systems.

Fluid saturation, fluid salinity and simultaneous saturation with vapor and brine are all strongly dependent on ambient magmatic conditions (cooling vs. decompression) and progress of crystallization (magma composition), and are in detail controlled by the miscibility gap in the H2O-NaCl-KCl system. In general, crystallizing magmas saturate with vapor, brine or both, depending on the pressure-temperature path and degree of crystallization. In melts that have near-eutectic or minimum composition, fluid saturation is dictated solely by the H2O solubility. Upon cooling, these melts become fluid-undersaturated until second boiling is encountered at the solidus. Hence fluid exsolution is discontinuous and episodic. By contrast, during decompression, fluid exsolution is driven by falling H2O solubility in the melt and manifested by continuous release of low-salinity vapor. In both cases, rapid crystallization at the solidus induces invariant co-exsolution of vapor and brine, with salinities dictated by the H2O-NaCl-KCl solvus (1–2 vs. 70–84 wt% NaCl + KCl in our simulations).

Magmas that are solid-saturated and steadily crystallize promote transfer of volatiles from diminishing amount of residual melt to fluid(s). This “continuous second boiling” is universally responsible for early or exclusive saturation with high-salinity brines. In low-pressure systems (~100 MPa), fluid exsolution will occur early on conjugate sides of the solvus and continue so until the solidus is reached. In high-pressure systems (~200 MPa), the brine quasi-continuously evolves to low-salinity vapor.

Chlorine and water concentrations in evolving melts vary according to the devolatilization path. The decompressing melts have lowered H2O contents, whereas the cooling magmas show chlorine depletion. However, the magnitude of the chlorine depletion increases and becomes analytically traceable only when magmas simultaneously crystallize solid phases. Fluid salinities do not vary appreciably in several evolutionary scenarios, therefore the information from fluid inclusions may not be useful for tracking the progress of devolatilization. However, the salinity of conjugate vapor and brine is a sensitive pressure indicator.

In systems where pre-enrichment of metals by incompatible accumulation in residual melts is required, high metal concentrations in hydrothermal fluids can only be reached if brine exsolution occurs late and close to the solidus. This is mainly fulfilled at low pressures and in near-eutectic melts. By contrast, magmas with early mineral saturation and/or evolving at high pressures are unlikely to produce economic mineralization.

Acknowledgements

The assistance of Vincenzo Stagno with laboratory experiments and electron microprobe analyses at the Bayerisches Geoinstitut, University of Bayreuth (Germany) is gratefully acknowledged. I appreciate careful and detailed review by Jamie Wilkinson.

References

Harlov DE, Aranovich L (eds) The role of halogens in terrestrial and extraterrestrial geochemical processes. Springer, Cham, 1030 p
Abstract. Deposit- to camp-scale quantified mineral maps have been generated for numerous Archean gold systems within the Yilgarn Craton to delineate gold mineral systems. Zoning of minerals produced by hydrothermal alteration are traced using energy-dispersive x-ray spectral measurements from the scanning electron microscope (SEM; 1000s of samples), textural SEM phase maps, whole-rock multi-element geochemistry and trace elements of select mineral phases. We show that fluid pathways in Archean gold systems can be strongly controlled by the architecture (both structural and lithological). Impermeable or weakly permeable talc-rich ultramafic and thick coherent phenocryst-rich mafic volcanics occur in the hanging-wall of ore-zones. Footwall domains contain broad (>100m) alteration zones with minerals, such as anhydrite paragenetically linked to mineralisation. Footwall pyrite-anhydrite domains transition into pyrrhotite-domains into mineralised zones, indicating chemical redox gradients. Other minerals (micas, chlorite, sulphides, amphibole, Ti-phases and feldspars) also display complex spatial distributions that are controlled by fluid pathways as well as the precursor lithology. Textural relationships demonstrate syn-mineral stage alteration that extends significant distances from the main structures which host ore zones. These data reflect the chemical evolution of gold mineral systems, ultimately driven by changes in fluid chemistry, T and P.

1 Introduction

Late Archean orogenic gold deposits are known from five continents and represent one of the great epochs of gold metallogeny in Earth’s history. The Yilgarn craton, one of the world’s most well-endowed cratons, has a resource of >250 Moz of Au (Goldfarb et al. 2005) with approximately half of this resource occurring in the Kalgoorlie Terrane (Fig 1). Despite extensive work there is still debate about the source of gold and fluids, time and length scales of transport, nature and chemistry of the transport medium and mechanisms of precipitation for these systems (Phillips and Evans, 2004; Goldfarb et al., 2005; Large et al., 2007). Fluid–rock reactions are considered essential in forming world-class orogenic gold deposits, with precipitation of gold driven by physicochemical changes as the gold-bearing fluid equilibrates with the wall-rocks (Evans, 2010). Rocks with high Fe/(Fe+Mg) are seen as favorable reactants to destabilize gold–sulphide ligands (Evans, 2010), leading to coeval gold and sulphide deposition. However, this model is not universal, as many deposits are hosted in rocks with low Fe/(Fe+Mg) ratios (Groves and Foster, 1991). Fluid immiscibility and the generation of two different fluid phases (e.g. boiling) has also been proposed as an effective depositional mechanism (Sibson, 1987). Separation of acid-generating volatiles (i.e. CO₂ and H₂S) raises the pH of the residual fluid and promotes the deposition of native metal, carbonate and sulphide phases (Drummond and Ohmoto, 1985).

In addition to uncertainty around processes related to the transport and deposition of gold are the size of alteration footprints and critical fluid pathways. These systems are considered relatively difficult to explore due to the fact that alteration halos are considered cryptic and less well-developed compared with many other hydrothermal mineral deposits (Goldfarb et al. 2005). However technological advances allow new and novel approaches to mapping cryptic alteration patterns at a range of scales, delineating fluid pathways. To predict using minerals requires key data-sets on host-rock chemistry/lithology, geological framework (i.e., structure and lithological boundaries), paragenesis (textural data), and an understanding of how key styles of alteration relate to fluid chemistry (i.e. CO₂-rich fluids, aH₂S, temperature etc.). Here we provide examples of detailed mineral mapping at the camp- and deposit-scale from important Au camps (e.g., St Ives and Kundana) from Western Australia’s Eastern Goldfields. In this paper we summarize some salient conclusions regarding

Figure 1. Map of the major terranes of the Yilgarn Craton.
architecture (structural, lithological) controls on fluid-flow and mineralogical zoning in Late Archean Gold Systems of the eastern Yilgarn Craton.

2 Architectural controls: Terrane- to deposit-scale

Major Au camps of the Eastern Goldfields straddle late Archean, granite-cored domes and related architecture (Blewett et al. 2010, Davis et al. 2010). The domes are considered the first-order pathways for advection of lower crust/ mantle energy and volatiles into hydrothermal systems in the mid-upper crust. The impacts of dome architecture on fluid flow patterns were complex. Flat architectural elements of domes (extensional structures and basins, thrusts and associated stacked lithologies) commonly created regional-scale aquitards as well as aquifers. In contrast steeply dipping intrusive rocks within domes provided major sub-vertical pathways for advection of deep-seated crust/mantle fluids. Secondary porosity in albitised porphyries (Bath et al. 2013) allow the possibility of significant fluid flow within steeply-dipping porphyry bodies, not just on the contacts.

Faults as aquicludes: Extant fluid-flow models for the formation of the St Ives camp consider the Repulse–Playa Fault as a major fluid pathway linked to the Boulder–Lefroy Fault System (Cox and Ruming 2004). The Boulder–Lefroy Fault System forms part of a crustal-scale fault architecture (Blewett et al. 2010) and gold camps such as St Ives ultimately reflect the fluid flux within this crustal architecture (Groves 1993, Hagemann and Cassidy 2000). However systematic S- and C-isotope mapping of reduced and oxidised assemblages within the Victory-Defiance complex (Neumayr et al., 2008) shows major changes in redox conditions across the Repulse and Britannia Shears (Fig 2). The most oxidised fluids (negative δ34S values in sulphides) were focused below the Repulse Shear and the most reduced fluids (positive δ13C values in carbonate) above the Britannia thrust. These patterns imply that Repulse and Britannia structures acted as aquicludes rather than aquifers, at least in the vicinity of the East Repulse deposit and on the eastern side of the Victory-Defiance complex. The seal above the East Repulse deposit appears to have a significant factor in the location of the mineralisation. Breaching of the seal led to mixing of SO2±HSO4⁻ fluids with CH4-rich fluids, creating a halo of strongly negative δ13C values above the deposit.

The distribution of trace-elements (Mo, W, Bi), commonly associated with oxidised fluids, on the footwall of the Playa-Repulse Fault hints that the Repulse–Playa segment of the Boulder–Lefroy Fault System behaved as a district-scale aquiclade rather than as a major aquifer. The fault system possibly operated in tandem with talc–carbonate altered Kambalda Komatiite to separate domains of dominantly oxidised and reduced fluids. Based on the identification of a sub-vertical pathway of highly oxidised fluid, spatially associated with porphyries beneath the East Repulse deposit (Bath et al., 2013), it is suggested the NW–SE trending porphyry dikes across the Victory-Defiance complex provided the major sub-vertical pathways for oxidised fluids, either within or on the contacts of the porphyries.

Lithological aquicludes and aquifers: Significant gold deposits occur in almost every rock type of the Kalgoorlie Terrane. The Golden Mile Deposit is hosted in dolerite, Wattle Dam in ultramafics, Athena and Hamlet (St Ives Gold Camp) in basalts, Invincible (St Ives Gold Camp) in Black Flag Beds, Wallaby in Late Basin conglomerates and the Kanowna Belle Au deposit in porphyries. This diversity of rock types hosting both high-grade and large-tonnage deposits strongly suggests that fluid-rock reactions are not the primary control on physicochemical changes driving gold deposition. Nonetheless, commonly observed but not unique associations with host rocks do occur, the most widely recognized being the association of mineralisation with Fe-rich dolerites. An alternate explanation is that it is the rheological properties of the rock that is the important factor. Rocks that are inherently strong and fail brittlely may act as either aquicludes or aquifers. There are a number of rock types in addition to Fe-rich dolerites, including the variole-rich middle Paringa Basalt (St Ives Camp) and the phenocryst-rich Victorious Basalt (Kundana Camp) that potentially acted as “strong beams” within the architecture, influencing fluid flow and ultimately deposit location. In the St Ives camp the Paringa basalt has been subdivided into Lower, Middle and Upper Paringa on the basis the Cr/Ti ratio coupled with coherent map patterns (Walshe et al. 2014). The geochemical subdivision is supported by visual logging of textural characteristics. The Upper Paringa Basalt is fine grained and massive, the Middle Paringa Basalt is visually identified by abundant varioles. The Lower Paringa Basalt is also variolitic but to a lesser degree. The best gold shoots with the Athena and Hamlet shears are hosted by the Middle Paringa Basalt.

3 Alteration zonation of the East Repulse deposit

The Eastern Repulse deposit occurs within the Victory-Defiance Complex, Yilgarn Craton, Western Australia (approx. 60 km south of Kalgoorlie; Fig 1). Rocks consist of mafic to ultramafic volcanics of the Kambalda Sequence, which occur within an antiform that plunges gently towards the south (~2710-2690 Ma; Blewett et al., 2010). The Kambalda Sequence is intruded by intermediate to felsic intrusions, which commonly show ages of ca. 2670 and 2650 Ma; although younger and older age intrusions have also been documented (Fig 2; Nelson, 1997; Neumayr et al., 2008; Watchorn, 1998; Yeats et al., 1999). Rocks were metamorphosed to upper greenschist and lower amphibolite facies through four main deformation events between ca. 2700 and 2630 Ma (Swager, 1997). Gold mineralisation in the Kalgoorlie Terrane is thought to have occurred between ca. 2640 and 2630 Ma following peak metamorphism. Gold mineralisation within the East Repulse deposit occurs at a depth of about 250 meters below the present surface (Fig 2). Much of the mineralisation occurs along the shallowly-dipping Repulse thrust.

Three dominant stages of alteration have been
established relative to mineralisation at the East Repulse deposit (Bath et al., 2013). These include: (1) early-stage albite-carbonate-sulphate-magnetite ± chlorite and/or epidote; (2) main-stage biotite-amphibole-anhydrite-carbonate ± pyrite and gold; and (3) late-stage carbonate-albite-pyrite-sulphite ± chlorite and/or epidote alteration (Bath et al. 2013). These stages of alteration overprint komatiite, basalt, dolerite, metasediments and granitoids. Alteration assemblages of the East Repulse deposit have also been divided into domains that reflect the distribution of alteration assemblages from the footwall through to the hanging wall of the deposit (Bath et al. 2013). Main domains include upper, transitional, ore and lower and these zones are reflected in the sulphide-sulphate mineralogy (Fig. 2). The upper domain contains pyrite and pyrrhotite, as well as nickel sulphides (e.g., millerite, pentlandite and seigenite) and cobaltite. The transitional domain occurs above the ore-domain and contains bismuthinite and galena. The ore-domain is dominated by sulphides, but contains minor amounts of sulphate minerals. Sulphate occurs in the form of barite and celestine — anhydrite is less common. Sulphides in the form of pyrite, chalcopyrite, molybdenite, galena and rare bismuthinite. The lower domain contains sulphates (anhydrite, celestine and/or barite) and sulphides (pyrite, molybdenite, galena and chalcopyrite). These reflect a strong redox gradient between the hanging and footwall.

4 Alteration zonation Kundana gold camp

The Kundana gold camp is located approximately 20 km west of Kalgoorlie along the Zuleika Shear Zone in the Kundana mining district (Fig. 1). The camp lies within the Coolgardie Domain of the Kalgoorlie Terrane (Swager, 1997). Mineralisation occurs along a main K2 lode centered on a shale unit that is bounded by plagioclase-phryic basalt (hanging-wall) and intermediate volcaniclastic units (footwall). The main high-grade K2 lode contains laminated or massive quartz veins. Free-gold occurs with scheelite, galena, sphalerite, pyrrhotite and pyrite along micro-fractures that cross-cut quartz veins. Surrounding wall rocks are variably mineralised and show evidence of weak to pervasive muscovite-albite-arsenopyrite-pyrrhotite alteration or biotite-anorthite ± anorthite ± calcite alteration. Pervasive albite-calcite-dolomite-pyrrhotite ± barite alteration occurs in the footwall and overprints intermediate volcaniclastics. Lower-grade mineralized lodes occur in the hanging wall of the deposit (K2A lodes). There K2A lodes cross-cut equigranular basalt and volcaniclastic units. K2A lodes show biotite-anorthite-calcite-arsenopyrite-scheelite-calcoanalcite (CaCe(CO₃)₂(OH)(H₂O)) ± muscovite (often quartz-undersaturated rock matrix) alteration with peripheral albited domains, which are enriched in ullmannite (NiSbS). Cobaltite (CoAsS) enrichment domains also form halos around main K2 lode and K2A lodes. These patterns reflect chemical gradients and predictable mineral zonation patterns around gold lodes.

Figure 2. Geological and alteration cross-section of the East Repulse gold deposit from the >12 Moz St Ives gold camp.
≈ 5.5 at 400°C. Auriferous fluids may have been alkaline. Fluid-mixing between reduced water-rich acid and CO₂-rich relatively alkaline fluids at the time of mineralisation may have played an important role in destabilising Au(HS)₂ complexes at the time high-grade gold was deposited.

Figure 3. Distribution of anhydrite and pyrrhotite along the K2 mineralised zone from the >8 Moz Kundana gold camp. Much of the mineralization occurs with pyrrhotite where sediments (yellow, blue and orange) form contacts with mafic volcanics or intrusives (green).

5 Conclusions

Mineralisation in camps from the World class Kalgoorlie Terrane are hosted along the contact between impermeable or weakly permeable talc-rich ultramafic and thick coherent phenocryst-rich mafic volcanics and permeable albite altered rocks in the footwall. Footwall domains contain broad (>100m) alteration zones with minerals, such as anhydrite, mapped and linked to mineralisation. Footwall pyrite-anhydrite domains transition into pyrrhotite-domains into mineralised zones, indicating chemical redox gradients. Other chemical gradients such fCO₂, aH₂O and pH likely also played a role in the deposition of gold in these key zones.

References


Critical mineral systems under cover: insights from magnetic, gravity, and magnetotelluric 3D inversion models, Southern Midcontinent, USA

A.E. McCafferty, P.A. Bedrosian, J.D. Phillips
U.S. Geological Survey, Geology, Geophysics, and Geochemistry Science Center, Denver, USA

Abstract. 3D inversion models of magnetic, gravity, and magnetotelluric (MT) data reveal evidence for concealed critical metal mineral systems at regional scales in the US southern Midcontinent. The region contains several igneous-related critical-element-bearing ore deposits of different types and ages that have been sourced from ore-forming fluids originating from the upper mantle to shallow crustal levels. These include the Mesoproterozoic IOCG-Co and IOA-REE deposits, which are part of the southeast Missouri iron metallogenic province. A depth slice along the top of the mantle from the 3D models reveals feeder zones that allowed development of large ca 1.4 Ga magmatic systems that host mineralization in the upper crust. Shallow crust to upper mantle conductivity sources dip under the iron province and may reflect a potential sulfur source for IOCG mineralization. Our findings indicate that the iron deposits show an unambiguous connection at depth by means of an inferred magmatic system that is traceable to the mantle and that different IOA, IOA±REE and IOCG deposits may be located in distinct parts of the same magmatic system. Several trans-crustal to trans-lithospheric magmatic plumbing systems are revealed and show how the Mesoproterozoic architecture may have influenced subsequent carbonatite and peralkaline igneous activity.

1 Introduction

Gravity, magnetic, and magnetotelluric data covering a large part of the US Midcontinent were inverted to 3D models of density, magnetic susceptibility, and electrical resistivity (Fig. 1). Regional- to continental-scale coverages such as these are required to adequately map and model the overall crustal architecture underlying large mineral provinces.

The mining community, along with federal governments and academia, has shown an increasing interest in large-scale geophysical data sets and their utility in exploration. A few examples include Laurentian University’s Metal Earth Project, Australia’s UNCOVER initiative, and the recently announced U.S. Geological Survey’s Earth Mapping Resource Initiative (Earth MRI) (Day 2019). The growing interest is driven, in large part, by a global shift to improve resource exploration undercover and identify large regions for further study.
2.1 Mineral Resources

The Mesoproterozoic iron metallogenic province in southeast Missouri (Kisvarsanyi and Proctor 1967) occurs within a 35- by 115-km region and is comprised of several iron, copper, cobalt, manganese, and rare-earth element deposits and prospects (Fig. 2), including one iron oxide-copper gold (IOCG) deposit and seven known iron oxide-apatite ± rare earth element (IOA ± REE) deposits (Nold et al. 2014). The deposits are hosted in 1.48 to 1.44 Ga high-silica rhyolites and intermediate to mafic-composition volcanic rocks. Most of the known deposits are located within or near Precambrian outcrops in the St. Francois Mountains. To date, no mineralization has been discovered in the contemporaneous ca 1.46 Ga granitoids or in the younger (ca 1.35 Ga) assemblage of two-mica granites and minor mafic intrusions that intrude the older Mesoproterozoic igneous rocks.

In addition to the mineral potential associated with the Mesoproterozoic IOA/IOCG deposits, other geologic terranes in the southern Midcontinent have a high potential for several valuable critical mineral and base metal commodities. The USGS has identified 35 critical minerals that either have important technological uses or are an import supply risk for the United States (Schultz et al. 2017; Fortier et al. 2018). Critical mineral commodities or commodity groups that are known to occur within our study area include aluminum, barite, beryllium, cobalt, fluorspar, gallium, germanium, manganese, niobium, rare-earth elements, titanium, and vanadium. Base and precious metal commodities present in various deposit types include copper, lead, zinc, and gold.

Critical mineral, base-, and precious-metal mineral commodities occur in various deposit types across a range of geologic terranes in the basement and in the overlying sedimentary section. Igneous deposit types include the southeast Missouri IOA+REE and IOCG+Co deposits; the Nb-REE-bearing carbonatite at Elk Creek, Nebraska; and a peralkaline intrusion complex with HREE-enriched fluorspar mineralization at Hicks Dome, Illinois. Sedimentary-hosted MVT Co, F, Ge, and Ba deposits are also present. A goal of our study is to evaluate how these various mineral systems might relate.

3 Data and Models

National-scale potential field databases of magnetic and gravity data (Phillips et al. 1993; Ravat et al. 2009) were inverted to 3D models of density and magnetic susceptibility, respectively. National-scale EarthScope magnetotelluric data, supplemented with stations collected by the USGS, which provided an increased site density, were used to construct the 3D resistivity model. Model constraints were provided by a database of Precambrian basement topographic elevations (Marshak et al. 2016) and a database of continental crust thickness (Shen and Ritzwoller 2016). The surfaces define the top and bottom elevations of the potential field inversion models and are especially important given the extreme structural relief in some parts of the Precambrian basement. The crustal thickness data are derived from inversion of USArray/Transportable Array seismic measurements from the EarthScope initiative and provide estimates related to variations in the depth to the Moho relative to the topographic surface.
A west to east vertical section was extracted through the magnetic susceptibility and density models (A-A’ in Fig. 2) along a profile that includes several iron deposits located in the St. Francois Mountains and major geologic features. An interpretation was produced that combined the density and susceptibility properties across the section (Fig. 3). Map sections from the 3D density and magnetic susceptibility models of the deep crust were generated by extracting voxels along an irregular surface just above the Moho surface (Figs. 4a, b). Depths to this surface range from 34 to 42 km-equivalent to the variable thickness of crust across the study. A depth slice of crustal resistivity was extracted at 27 km from the 3D resistivity model (Fig. 4c).

4 Results

The mineral system below IOA/IOCG deposits is visualized on a schematic cross section that transects the major iron deposits (Fig. 3) and depicts a regional crustal framework that highlights important physical property manifestations related to the formation of the deposits. The susceptibility inversion section is used as a backdrop but the illustration incorporates important information from the density inversion, geology and geochronology of the St. Francois Mountains and a model for the genesis of the iron deposits.

Our findings suggest that the iron deposits in southeast Missouri, with no obvious connection at the surface, are part of one large magmatic system at depth (Fig. 3). At deep crustal levels, the section along A-A’ shows the crust beneath the iron province contains broad (up to 75 km-wide) column of high magnetic susceptibility material, which serves to anchor the upper caldera-forming parts of the crust to the mantle. The magnetic column splays up and outward from the mantle and through the crust to develop moderate to high susceptibility apotostases that envelope both the ca 1.4 Ga caldera structures and ca 1.3 Ga plutons at mid to shallow depths. We assume that areas where the high susceptibility column is also dense, larger volumes of mafic rock are present in the crust that were part of the IOA/IOCG ore-forming system.

The distinct nonmagnetic masses under the ca 1.3 Ga Graniteville and Buick granitic plutons extend to somewhat greater depths and yield lower susceptibilities compared to that observed under the older Butler Hill caldera (Fig. 3). The model results are consistent with magnetic susceptibility measurements on hand and drill core samples that show the ca 1.3 plutons have the lowest magnetic susceptibilities compared to the older granites. While not conclusive, the lower susceptibility to greater depths indicated on the magnetic susceptibility inversion model, may help to distinguish younger plutons from older caldera structures in concealed parts of the Precambrian basement. Differentiating these two features may aid targeting of favorable exploration areas for IOA/IOCG deposits. Similar trans-crustal boundaries such as those present in Fig. 3 are also imaged near the Hicks Dome peralkaline complex (Fig. 2), which suggests Hicks Dome may be located along a reactivated Mesoproterozoic structure.

The nature of the lower crust across the southern Midcontinent is revealed in the susceptibility and density depth slices (Figs. 4a, b). Results show that the iron deposits formed above a magmatic system that extends over 170 km within a 40 to 50 km-wide elongate-track of high magnetization/moderately dense rocks that trends northwesterly. The IOA deposits sit directly over the high magnetization track while the Boss IOCG and the Camel’s Hump IOA(?) deposits sit within 30 km of the central axis of the base of the proposed magmatic system. Other similar magnetic tracks along the top of the mantle are interpreted to represent the base of other
prospective regions for iron mineralization.

Inversion of long-period magnetotelluric data to electrical resistivity, provides a third physical property that informs changes in the deep crust related to the tectonic and magmatic history across the southern Midcontinent.

An enhanced conductivity anomaly, calculated from EarthScope magnetotelluric data, coincides with the northwest-trending Missouri Gravity Low (DeLucia et al. 2019). Major and minor IOA and IOCG deposits are located along the northeast edge of the anomaly. Shorter period magnetotelluric data used in this report show two parallel tracts of high conductivity exist at mid crust to mantle depths (Fig. 4c). A permissive source for the high conductivity may be older metasedimentary rock that underlies the more extensive granite and rhyolite. A metasedimentary package could be a potential source for sulfide mineralization in the iron deposits.

Acknowledgements

This work was supported by the U.S. Geological Survey Mineral Resource Program.

References


Marshak S Domrois S Abert C Larson T (2016) DEM of the great unconformity, USA cratonic platform: Univ of Illinois at Urbana-Champaign, doi:10.13012/B2IDB-546972_V1


Fig.4 (A) Magnetic susceptibility of the deep crust; (B) density of the deep crust and (C) resistivity at 27 km depth.

An enhanced conductivity anomaly, calculated from EarthScope magnetotelluric data, coincides with the
Automated facies classification and gold grade prediction using machine learning algorithms

Glen T. Nwaila, Steven E. Zhang
School of Geosciences, University of the Witwatersrand, South Africa

Hartwig E. Frimmel
Bavarian Georesources Centre, Institute of Geography and Geology, University of Würzburg, Germany

Abstract. Point-wise gold grade data are commonly used to guide exploration and resource estimation with the application of spatial interpolation techniques such as kriging. The application of kriging is not optimal where high nugget thresholds exist, such as the gold deposits in the Witwatersrand Basin of South Africa. To reduce the impact of subjective grade interpolation and geological interpretation, as well as to exploit currently unused geological descriptions, we present a novel machine learning-based algorithm called GS-Pred. It combines both sedimentological and gold assay data for point-wise gold grade prediction and automated facies identification in a conglomerate-hosted gold deposit. For this application, GS-Pred requires an input database of sedimentological descriptions, spatial information and gold grades, and makes predictions of gold grades at any point within the spatial coverage of the input database, provided that it has appropriate sedimentological descriptions. This novel machine-learning algorithm is entirely data-driven. We have shown its successful application in a complex geological setting of the Witwatersrand basin.

1 Introduction

Conglomerate-hosted gold deposits in the Witwatersrand Supergroup (South Africa) include the largest palaeoplacer deposits known in the world. Although their genesis is still debated, a present-day understanding suggests a synsedimentary gold concentration with post-depositional hydrothermal remobilisation of some of the gold particles over short, economically insignificant, distances (Frimmel 2018). A significant amount of high-dimensionality (i.e. more than 10 attributes) sedimentological and metal grade data has been accumulated for most of the time these deposits have been mined (over a century) from various Witwatersrand goldfields. Qualitative relationships between the sedimentology and the gold grade in the Witwatersrand Supergroup have long been recognised through the daily practice of core-logging, underground mapping and sampling (Nami and Verrezen 1986), but these relationships exhibit spatial variability and can be complex. The evolution and adoption of computer technology and machine learning in resource exploration and exploitation has made this data more meaningful and contextually relevant. Techniques using machine-learning algorithms are well-suited for high-dimensionality data, complex processes and spatially-dispersed data (Kanevski et al. 2009).

Here we introduce a set of algorithms to predict gold grade and perform facies identification called GS-Pred, which uses geological descriptions and gold assay data. GS-Pred consists of data pre-processing, weighted and spatially-localised linear regressions, and cluster analysis. GS-Pred infers unknown metal grades at points that are within the vicinity of previously sampled areas and in its present form requires knowledge of the deposits on a mine- and regional-scale. Compared to the standard approach of chemical assays, GS-Pred is less accurate but rapid and highly automatable. This makes GS-Pred a viable tool for mine production, planning and target exploration.

We evaluate the performance of GS-Pred on a test dataset consisting of sedimentological and gold grade data from the Witwatersrand Basin of South Africa. In particular, we compare our regression algorithm to the elastic net, K-nearest neighbours, non-linear support vector regression and ordinary kriging. We show that our algorithm is generally more accurate over the test dataset and that under similar circumstances, the machine learning algorithms are more capable than traditional geostatistical methods. In addition, we show that a simple mixture of kriging and machine learning predictions enhances the prediction performance.

2 Machine learning, geostatistics and geologic background

2.1 Machine learning and geostatistics

Machine-learning algorithms are applied by computers on data to recognise patterns using automated mathematical induction. They are highly successful in geosciences and closely-related fields (e.g. Melo et al. 2017). In this paper, we explore several multivariate regression algorithms including LRPCC, non-linear support vector regression (SVR) with a radial basis function kernel, non-parametric regression, K-nearest neighbours (KNN) and penalised linear regression in the form of elastic net regression with cross-validation (“ElasticNetCV”). The unique parameters in each method can be determined through cross-validation testing. In addition, we use the K-means clustering algorithm to identify rock facies using sedimentological descriptions. Kriging is a progressive interpolation method using a spatial model for point-wise estimations of a regionalised variable. It is a popular technique in the geosciences, such as in ore and natural
2.2 Geologic background

The Witwatersrand Supergroup, located near the centre of the Kaapvaal Craton (South Africa), is one of the best preserved Mesoarchaean sediment archives that records the development of a cratonic sedimentary basin in a tectono-sedimentary environment (Fig. 1). It is known to cover an area that stretches for about 350 km in a northeasterly, and about 200 km in a northwesterly, direction and is the largest known gold province in the world. The Witwatersrand Supergroup has been subdivided into the lower gold-poor West Rand Group (2.99–2.91 Ga) and the upper gold- (and uranium-) rich Central Rand Group (2.90–2.79 Ga; Kositcin and Krapež 2004).

3 Material and methods

3.1 Data

Rocks of the Witwatersrand Supergroup are best studied in underground mine exposures and drill cores. We collected 1964 samples (Fig. 2) comprising sedimentological data and gold assays that have been declared as qualified for resource and reserve estimations from published industry reports and dissertations that focused on the West Rand goldfields.

The information contained in the datasets are sample coordinates (x, y, z); conglomerate thickness (CW); volume percentage of conglomerate; quartz/chert pebble size; pebble packing; pebble roundness and sorting; % pyrite; the colour of the conglomerate matrix; the type of the conglomerate basal contact. This dataset covers an area of about 46 km².

3.2 Development of the prediction model

The mean gold grade in the dataset is 14.91 g/t with a standard deviation of 45.62 g/t. Within the dataset are samples with 0 g/t (the detection limit is 0.001 g/t) and high gold grade (e.g. 1402 g/t). Data below the 2nd percentile (about 2 % of the data) was removed as outliers. The gold grade is approximately log-normally distributed. Normalisation is unnecessary for machine learning algorithms in general, but is necessary for many geostatistical techniques. GS-Pred normalises the gold grade data using a three-parameter log-transformation with an additional small positive constant, β, that is added to the gold grade to minimise the D’Agostino’s K-squared omnibus test results (D’Agostino and Pearson 1973). The transformation for the gold grades can be written as

\[ \Gamma = \ln(Au[g/t] + \beta), \]

where Au [g/t] are gold grades in grams per ton and \( \Gamma \) are log-transformed gold grades.

The test statistics of the D’Agostino’s K-squared, Anderson-Darling and Shapiro-Wilks tests on the untransformed gold grade data are 1246.11, 102.88 and 0.75 respectively. After the transformation, the mean is 1.97 and the standard deviation is 1.18. The test statistics of the D’Agostino’s K-squared, Anderson-Darling and Shapiro-Wilks tests are 18.24, 2.49 and 0.99, respectively. GS-Pred also maps the sedimentological descriptions into numeric feature labels (e.g. shades of colours into a sequence of integers) that are suitable for regression algorithms.

GS-Pred includes four main steps: (1) an automated semi-variance modelling routine that incorporates the spherical model to determine the range and sill within the dataset; (2) a linear regression and Pearson correlation-based prediction algorithm that predicts metal grades with sedimentological features using training data localised within an Euclidean neighbourhood based on the range (LRPCC); (3) a K-means clustering analysis on the sedimentological features of the entire dataset to
automatically identify rock facies; (4) leave-one-out cross-validation testing and facies-specific prediction performance evaluation.

In LRPCC, feature weighting and training occurs on a per-target basis. For each target, the algorithm can be written as:

\[ Y = \sum_i f(\Gamma, \omega_i) \cdot \left( \frac{\rho_i^2}{\sum_j \rho^2_j} \right) \cdot \left( \sum_i \rho^2_i \geq c \right) \]

where each feature (“\( f \)”) is used in a univariate linear regression to make a prediction \( Y_i \approx f(\Gamma, \omega_i) \), where \( \Gamma \) is a set of known labels (e.g. metal grades). The output is normalised by the sum of the squares of the Pearson correlation coefficients (“\( \rho^2_i \)”) between all features and the labels \( \bar{Y}_i = Y_i \cdot \rho^2_i / \sum_j \rho^2_j \). The algorithm output is the sum of all feature’s contributions, \( Y = \sum_i \bar{Y}_i \). A small positive threshold parameter \( 0 \leq c < 1 \) can mute features that are poorly correlated with the metal grade per prediction target (where \( \rho^2_i < c \)). Fixing all other algorithms in GS-Pred, LRPCC is compared with ElasticNetCV, SVR and KNN algorithms to assess its prediction performance. The parameter \( c \) in LRPCC can range between 0 and 1. For all other regression methods, the parameters are determined through cross-validation, and for the elastic net method, on a per-target basis. Prediction performance is evaluated through the mean and median of the absolute value of the relative errors (MRE and MERE). For the K-means cluster analysis, feature rescaling was applied to ensure that each feature spans an identical range.

4 Results

From the automated semi-variogram modelling, the correlation range in the test dataset is about 14 m; the nugget threshold is 0.54 and the sill 0.87. Cross-validation testing during feature selection reveals that sedimentology and CW consistently produces lower MREs. This combination is used for all subsequent evaluations. For the parameter \( c \), higher values result in lower prediction errors at the expense of the predictable fraction of samples. For comparison purposes, we adopt \( c=0.1 \), which does not decrease the predictable fraction noticeably (average relative loss of roughly 3 %).

The best kriging results obtained by cross-validation testing features an MRE of ~1.2 with ~0.9 of the dataset predictable. On average, LRPCC is more accurate than any other algorithm, and machine learning algorithms are usually better than ordinary kriging (Fig. 3). There are many ways to integrate regression and interpolation results to improve the overall prediction performance. Here we use a mixture parameter \( p \) based on the kriging standard uncertainty estimates \( s \), such that \( p=e^{-s} \). In our test dataset, the maximum kriging contribution is about 76 % and the minimum is 0 %. Results show that LRPCC+kriging is more accurate at larger radii compared to LRPCC-alone (Fig. 3).

Cluster analysis of the sedimentological features resulted in at most four unique clusters that appear to be correlated with the samples spatial coordinates (Fig. 4). These clusters respond very differently to prediction, which produces distinct MRE profiles (Fig. 5).

5 Discussion
For LRPCC, the peak prediction accuracy occurs at a neighbourhood radius from 9 to 11 m (Fig. 3). Below 9 m distance, prediction performance degrades. LRPCC is able to reject a very small population of very-poorly predicted targets and eliminate poorly-correlated features. As a result, its MRE profile shows drastic dips in MRE at various radii. These points almost entirely belong to a particular facies (Figs. 4 and 5) that is located at mid to deeper depths of the sampled volume. Cluster analysis combined with gold grade predictions suggests that this facies consistently feature gold grades that are poorly correlated with the sedimentology. Detailed analysis suggests that members of this facies constitute less than about 15 % of the dataset population, 1/3rd of which feature high prediction errors that heavily inflate the MRE. The gold in this facies may be associated with non-sedimentary mineralisation processes and/or that additional processes have significantly modified the primary mineralisation processes, such as remobilisation via secondary hydrothermal processes (Phillips and Powel 2011). This is an interesting discovery and could contribute to the understanding of the genesis of the Witwatersrand gold deposits and the relative contributions of the various genetic hypotheses. Moreover, it is possible to employ GS-Pred to anticipate prediction behaviours for different facies and then generalise that knowledge to new exploration targets based on their geological descriptions.

There are at least two other probable causes for poorly correlated metal grades in samples that are not facies-specific. One is the qualitative nature of most of the sedimentological descriptions that imposes prediction errors of an unknown magnitude. Traditional interpolation techniques are at an inherent advantage in the sense that the assay data have well-constrained uncertainties and are fully-quantitative. Another probable cause is multiple remobilisation events of gold by various processes (be it by mechanical and/or chemical processes; Frimmel 2018).

Given that the dataset was originally unintended for machine-learning purposes, to be able to predict gold grade with low MERE demonstrates the potential of these algorithms and information within such datasets. Combining both GS-Pred and kriging can significantly improve prediction results at higher radii, because spatial correlations become progressively more significant with higher radii compared to localised relationships between gold grade and sedimentology. The best combination of the two still warrants further investigation.

6 Conclusion

We have proposed a set of algorithms called GS-Pred that use geological descriptions and assay data to predict gold grade and perform automated facies identification. GS-Pred was validated on a dataset of samples from the Witwatersrand Basin. It was able to classify samples into unique facies that feature different strengths of sedimentological control on the gold grade, and which are distributed differently in the sample coordinate space. Samples that cluster primarily with control sites for high gold mineralisation potential and feature a good prediction performance are good candidates for future exploration and site characterisation. The incorporation of both qualitative and quantitative geological and gold assay data in resource estimation of complex mineral deposits has the potential to expose hidden patterns of mineralisation diversity, that is of both an academic and industry interest.

Acknowledgements

Glen Nwaila thanks CIMERA (Centre of Excellence for Integrated Mineral and Energy Resource Analysis) for funding this research, and Sibanye Stillwater for providing the data.

References

Comparisons of Metallogenesis within the Pyrenees-Alps-Zagros-Himalaya collisional orogens

Hongrui Zhang, Zengqian Hou
Key Laboratory of Deep-Earth Dynamics of Ministry of Natural Resources, Institute of Geology, Chinese Academy of Geological Sciences, China

Abstract. Modern collisional orogens represent a natural laboratory for the study of mineral deposit distribution in different tectonic environments. The Pyrenees, Alps, Zagros and Himalaya are all associated with Neo-Tethyan subduction and represent the youngest collisional orogens on Earth. Here, we compare these four orogens in terms of their composition, architecture, tectonic evolution, and metallogenic systems. The four orogens can be divided into simple and composite types. Simple orogens are represented by the Pyrenees and the Alps, and are characterized by narrow linear shapes in plain view and symmetric structures in cross-section, are free of arc magmatism, and are associated with Mississippi Valley-type Pb-Zn and orogenic gold deposits. In contrast, composite orogens, as exemplified by the Zagros-Iranian and Himalayan-Tibetan Plateaus, are associated with broad orogenic plateaus in plain view and asymmetrical structures in cross-section. These record extensive arc magmatism in continental margins, and are associated with a variety of deposit types including porphyry Cu-Mo, orogenic Au, Mississippi Valley type Pb-Zn, and detachment-fault-related polymetallic deposits.

1 Introduction

Collisional orogens are one of the most recognizable geotectonic features along convergent continental boundaries. The Pyrenees-Alps-Zagros-Himalaya mountain chain is a series of modern collisional orogens that are located along the southern margin of the Eurasian continent (Figure 1) and were generated following the closure of the Neo-Tethys Ocean. These four orogens have different patterns of collisional orogeny and tectonic histories, and are associated with different metallogenic systems (e.g., Hou and Zhang 2015). This study presents a review on these four orogens with the aim of gaining new insights into the metallogenesis across the region.

2 Architecture and evolution of the orogens

The Pyrenean orogen is a narrow linear mountain belt in the northern margin of the Iberian Peninsula. It is a typical symmetrical orogenic belt with a central axial zone that is surrounded by double-wedged ranges on each side (Verges and Fernandez 2012). It is formed by rifted and amalgamated of the Iberian plate with the Eurasian continent from Jurassic to Cenozoic.

The Alpine orogen within the Apennine region of southern Europe is a nearly E-W trending narrow linear mountain belt that formed by the underthrusting of the Eurasian continent beneath the Adriatic Plate (Coward and Dietrich 1989). The Alps is similar to the Pyrenees in that the Alpine orogen is a symmetrical orogenic belt (Dal Piaz et al. 2003). However, the axial zone within the Alpine orogen is more complex than that in the Pyrenees and is divided into three units (Schmid et al. 2004): the Austroalpine domain, the Penninic domain, and the Helvetic domain. The tectonic evolution of the Alpine orogen is similar to that of the Pyrenean orogen in that it is divided into two phases: Mesozoic breakup and Cenozoic collision.

The structure of the Zagros-Iranian Plateau is different to that of the Pyrenean and Alpine orogens in that this region does not contain fold-and-thrust belts or an associated foreland basin on the upper side of the collision zone, but contains a broad tectono-magmatic zone that is present within the Sanandaj-Sirjan magmatic and metamorphic belt (SSZ) and the Urumieh-Dokhtar magmatic assemblage (UDMA) (Agard et al. 2011), indicating the Zagros-Iranian Plateau has an asymmetrical structure.

The Himalayan-Tibetan Plateau represents a composite accretionary-collisional orogen (Pan et al. 2012; Zhang et al. 2017a). The plateau also contains a huge tectono-magmatic zone that spans thousands of kilometers. The collisional related tectonism and magmatism of the four orogens are summarized in Figure 2.

3 Mineral deposits of the orogens

The Pyrenean orogen contains numerous Pb-Zn deposits (Figures 3a) that are generally located within foreland basins on both sides of the orogen (Leach et al. 2006).

The collision-related deposits of the Alpine orogen include orogenic Au gold deposits and MVT-type Pb-Zn deposits (Figures 3b). The orogenic Au deposits are generally located in the western Monte Rosa (Pettke et al. 2000) and eastern Hohe Tauern areas (Horner et al. 1997). The Alpine MVT-type Pb-Zn deposits are generally located within the Drau Range area of the middle and eastern parts of the orogen (Henjes-Kunst et al. 2017).

The Zagros-Iranian Plateau hosts a number of economically significant mineral deposits and contains various styles of mineralization. Mineral deposits related to continental collision include porphyry Cu-Mo-Au, MVT Pb-Zn, and orogenic Au deposits (Figure 3c). The main metallogenic belts include the Arasbaran-Kerman porphyry copper belt (Aghazadeh et al. 2015), the Takab-
Yazd MVT Pb-Zn belt (Ehya et al. 2010)), and the Piranshahr-Sahez-Sardasht orogenic Au district (Aliyari et al. 2012).

Numerous large and giant metal deposits within the Himalayan-Tibetan Plateau (Figure 3d). These include the Gangdese and Yulong porphyry copper belts (Hou et al. 2009a), the Sanjiang MVT-type Pb-Zn belt (Zhang et al. 2017b), the Ailaoshan orogenic Au belt (Deng et al. 2014), the Western Sichuan carbonatite-related rare earth element (REE) belt (Hou et al. 2009b) and the southern Tibet detachment-fault-related polymetallic belt (Li et al. 2017).

4 Comparison and discussion

4.1 Basic types of collisional orogenic belt

Continental collision orogens can be classified into simple and composite types, as evidenced by the four examples outlined above. Simple collisional orogens are characterized by a narrow linear orogenic belt, and has associated metallogenic systems that are dominated by processes within the middle and upper crust, forming mineralization such as MVT Pb-Zn and orogenic Au deposits, as exemplified by the Pyrenees and the Alps. Although collisional related calc-alkaline and potassic magmatism may develop, no pre-collisional magmatism recorded in this type of collision. In comparison, composite collisional orogens are characterized by the occurrence of continental arc magmatism with a broad orogenic plateau. The metallogenic systems in these types of collisional environments are associated with both crust and mantle processes, and form mineralization such as carbonatite-related REE deposits, collisional porphyry copper deposits (PCDs), orogenic Au deposits, MVT-like Pb-Zn deposits, and detachment-fault-related polymetallic deposits. This type of collision is exemplified by the Zagros-Iran and Himalayan-Tibetan plateaux.

Simple collisional orogens have symmetrical structures (Figure 4a) that consist of a central axial zone surrounded by fold-and-thrust belts and foreland basins. In contrast, composite collisional belts have asymmetrical structures (Figure 4b). For example, the Zagros orogenic belt contains a broad tectono-magmatic zone that contains the SSZ, the UDMA, and even part of the Central Iran block. The SSZ and UDMA are related to continental arc formation associated with subduction of the Neo-Tethys oceanic crust, whereas the Central Iran block contains continental lithospheric material that was located above the Paleo-Tethyan subduction zone. For the Himalayan orogeny, its influence has extended to a broad tectono-magmatic zone that includes the Lhasa, Southern Qiangtang, and Northern Qingtang blocks. These blocks were amalgamated by multiple accretionary and collisional processes between the Mesozoic and the Paleozoic, and the continental arc lithosphere in the Lhasa block was generated by subduction of the Neo-Tethys oceanic crust.

4.2 Mineralization within different types of continental collisional orogen

Different types of collisional orogens have similarities in terms of metallogenesis. For example, sediment-hosted Pb-Zn deposits (in the form of MVT-type and MVT-like deposits) are present in all four of the continental collisional orogenic belts. Three of the four orogenic belts considered here (except the Pyrenees) contain limited orogenic Au deposits. This type of gold deposit generally forms in accretionary orogenic settings and is closely related to metamorphic fluids that can leach gold from source rocks, be transported along major fault zones, and precipitate gold at sites of local extension (Goldfarb et al. 2005). During continental collision, metamorphic fluids can be produced by dehydration of the subducting crust and transported along translithospheric faults, including sutures and large shear zones, which provide ideal pathways for migration of the metamorphic fluids.

However, there are also some differences in the mineral deposits that form in different types of collisional orogen. The simple collisional orogens are absent of magmatic arcs and do not generally contain magmatism-related ore deposits, including carbonatite-related REE, PCD mineralization associated with magmas generated by the decompressional melting of sublithospheric mantle, and polymetallic deposits related to partial melting of the middle and upper crust. All of these ore deposits are present within the composite collisional orogens in addition to the occurrence of continental margin arcs. This indicates that these composite collisional orogens involve the intense reactivation and migration of crust and mantle materials as well as the formation of large ore deposits in shallow crustal environments.
Figure 1. Global distribution of collisional orogens (modified from www.ngdc.noaa.gov).

Figure 2. Tectonism and magmatism recorded by the Pyrenean, Alpine, Zagros-Iranian, and Himalayan-Tibetan collisional orogens.

Figure 3. Temporal distribution of mineral deposit types within the Pyrenean, Alpine, Zagros-Iranian, and Himalayan-Tibetan collisional orogens.

Figure 4. Sketch diagram showing the relationship between structures and the main mineral deposit types within (A) simple and (B) composite types of collisional orogen (not to scale)
Acknowledgements

This research was supported by the National Natural Science Foundation of China (Grant Nos. 41772088, 41773042, 41773043), and the China Geological Survey (Grant No. DD20190001). Contribution to IGCP 662.

References


500 Myrs in the making: control of Gondwana margin assembly on Carboniferous orogenic gold in Peru

Daniel Wiemer, Steffen G. Hagemann, Nicolas Thébaud
University of Western Australia
Carlos Villanes
Compañía Minera Poderosa S.A.

Abstract. Carboniferous intrusion-related orogenic gold deposits in the Eastern Andean Cordillera display a high distribution-density in northern Peru. New geological-structural mapping suggests a basement domain boundary controlling the emplacement of large plutonic complexes and associated hydrothermal gold deposits. The southern Montanitas Domain basement comprises thrust nappes of imbricated ophiolite slices and granitic gneiss. The basement of the northern Pataz Domain forms a fold-and-thrust belt, where low-grade Ordovician volcanic arc rocks and marginal sedimentary rocks are thrust over semi-pelitic schists. Structural data indicates that both domains were deformed during a common orogeny, ascribed to the Late Famatinian (ca. 440 Ma) that affected the Eastern Cordillera to the south. North of the study area, no Late Famatinian imprints are documented. It is proposed that the study area is situated at the northernmost extent of an orogenic belt that formed through re-collision with the putative Paracas terrane that detached from Amazonia during Rodinia break-up. Carboniferous compression was accommodated in dextral strike-slip along the trans-crustal Rio Maranon Fault. We suggest that the greater width of the basement orogen to the south led to magma and fluid channeling at its northern tip. Gold mineralization focused in a narrow, strike-slip-induced dilation zone north of the basement block.

1 Introduction

The Eastern Andean Cordillera (EAC) of Peru is punctuated by numerous Carboniferous granitoid-hosted orogenic gold districts. The highest density and most productive (i.e., Pataz-Parcoy) known deposits are situated in a narrow belt at the latitude of Trujillo in northern Peru (Fig. 1; Haeberlin et al. 2004). Considering that the gold-hosting Carboniferous plutonic belt extends over hundreds of km along strike, the spatially restricted distribution of most productive deposits is intriguing. Specific sites in the tectonic framework of the EAC may have favored concentration of magmatic-hydrothermal gold-bearing fluids. Indeed, the pre-Carboniferous EAC formed through complex tectono-magmatic events associated with repeated terrane detachments and recollisions along the (paleo-)Gondwana margin since the Mesoproterozoic (Chew et al. 2007, 2016; Mišković et al. 2009). The spatial delineation of crustal blocks/terranes, and their significance in shaping the basement tectonic framework(s) for the Carboniferous gold systems, however, remain to be demonstrated.

Geological-structural mapping of a key area was conducted in the high production Pataz-Parcoy districts, and extends southward into the Montanitas-Ongon prospects (Fig. 1). Previous zircon isotopic data from Carboniferous igneous rocks, and basement depositional and metamorphic ages, indicate along strike variation in magmatic processes and basement components in the area (Chew et al. 2016; Angerer et al. 2018). Our results support the presence of distinct basement domains. We present a refined model of terrane assembly at the Peruvian Gondwana margin and discuss the role of basement inheritance on Carboniferous gold formation and distribution.
in the EAC. However, putative ophiolite vestiges (Tarma, Fig. 1) indicate oceanic crust formation at ca. 720 Ma (Sm-Nd isochron; Tessinari et al. 2011). Ordovician arc magmatism along the entire EAC occurred at ca. 480 Ma during the Early Famatinian orogenic cycle (Chew et al. 2007). A Late Famatinian cycle is recorded in ~445 Ma granitic magmatism and subsequent metamorphism at ca. ~435 Ma (U-Pb zircon and titanite, respectively; Chew et al. 2016). Importantly, Late Famatinian imprints are only observed as far north as the present study area (Fig. 1), affecting sedimentary rocks with maximum depositional ages consistent with Early Famatinian sources (“Young” Maranon Complex). Towards the north, no Late Famatinian imprints are documented, and maximum depositional ages are ~750 Ma (“Old” Maranon Complex) (Chew et al. 2007; Witt et al. 2013). Geochronological data from offshore boreholes attest to the presence of Grenvillian to Ordovician basement, which led to the interpretation of the existence of the Paracas and possibly the Oaxaquia (further west) terranes, interpreted interpretation of the existence of the Paracas and Grenvillian to Ordovician basement, which led to the interpretation of the existence of the Paracas and possibly the Oaxaquia (further west) terranes, interpreted to have been detached during Rodinia break-up and recollided with the Gondwana margin. In fact, recent metamorphic constraints indicate the formation of a paired HP/LT collisional belt, which incorporated the Tarma ophiolite during the Late Famatinian orogeny (Willner et al. 2014). However, the northernmost extent of Paracas offshore basement is located at the Isla de las Hormigas de Afluera (Fig. 1), whereas further to the north Permian ages are detected (Romero et al. 2013). Hence, the northern delineation of the putative Paracas terrane remains unknown.

Voluminous Carboniferous I-type magmatism largely affected the central to northern EAC (Fig. 1) and peaked between ca. 340-320 Ma (Witt et al. 2013). The Carboniferous gold deposits focus along the Rio Maranon Fault, a major trans-crustal structure and likely Famatinian suture (Schreiber et al. 1990; Fig. 1). Gold is found in quartz-sulfide veins, hosted in the Carboniferous granitic plutons.

3 Results from the study area

Geological-structural mapping revealed a significant change in basement lithologies from north to south that spatially coincides with a bend in the Rio Maranon Fault (Fig. 2). We defined a northern Pataz Domain and a southern Montanitas Domain, and provide evidence for their distinct basement lithological-structural inventories and Carboniferous magmatism emplacement style, below. **Pataz Domain:** In the Pataz Domain, Carboniferous gold system-hosting granitoid suites intrude a narrow NNE-trending corridor parallel, and directly adjacent to the Rio Maranon Fault (Fig. 2). The granitic suites intrude two greenschist facies basement tectonic units: (i) semipelitic schists with rare m-thick quartzite intercalations, ascribed to the “Young” Maranon Complex (MC; max U-Pb detrital zircon depositional age of ~461 Ma; Chew et al. 2007) to the west, and (ii) easterly adjacent, tectonically overlying volcanic, volcanioclastic, and sedimentary rocks belonging to the Eastern Andean Cordillera Group (EACG; max depositional age of ~467 Ma; Witt et al. 2013). Sedimentary rocks of the EACG are part of the Contaya Formation, comprising Graptolite strata and turbidite sequences (Hughes et al. 1980; Schreiber et al. 1990), and volcanic rocks of the EACG display characteristic arc signatures.

![Figure 2. Simplified geological-structural map of the study area (location shown in figure 1). Description in text.](image)

The basement tectonic units of the Pataz Domain show a common deformation history (D1-D3). Early S1-foliation developed parallel to bedding (S0) planes. S0/S1-planes strike NNW and dip dominantly to the E-/NE (D1). Subsequent F2-folding around S1-strike-parallel sub-horizontal axes is evident in dm-scale S-/Z-type parasitic folds within up- or downward verging limbs of transposed larger-scale folds. Transposition of high intensity fold hinge zones led to local S2 foliations. The S2 planes correlate geometrically with brittle-ductile D2 fault arrays. These E-/NE-dipping faults caused the tectonic juxtapositioning of the MC and the EACG through top to the W-/SW thrusting. A D3 event locally reactivated these faults as ductile to brittle normal shear zones.

The Carboniferous plutonic rocks (Fig. 2) display a clear relative timing of distinct magma emplacements: (i) diorite, (ii) granodiorite/tonalite, and (iii) late-stage monzogranite, and pegmatite/aplite dikes. These components successively intruded to form the presently exposed batholith, without showing systematic spatial-compositional trends. It is noted, however, that the eastern extent of the batholith is unknown and tectonically delineated by over-thrusting extrusive equivalents (volcanic carapace, Fig. 2). Magma emplacement followed the NE-dipping S0/S1 planes of the basement, as evident in numerous parallel 10- to 100-m-wide supra-solidus magmatic flow zones of elongated diorite enclaves in granodiorite.

The Pataz Domain experienced a syn- to post-batholith syn-mineralization D3 event that produced F4-kink folds and faults in the basement, and faults and fault-
fill veins in the batholith. Auriferous quartz-sulfide fault-fill veins follow three orientations: (i) the steep N/NNW-trending western batholith contact, (ii) the medium ENE-dipping basement inherited S₂-plane in the magmatic architecture, and (iii) shallow-medium NE-dipping veins observed in the footwall of the mineralized system. Type-iii veins formed as thrust faults that match Andersonian-type orientations assuming NE-SW compression. Type-ii veins display progressive textural dextral shear development. All veins formed during an early quartz-pyrite paragenetic stage (Fig. 3, D4a). WNW-trending steep faulting accompanied early vein formation, as evident in syn-mineralization drag-folds. A second quartz-pyrite-sphalerite-galena paragenetic stage fills dilational sites indicating re-opening of former shear/fault veins associated with N-/NE-trending normal faults. The normal faults indicate NW-SE extension consistent with horst-and-graben development during late-stage deposition of the volcanic carapace (Fig. 3, D4b).

**Montanitas Domain:** In the Montanitas Domain, the western demarcation of the Carboniferous batholith is markedly offset eastward from the present surface exposure of the Rio Maranon Fault (Fig. 2). Here, the magmatic suites extend over a much wider area towards the east, and display a more systematic spatial trend of eastward increase in more differentiated magmas (diorite, granodiorite, potassic granite; not shown in Fig. 2).

The basement between the Rio Maranon Fault and the Carboniferous igneous rocks constitutes imbricated orogenic nappes, comprising the newly identified Tomac Ophiolite and Alberado Gneiss (Fig. 2). Where relatively undeformed, the Tomac Ophiolite comprises alternating pillow basalt (Fig. 4a) and more massive basalt and dolerite (i.e., diabase). Deformation intensity increases towards high-strain thrust zones within the nappe stack, where sheared pillows and/or mafic schists are observed. The highest strain occurred where the Alberado Gneiss nappes are thrust over the mafic rocks (top to SW). Here, the two basement units are interfolded isoclinal (D₂) over 10-50 m-wide zones (Fig. 4b). Geochemical data of the Tomac Ophiolite indicates MORB affinity (Fig. 4c). The Alberado Gneiss comprises remnant former upper amphibolite facies mineralogy (plagioclase, biotite, amphibole), but are often overprinted by retrograde chlorite-bearing assemblages. Both basement units were affected by cm-scale recumbent folds and associated incipient hinge faults, which we correlate to the F₄ kink-folds and associated faults in the Pataz Domain basement.

Auriferous quartz-sulfide veins in the Montanitas Domain mostly form arrays sub-parallel to steep NNW-striking contacts between distinct Carboniferous intrusions, or sub-parallel to NW-striking faults similar to those observed in the Pataz Domain.

**Figure 3.** Schematic structural model for gold vein system formation during D₁ in the northern Pataz Domain.

**Figure 4.** a. Pillow basalt (Tomac Ophiolite). b. F₂-isoclinal interfolding of the Tomac Ophiolite and the Alberado Gneiss in high-strain thrust zone. c. MORB-type REE pattern for the Tomac Ophiolite and trace element arc-signature of Alberado Gneiss (Primitive Mantle normalized after McDonough and Sun, 1995).

**4 Discussion**

Based on presented data, we propose the following model:

1. We correlate the newly identified Tomac Ophiolite with previously identified ophiolites to the south (e.g., in Tarma, Huanuco). Oceanic protoliths formed during Rodinia break-up at ~720 Ma (Tessinari et al. 2011; Fig. 5a).
2. EACG volcanic activity was part of extensive Early Famatinian arc formation along the EAC (Fig. 5b). Based on the similar deformation history, it is likely that the Alberado Gneiss protoliths were emplaced at this time.
3. Based on previous constraints for synchronous deposition of EACG and “Young” MC detritus, we propose a marginal to sub-marine arc-forearc environment. During this inter-Famatinian phase, Graptolite shales, turbidites (EACG) and outboard deep-marine sediments (MC) were deposited (Fig. 5c).
4. In line with evidence for paired metamorphic belt formation and associated Tarma Ophiolite emplacement further south, we propose that Late Famatinian collisional orogeny affected the study area (D₁-D₂; Fig. 5d). As ophiolite and gneiss nappes are only observed in the Montanitas Domain, and no Late Famatinian imprints are recorded north of the study area, we suggest that the study area was situated at the northern extent of this
orogeny. We propose that this marks the northern delineation of the Paracas terrane and therefore limits its re-collision impact on the Gondwana margin.

Figure 5. Illustration of model for micro-terranne assembly in north-central Peru. Refer to text for description of a-h.

(5) Normal fault reactivation in the Pataz Domain (D₃) records post-orogenic collapse (Fig. 5e).

(6) Carboniferous arc formation affected the entire central-north Peruvian EAC (Fig. 5f). Magma and fluid were channeled into a narrow corridor in the Pataz Domain. Upon batholith crystallization, initial veins formed through energy release(s) accommodating ongoing strike-slip (D₄a). The southern basement block caused a dilational jog, where block rotation and normal faulting accompanied mineralization of the gold-bearing second paragenetic stage (D₄b; Fig. 5g).

(7) Permo-Triassic S- and A-type magmatism focused along the southern Famatinian suture (Fig. 5h).

5 Implications

A new model for Gondwana margin assembly in the EAC provides insights into the formation of gold deposits in northern Peru. The northern delineation of the Paracas terrane is recorded in the newly identified Tomac-Ophiolite and Alberado Gneiss. Carboniferous intrusion-related orogenic gold formed in a strike-slip-induced dilational corridor north of this Late Famatinian basement. The Paracas detachment may have isolated an upper mantle reservoir, fertilized during renewed subduction onset, and tapped in the Carboniferous.

Acknowledgements

We thank the Compania Minera Poderosa S.A., particularly F. Cueva. Geochemical analyses were performed by the Bureau Veritas, Vancouver, Canada.

References


Geodynamic and metallogenetnic reconstruction of the Neoarchean Qingyuan greenstone belt: evidence from petrogeochemistry and U-Pb geochronology

Zidong Peng, Lianchang Zhang, Changle Wang, Xiaoxue Tong
Institute of Geology and Geophysics, Chinese Academy of Sciences, China

Abstract. The Neoarchean Qingyuan greenstone belt (QGB) is located on the northern margin of the North China Craton (NCC). Despite close geological similarities with other greenstone terranes in the NCC, the QGB are characterized by hosts the oldest volcanogenic massive sulphide (VMS) deposit (Hongtoushan VMS, with 0.15 Mt Cu at 1.6% and 0.21 Mt Zn at 2.3%) in China. Moreover, there are also several economic banded iron formation-type iron deposits (e.g., Xiaolaihe, Yujiabu, and Xiadianzi BIF) in this belt. Despite previous work in the area, the tectonic setting of the QGB is under debated; whereas the genetic relationship between mineralization and chemostratigraphic evolution of the area has also remained enigmatic. In this study, we present an integrated study of the supracrustal rocks in the QGB, including field and petrographic observations, whole-rock lithogeochemical data, and U-Pb geochronology of meta-felsic rocks that are interlayered with the BIF. The objectives are to (1) elucidate the petrogenetic history of these mafic and felsic volcanic rocks, and reconstruct their geodynamic setting, and (2) decode the metallogenetnic history of VMS and BIF in the QGB.

1 Introduction

Archean greenstone belts are fertile terranes for various mineral deposits, among which the volcanogenic massive sulphide (VMS) deposits and banded iron formations (BIFs) of Algoma type have significant research and economic significance (Bekker et al. 2010; Mercier-Langevin et al. 2014). In general, there has been unprecedented research on virtually all aspects of VMS and BIF has mushroomed in the past fifty years (e.g., Franklin et al., 2005; Bekker et al., 2010; Piercey 2011). Interestingly, some of these research illustrates that in the Precambrian VMS and BIF usually have close spatial and temporal associations (e.g., Huston and Logan, 2004), and in most cases they are recognized as syngenetic and strata bounded within the supracrustal rocks of old craton (e.g., Zaleski and Peterson 1995; Slack et al. 2007). Although great progress has been made to figure out the cause and connection of VMS-BIF paragenetic assemblages, but there are still some aspects remain poorly constrained, such as their tectonic setting and the relationship between geodynamic evolution of the greenstone belt and its mineralization.

The Neoarchean Qingyuan greenstone belt (QGB) is located on the northern margin of the North China Craton (NCC) (Fig. 1a), it hosts several VMS and BIF-type iron deposits that formed synchronously (Wan et al. 2012; Zhang 2014; Zhu et al. 2015). Nevertheless, for a long time the tectonic setting of the QGB is under debated, whether it represents an intra-continental rift (Zhai et al. 1985) or formed above a mantle plume (Wu et al. 2013) or was similar to modern arcs (Peng et al. 2015). Furthermore, the relationship between its mineralization and chemostratigraphic evolution has also remained enigmatic. Hence, a detailed work on the supracrustal rock sequences of the QGB may be a fruitful approach to achieve these attempting targets, and is presented herein.

2 Geological background

The QGB is situated in the northern margin of the EB, covering an area of ~25,000 km2 (Peng et al. 2015). It comprises Archean plutons (covering about 70% of the area) and supracrustal rocks, some of which are unconformable covered by Mesozoic sedimentary rocks and intruded by Neopaleozoic plutons as partly showing in Fig. 1b. The Neoarchean plutons in Qingyuan area were grouped into two major episodes by Wang et al. (2016) based on U-Pb isotopic data, the older ~2.56-2.53 Ga strongly gneissic quartz dioritic and tonalitic to trondhjemitic gneisses series, and the younger ~2.52-2.49 Ga weakly gneissic to massive quartz monzodioritic and monzogranitic gneisses series. These plutons are present as domes and as irregularly shaped outcrops,
which control the distribution of greenstone units within the study area. Meanwhile, the Neoarchean supracrustal rocks were subdivided into three main assemblages from bottom to top mainly based on their lithologic association and metamorphic grade (Zhai et al. 1985; Shen et al. 1994): the Shipengzi Formation (SF) composed of tholeiitic to calc-alkalic meta-mafic volcanic rocks with some bimodal lithofacies and BIFs, the Hongsoushan Formation (HF) composed of meta-calc-alkaline bimodal volcanic rocks with VMS and minor BIFs, and the Nantianmen Formation (NF) composed of sedimentary lithofacies with lesser amount of tholeiitic to transitional meta-mafic volcanics and BIFs.

3 Results and Discussion

3.1 Chronology

The analysed zircons can be divided into three groups according to its CL textures and Th/U values. Group I and Group II both are mostly subhedral to euhedral prismatic crystals with blurred oscillatory- or sector-zoning, but their Th/U ratios are different. The former possess a high Th/U ratio (average 0.63) and define an upper intercept age of 2616.9±3.6 Ma, whereas the latter have a moderate Th/U value (average 0.40) and yielded an upper intercept age of 2565±7.8 Ma. Group III are mostly subhedral prismatic crystals with fairy dark in colour and misty internal textures, their Th/U ratios are very low (average 0.07) and define an upper intercept age of 2516.7±6.1 Ma. Combined with previous geochronology (Zhu et al. 2015) in the QGB, we suggest that the 2565±7.8 Ma age is the formation age of these felsic metavolcanics, and also it represents the deposition age of the Xiadianzi BIF. In contrast, the older 2616.9±3.6 Ma age is the crystallization age of the inherited zircon, which indicates the existence of old crust in the Qingyuan area, the younger 2516.7±6.1 Ma age is similar to those metamorphic age presented by previous researcher (Wan et al. 2012).

3.2 Petrochemical and Petrogenesis

The systematic stratigraphic variations in the trace elements geochemical characteristics of the QGB (Fig. 2 and Fig. 3) provide an optimized opportunity to decipher the petrogenesis of its volcanics. On the La/Sm vs. La/Ta diagram, all basalt samples show minimal contamination by continental materials (Fig. 4a), suggesting that they were formed by uncontaminated magma precursors. Among them, the geochemical features of groups I basalts are comparable to those of Mid-Ocean Ridge Basalts (MORB), which are further supported by the samples falling into the MORB field on the La/Nb vs. La and Th/Yb vs. Nb/Yb diagrams (Fig. 4b, c). Hence, the magmatic precursors of these rocks are inferred to have formed by the partial melting of depleted mantle, this inference are supported by their low (La/Sm)_N (average 1.3), (La/Yb)_N (average 1.4), Nb/Ta (average 16.4, primitive mantle 17.6) and Zr/Hf (average 34.5, primitive mantle 36) ratios.

Basalts samples from group II and group III all fall into the IAB (island arc basalt) field on the La/Nb vs. La diagram (Fig. 4b). However, among them the group II basalts are characterized by slightly fractionated REE patterns and pronounced negative Nb anomalies, which closely compare with calc-alkaline island arc andesites-basalts. Similarly, on the Th/Yb vs. Nb/Yb diagram the group II basalts all plot in the calc-alkaline area within Cenozoic counterparts region (Polat et al. 2011), further supporting their genetic link with arc magmatism formed by slab dehydration and wedge melting. In contrast, group III basalts are characterized by unfractonated REE patterns, moderate negative Nb anomalies and devoid of pronounced HFSE anomalies, which are compositionally comparable to the typical primitive arc basalts (Hollings and Kerrich 2000). As a corollary, the group III basalts might source from partial melting of the sub-arc mantle wedge at high level, and accompanied by addition of limited fluids derived from subducted slab (Pearce and Parkinson 1993; Polat et al. 2011).

Figure 2. Chondrite-normalized REE diagrams and primitive mantle-normalized trace element diagrams for felsic rocks from the QGB (Normalizing values from Sun and McDonough, 1989)

Figure 3. Chondrite-normalized REE diagrams and primitive mantle-normalized trace element diagrams for mafic rocks from the QGB (N-MORB and the normalizing values from Sun and McDonough, 1989)
temperature, medium pressure petrogenesis of partial melting at shallow (10-15 km perhaps) crustal levels with amphibole and plagioclase as residual mineral phases, as testified by the LREE-enriched REE patterns, high contents of HFSE and obviously negative Eu anomalies (Lesher et al. 1986) (Fig. 2a, b). While, group II felsic volcanics from bimodal volcanic sequence of the SF are characterized by high Zr/Y values (average 29.8), fractionated REE patterns (La/YbCN = 16.5-187.9) and weakly negative to positive Eu anomalies (Fig. 2c, d), which are consistent with the typical features of FI type felsic volcanics, indicating that they might generate by low-degree partial melting of mafic source at high pressure (> 0.7 Gpa) with minimal fractionation (Lesher et al. 1986).

3.3 Tectonic evolution and mineralization

As documented earlier, the extensively exposed tholeiitic basalts (group III) with shallow negative Nb anomalies and transitional to calc-alkaline basalts (group II; the SF) with deeper negative Nb anomalies (Fig. 3) recorded the evolution from primitive arc to mature arc magmatism, while the stratigraphic younger sequences (the HF) composed of interlayered N-MORB type basalts (group I) with FI (group II) to FII (group I) felsic volcanics (Fig. 2, 3) are petrogenetic in response to rifting processes. Therefore, an extensional arc setting is proposed for the QGB, however, given the presence of slightly continental crust signatures, such as crustal contamination and xenocrystic zircons, in some supracrustal rocks the arc are more likely formed along the continental margin rather than intra-oceanic.

Based on an extensive database of compiled whole-rock geochemistry (Fig. 2, 3), U-Pb geochronology (not shown) and stratigraphic constraints, a simplified geodynamic scenario including the formation of an continental margin arc, the subsequent arc-rifting processes, and end of the extension is proposed for the formation of the SF, the HF and the NF in the QGB, respectively. The first stage is characterized by the generation of volume tholeiitic (group III) to calc-alkaline (group II) basalts in the lower most SF, it may reflect a gradual transition from depleted, weakly subduction altered to subduction metasomatized mantle melts (Manikyamba et al. 2015), because during early stage of subduction only limited flux generated by the dehydration process of oceanic slab, but as the increase of subduction depth more transitional to calc-alkaline basalts occurred attesting to an increasing contribution from slab-derived fluid and/or melt (Stern 2002). Studies of the Phanerozoic oceanic island arc indicate that the magmatism can transform form primitive island arc to calc-alkaline just in a few million years (Jicha and Singer 2006), which is totally comparable with that of the QGB. The second stage is an extension-dominated geodynamic setting in which rifting of the continental margin arc, perhaps triggered by the subduction slab rollback, induced the thinning of overriding plate and the formation of numerous normal faults (e.g., synvolcanic and synsedimentary faults), which would increase the permeability for fluid flow and provided an accommodation space for upwelling mantle melts to occupy, thereby elevated the geothermal gradient of the rift (e.g., Schardt et al. 2005; Piercey et al. 2011). These processes, in the end would provide the necessities for generation and evolution of sub-sea floor hydrothermal systems. Convection of seawater through mafic crust leached large quantities of elements (i.e., sulfur, copper, zinc, iron, lead, and gold), deposition of these elements as sulfides and/or ferric oxyhydroxides on the seafloor in
certain environment generated the VMS and BIF in the QGB. Finally, the last stage is characterized by the presence of dominated sedimentary rocks, such as marble, quartzite and minor BIF in the upper NF (Zhang 2014), which may represent termination of the extension process and the following sedimentation.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (No. 41572076).

References

Crustal architecture of the south-east Superior Craton

David R. Mole, Jeffrey H. Marsh, Phil Thurston, John A. Ayer
Mineral Exploration Research Centre (MERC), Harquail School of Earth Sciences and Goodman School of Mines, Laurentian University, Canada

Bal S. Kamber
Queensland University of Technology, Earth Environment and Biological Sciences, Australia

Abstract. The Neoarchean Abitibi sub-province of the south-east Superior Craton represents one of the most mineralized pieces of crust on Earth. Rich in both orogenic gold and base metal (Cu, Zn, Pb) VMS deposits, but relatively poorly endowed in komatiite-hosted Ni-Cu-PGE systems, the region appears to have a different mineral systems story to its Neoarchean counterpart: the Yilgarn Craton in Western Australia. Large-scale isotopic mapping using Sm-Nd and Lu-Hf systems have proven useful in understanding the large-scale crustal architecture that controls metal endowment in the Yilgarn, and hence a major component of the Metal Earth project is to produce similar mapping products for the Superior Craton. Initial results from a small Lu-Hf dataset demonstrate a clear spatial variation in εHf across the Ontario Abitibi region. The area as a whole is juvenile, but small variations within these data correspond to east-west trending zones of relatively more- or less-juvenile crust. The occurrence of VMS systems and orogenic gold deposits correlate with the most juvenile zones, while the edge of these zones correlate with major structures important for mineralization, such as the Porcupine-Destor Fault. These observations suggest that crustal architecture has a fundamental large-scale control on regional metal endowment in the Abitibi sub-province.

1 Introduction

Lithospheric and crustal architecture – the framework of major tectonic blocks, terranes and their boundaries – represent a fundamental first-order control on major geological systems, including ore deposits and the location of world-class mineral camps. Existing work has demonstrated the ability of radiogenic isotope systems (i.e. Sm-Nd, Lu-Hf) to constrain time-resolved intracratonic lithospheric architecture. Champion and Cassidy (2007) used regional Sm-Nd isotopic data to map the crustal architecture of the Yilgarn Craton, while Mole et al. (2013) and Huston et al. (2014) demonstrated the association between that lithospheric architecture and BIF-hosted iron, orogenic gold, and komatiite-hosted Ni-Cu-PGE systems.

Those results demonstrated the underlying control of lithospheric-crustal architecture and the potential for isotopic mapping as a greenfields area selection tool. Further work by Mole et al. (2014), using Lu-Hf isotopes, demonstrated that the technique could account for rocks, events, and mineral systems of different ages, showing how Ni-Cu-PGE mineralized komatiite systems of the Yilgarn Craton migrated with the changing lithospheric boundary (craton margin) from 2.9 to 2.7 Ga.

Beyond mineral systems science, the data collected in these studies allow a time-space assessment of craton construction and evolution, which provide vital information on the tectonic environment/s active on the Archean Earth.

Despite the increasing prevalence and use of the isotopic mapping technique in China (Hou et al. 2015) and West Africa (Parra-Avila et al. 2017), it is yet to be applied across the Earth’s largest Archean craton – the Superior.

2 Isotopic mapping of the Superior Craton: the craton-scale module of Metal Earth

In the Superior Craton, the isotopic mapping technique has been applied locally to the Wabigoon region by Lu et al. (2013) and Bjorkman (2017), but information from other regions is currently sparse, or has not been collated to produce a spatial product. A primary goal of the new Metal Earth project at Laurentian University is to apply this technique to the entire Superior Craton, producing a craton-wide Lu-Hf isotopic map that will be used to: (1) Understand the development and evolution of the craton; (2) evaluate the spatial variability in magmatism and metal endowment; and (3) be available as an area selection tool for large-scale exploration activities.

3 Methodology

The isotopic mapping of the Superior Craton will be approached in an incremental method. The craton has been sub-divided into six main zones, based on geology, geography, and administration. Each zone is approached individually, with integration between zones as the project progresses. Samples are selected from a new, in-house geochronology database that contains the location of all current Superior zircon geochronology samples; all are felsic volcanics or granitoid rocks, which represent a physical sample of the Archean crust. These samples are then located in the relevant archive and sub-sampled. Once mounted and imaged, zircons undergo oxygen isotope analyses by secondary ion mass spectrometry (SIMS) at the Centre for Isotopic Microanalysis (CCIM) at the University of Alberta, before laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) for U-Pb geochronology, Lu-Hf isotopes, and zircon trace element analyses at the Minerals Exploration...
Research Centre Isotope Geochemistry Laboratory (MERC-IGL). The first zone to undergo this method is the south-east Superior, and data collection is on-going. The initial data presented here are solution ICP-MS zircon data provided by John Ayer and Balz Kamber.

4 Early results from the south-east Superior Craton

The south-east Superior Craton comprises the Quetico, Abitibi, Opatica, and Wawa subprovinces, and thereby some of the most well-mineralised crust on Earth, with the Abitibi producing >180 Moz of Au alone (Spooner and Barrie 1993).

Initial results from the Ontario portion of the Abitibi are displayed in Figures 1 and 2. Figure 2 shows the variation in εHf across this area of crust. This is essentially a time-slice of crustal architecture at 2740-2670 Ma, i.e. during the development of the major Abitibi volcanic sequences from the 2750-2735 Ma Pacaud Assemblage to the Upper Blake River (2701-2695 Ma) and syn-sedimentary Porcupine and Timiskaming Assemblages. As we collect more data, we will look to further define time-slices around major magmatic events (Thurston et al. 2008).

The first observation is that all the crust in this region of the south-east Superior is juvenile (Figures 2-3). All data fall between +5 and +2 εHf units, with no data below the chondrite uniform reservoir line (CHUR). This suggests that the crust of the Abitibi region has a short residence time. A number of interpretations are possible: (1) if the crust was extracted from a depleted mantle (DM) that corresponded to the DM model line (Figure 3), then it is possible an older element of the crust is 3100 Ma, and that this element may have mixed with younger crust between 2740-2670 Ma, resulting in the scatter in the εHf plot; (2) the data may represent newly-extracted crust which was extracted from a DM that was less radiogenic than the model DM line, in which case any DM model ages (two-stage) would not be accurate; (3) hypotheses one and two could be correct, but also involve an older crustal element not represented here due to dilution within a mixing system dominated by the juvenile crust.

![Figure 1. Geological map and location of Hf-isotope samples (black circles). Location of map is at the south-east corner of the Superior Craton. Shades of pink represent TTG-granitoid rocks, green = mafic rocks, yellow = felsic volcanics.](image)

![Figure 2. Contour map of Hf-isotope data (shown as εHf). Gold deposits, Kidd-Creek VMS (yellow star) and komatiite-hosted Ni-Cu-PGE deposits (red stars) are shown. Black dashed lines are interpreted east-west linear isotopic zones. The εHf group interval is based upon the analytical error, at 0.25 epsilon units (zircon solution ICP-MS data).](image)
Given the lack of zircon xenocrysts >2.9 Ga and the lack of any older component in existing Hf and Nd datasets (Corfu and Noble 1992), we suggest that the crust of the Abitibi represents either very young ca. 2.7 Ga ‘primary’ crust (two-stage evolution to felsic crust) extracted from a depleted mantle that is less radiogenic than the current DM model; or that the crust has a slightly older, 3.1-2.9 Ga component, that would still be relatively juvenile at 2.7 Ga (Figure 3).

The spatial representation of these data in Figure 2 show a series of east-west trending isotopic zones of slightly different isotopic character. The regions of ‘hotter’ colours are ca. +5 to +3.5 εHf, whilst the ‘cooler’ regions are ca. +3.25 to +2 Ga. If we assume this crust was extracted from a model DM, then the cooler regions would represent ca. 3.1 Ga crust, and the hotter regions ca. 2.9 Ga material.

Interestingly, the northern-most juvenile isotopic zone hosts the major gold camps, including Timmins and Kirkland Lake, as well as the Kidd Creek and Kirkland Lake VMS systems. The komatiite-hosted Ni-Cu-PGE systems appear to form a north-south trend that is normal to the isotopic zoning and not constrained to a particular zone, or type of zone.

The Au systems appear to prefer the southern region of this zone, which corresponds spatially to the Porcupine-Dester Fault (PDF), suggesting the edges of the isotopic zones have structural representatives. The southern juvenile zone is currently poorly constrained, but additional data will aim to constrain if the margins of this zone correspond to the highly prospective Cadillac-Larder-Lake Fault (CLLF). The komatiite-hosted Ni-Cu-PGE systems appear to be aligned with the margin of the Wawa sub-province to the west, suggesting this may have a control on the location of these systems, such as that observed in the Yilgarn (Mole et al. 2014). However, at this stage the isotopic dataset is too small to evaluate this hypothesis.

Figure 3. Age vs εHf plot for felsic volcanic and granitoid rocks shown in Figures 1-2. The 2-sigma analytical error is 0.25 epsilon units. The depleted mantle line is in red, CHUR is in blue.

A number of tectonic-scale processes may have formed the east-west isotopic zones and corresponding crustal architecture:

1. Rift-basin architecture, where the highly juvenile zones represent grabens of thin, hot crust, and the relatively less-juvenile zones horsts of cooler crust. Within this interpretation, the less juvenile crust also could be slightly older, 3.1 Ga pre-existing crust rifted by a later, ca. 2.7 Ga magmatic period.

2. The isotopic zones may represent accreted ribbon continents and/or island arcs, each with a different character and crustal history. However, long-lived (<2760 Ma?) shared magmatic events across these zones do not support this;

3. Within a complex vertical tectonic regime, with crustal upturns and ‘drip’-style tectonics in operation (Nebel et al. 2018; Wiemer et al. 2018), reworking within thickened mafic crust may result in spatial εHf variations depending on the age of the reworked crust and geometry of a ‘drip’.

Our preferred interpretation at this stage is that the εHf architecture in Figure 2 represents a rift basin similar to that in the Basin and Range province (Eaton 1982). This environment facilitated the formation of the VMS systems in the Abitibi and set-up the gold-rich source regions, prior to late compression, granitoid intrusion, and gold mineralizing events at <2.7 Ga.

This may suggest a rift- or extension-dominated volcanic evolution between ca. 2740-2690 Ma, followed by a brief period of ‘late’ subduction which drove compression, granitoid formation, basin formation (deposition of Porcupine and Timiskaming sediments), and ultimately orogenic gold mineralization. However, a possible alternative for late subduction could be the internal reworking of the 2740-2690 Ma greenstone sequence, to produce TTG, and reworking of existing TTG to form granitoids (Johnson et al. 2017; Bédard 2006; Sizova et al. 2015). This process would form basins and drive sedimentation processes, with late far-field compression driving the establishment if the final, current structural architecture. Further, detailed upcoming work is planned to try to address the tectonic setting for the south-east Superior Craton, and the role of subduction and/or any alternative tectonic processes.

5 Conclusions

Initial results from the isotopic mapping program of the Metal Earth project show a number of important features:

- The spatial distribution of crustal εHf data reconcile a number of east-west zones of differing isotopic character; all are juvenile but some are more juvenile (+5 to +3.5) than others (+3.25 to +2);
- The more juvenile zones correlate with the occurrence of VMS and orogenic gold systems, and the edge of the zones correspond to major structures associated with gold prospectivity;
- These relationships are consistent with those constrained in the Yilgarn Craton;
- Together, these data suggest an intimate relationship between architecture, crustal history, and endowment, which can be mapped using the
of the Abitibi.

This dataset represents a fragment of that being developed as part of Metal Earth’s isotopic mapping project. Work is ongoing to look in more detail at time-resolved architectural evolution within the 2740-2670 Ma period in order to separate out the various events vital in the formation and establishment of this world-class mineral system.

Acknowledgements

This is contribution number MERC-ME-2019-170 of the Metal Earth project, hosted by the Mineral Exploration Research Centre (MERC) at Laurentian University, Canada. The project is funded by the Canada First Research Excellence Fund. We thank our partners at the Geological Survey of Canada, Ontario Geological Survey, and Ministère de l'Énergie et des Ressources naturelles (MERN). The assistance of the Jack Satterly Geochronology Laboratory at the University of Toronto and Geotop at University of Quebec at Montreal (UQAM) are much appreciated. We thank our collaborators at the Canadian Centre for Isotopic Microanalysis (CCIM) at University of Alberta, whom acquire our O-isotopes in zircon via SIMS.

References


Isotopic and geochemical indicators on volcanic-hosted massive sulfide prospectivity: a review

David L Huston, David C Champion and Michael P Doublier
Geoscience Australia

Abstract. Well-mineralized Neoarchean volcanic-hosted massive sulfide (VHMS) provinces are characterized by rhyolites with specific geochemical features and juvenile radiogenic isotope signatures. Although well-mineralized Paleoproterozoic provinces share many similar characteristics, the signatures of fertile Phanerozoic provinces differ. These temporal changes not only have implications for the use of geochemical fertility signatures during VHMS exploration, but also for the secular evolution of tectonic process and metallogenesis. The changes in VHMS fertility indicators may relate to the change from unstable shallow slab break-off to stable deep break-off (modern-style) subduction during the Neoproterozoic.

1 Introduction

Black smokers, the modern analogue of volcanic-hosted massive sulfide (VHMS) deposits, presently form along mid-oceanic ridges and convergent margins, including back-arc settings (Hannington et al., 2005). Of these two settings, the former is highly likely to be destroyed by subsequent subduction, leaving the latter the dominant tectonic setting in which ancient VHMS deposits are preserved. The distribution of black smokers (Hannington et al., 2005) indicates that ancient VHMS deposits should be present in back-arc basins and rifted arcs that form above the subduction channel. Although a broad convergent margin setting is the main environment for VHMS formation, some ancient convergent margins appear to be better mineralized than others, raising the question as to whether better-mineralized can be distinguished from poorly-mineralized VHMS provinces using geological, geochemical and/or geophysical data.

A number of types of geochemical data have been used to distinguish better-mineralized VHMS provinces, including whole-rock rhyolite geochemistry, and the lead and neodymium characteristics of the province hosting the deposits (Lesher et al., 1986; Huston et al. 2005). These disparate signals probably reflect the tectonic environment in which the deposits form. Importantly, the geochemical characteristics of well-mineralized provinces change through time: well-mineralized Archean and Paleoproterozoic provinces have different geochemical and isotopic characteristics to well-mineralized Phanerozoic provinces. These changes probably relate to the evolution of tectonic processes through geological time.

The purpose of this contribution is to review geochemical and isotopic characteristics indicative of highly mineralized provinces and how these characteristics have changed through time, and then use these observations and models of secular variations in tectonic processes to develop an overall model which points to how geochemical characteristics could be used in exploration for VHMS deposits.

2 Geochemical indicators of VHMS potential

The pioneering study by Lesher et al. (1986) indicated that the geochemistry of high field strength and rare earth elements (REE) from rhyolites can be used to determine the potential of the host package to contain VHMS deposits. Lesher et al. (1986), who worked exclusively on Neoarchean deposits, grouped rhyolites into four categories (types FI to FIIIa: Fig. 1), of which two, FIIa and FIIb, had the highest potential to host VHMS deposits. Subsequent workers have largely confirmed the original results of Lesher et al. (1986), with some important wrinkles.

Hart et al. (2004) found that the geochemical characteristics of rhyolites in fertile host packages changed with time: although the characteristics of most fertile Archean and Paleoproterozoic packages were broadly similar, fertile packages in Phanerozoic provinces were dominated by FII and FIV, the latter a new rhyolite type not noted in the signatures of Archean (or Paleoproterozoic) provinces by Lesher et al. (1986). Moreover, Mercier-Langevin et al. (2007) noted that the host to the precious metal-rich, Neoarchean Bousquet district was dominated by FI rhyolites, indicating that some Neoarchean districts, in this case containing high sulfidation VHMS deposits, do not fit the results of Lesher et al. (1986). Other precious-metal rich deposits that formed on thicker crust, such as the Nimbus deposit in the Yilgarn Craton (Hollis et al. 2017), also do not fit with in the classification of Lesher et al. (1986).
The changes in REE geochemistry used by Lesher et al. (1986) and Hart et al. (2004) as VHMS fertility indicators relate to presence or absence of garnet in the source regions of the rhyolitic melts (e.g. Rollinson 1993), which in turn is related to the pressure (depth) at which melting occurs (e.g. Zhang et al. 2013). The geochemistry of FIIa and FIIb rhyolites, which are fertile in the Neoarchean and Paleoproterozoic, indicates high temperature, shallow melting in the absence of garnet in the crust, whereas the geochemistry of FI rhyolites, which are most prospective in the Phanerozoic, and, particularly, F1 rhyolites are indicative of deeper melting in the presence of garnet. This suggests that the depth of melting for VHMS-fertile rhyolites has increased with geological time, and that rhyolites associated with high-sulfidation VHMS deposits may have been sourced from a greater depth than “normal” VHMS deposits.

Barrie (1995) found zircon saturation temperatures, which are calculated from rhyolite geochemical data, are also indicative of VHMS fertility. Fertile volcanic packages have higher zircon saturation temperatures than less-fertile packages. The results of Barrie (1995) were based solely on Neoarchean districts, so potential secular changes in the indicator are not known.

3 Radiogenic isotope indicators of VHMS potential

Huston et al. (2005, 2014: Fig. 2) first noted that more fertile VHMS provinces were associated with juvenile crust as indicated by variations in granite Nd model ages (e.g. Champion and Cassidy 2008) and μ values (238U/204Pb) calculated from ore lead isotope data. Highly mineralized terranes (e.g. Abitibi-Wawa Subprovince, southeastern Canada), and more strongly mineralized zones within less mineralized provinces (e.g. Teutonic Zone in Eastern Goldfields Superterrane, and Cue Zone in Youanmi Terrane, Western Australia) have granite Nd model ages close to emplacement ages and/or low μ values (Fig. 2). In general, juvenile Archean provinces are more fertile for VHMS deposits than more evolved provinces (Fig. 3). This general relationship also applies to Paleoproterozoic provinces, but not to Phanerozoic provinces, where highly mineralized VHMS provinces are commonly present in more evolved crust (e.g. Mount Read Volcanics, Tasmania, Australia).

Figure 3. Plot of Cu, Zn, Pb, and combined Cu-Pb-Zn VHMS metal endowment (in tonnes of metal/km²) for Archean cratonic blocks in Canada and Australia, highlighting the much greater endowment in isotopically primitive blocks (after Champion and Huston 2016).
Volcanic-hosted massive sulfide fertility indicators in a tectonic context

Disparate geochemical data sets have been used to infer the fertility of volcanic successions for VHMS deposits. In most cases these fertility indicators were developed in Neoarchean VHMS provinces, and later research has indicated that indicators have changed through time, with the greatest changes between the Paleoproterozoic and Phanerozoic.

The style of tectonics also appear to have changed through geological time as a consequence of mantle cooling from some form of stagnant lid regime in the Paleoarchean through shallow slab break-off subduction in the Mesoarchean through the mid-Neoproterozoic to modern-style deep slab break-off subduction from the mid-Neoproterozoic to now (Sizova et al. 2010; Moyen and van Hunen 2012). Moreover, the style and, particularly, the duration of metallogenesis along convergent margins (Huston et al. 2018) has also changed, with Neoarchean to Paleoproterozoic margins characterized by a shorter duration of metallogenesis (<200 Myr) than those in the Phanerozoic (400-700 Myr). These changes in tectonic setting, metallogenesis and VHMS fertility indicators may be linked.

Figure 4 illustrates a model that accounts for changes in VHMS indicators between the Neoarchean-Paleoproterozoic and Phanerozoic as a consequence of changes in tectonics. In this model, subduction during the Neoarchean to Paleoproterozoic (Fig. 4a) is unstable due to repeated (and shallow) slab break-off, leading to relatively short periods of subduction and convergent-margin metallogenesis. Possibly, due to the shallow dip of subduction, arcs may not form. In contrast, from the late Neoproterozoic onwards (Fig. 4b), subduction is characterized by generally coherent and often steeper slab dips and is more stable with consistent development of volcanic arcs. This leads to significantly longer periods of subduction, with a greater flux of hydrated oceanic crust and eroded continental crust into the subduction channel, and also to a cooler environment in the subduction zone (Brown 2014). The cooler environment leads to melting at greater depths, commonly in the garnet present zone, leading to the formation of a greater association of VHMS deposits with type FII and FIV volcanics. Moreover, the introduction of greater amounts of evolved crustal material in the subduction channel along with greater crustal thicknesses lead to a breakdown in the relationship between juvenile crust and VHMS deposits seen in older deposits.
5 Summary, implications for exploration and future research

The review presented above suggests that although there appear to be reasonably reliable geochemical indicators of VHMS fertility at the province- to district-scale, these indicators appear to change with geological time. This means that caution needs to be exercised in applying the techniques during exploration; in particular the age of the mineralization must be considered.

The development of micro-analytical geochemical and isotopic techniques, including the geochemistry and isotopic composition of zircon, offers new opportunities to develop fertility indicators. These techniques have been developed for porphyry copper exploration (e.g. Dilles et al. 2015) and can be potentially adapted for VHMS exploration.

Acknowledgements

The authors acknowledge the input of our collaborators, both past and present, who have influenced our thoughts over the years. The collaborators include Kevin Cassidy, Bruce Eglington, Sally Pehrsson, Steve Piercey and Shen-Su Sun. Roger Skirrow and Steve Hollis are thanked for their reviews. This contribution is published with permission of the Chief Executive Officer of Geoscience Australia.

References

Champion DC, Cassidy KF (2008) Using geochemistry and isotopic signatures of granites to aid mineral systems studies: an example from the Yilgarn Craton. Geoscience Australia Record 2008/09.7–16
Hollis SP, Yeats CJ, Wyche S, Barnes SJ, Ivanic TJ (2017) VMS mineralization in the Yilgarn Craton, Western Australia: a review of known deposits and prospectivity analysis of felsic volcanic rocks. Geol Sur Western Austr Rep 166
Does heat matter? Magmatism and metallogeny in the IPB: assessment of future mineral exploration vectors

André Cravinho, Jorge MRS Relvas
Instituto Dom Luiz, Faculdade de Ciências, Universidade de Lisboa, Portugal

Rita Solá, Igor Morais, Luis Albardeiro, João X Matos, Rute Salgueiro, Daniel de Oliveira
Laboratório Nacional de Energia e Geologia / Centro de Estudos Geológicos e Mineiros do Alentejo, Portugal

Nelson Pacheco
Somincor-Lundin Mining, Castro Verde, Portugal

Abstract. The Iberian Pyrite Belt (IPB) is historically considered one of the most important VHMS (felsic-siliciclastic) provinces worldwide. Moreover, its seven deposits currently in operation represent the most important base-metal producers in Western Europe. Nevertheless, the number of massive and/or stringer sulfide intersections in the province is currently declining and, thus, new exploration vectors must be developed for new deposits to be found, probably at greater depths. Traditional approaches to brownfield VHMS exploration focuses mostly on detecting any geophysical and/or geochemical features possibly related to massive sulfide orebodies, but the understanding of the relation between these ore-forming systems and heat sources is still poorly constrained and can potentially prove to be critical in defining regional and/or local target areas for VHMS exploration. This on-going research project uses the Neves-Corvo deposit as a case-study and aims to constrain the relationships between petrogenesis and metallogeny, in order to assess which petrogenetic conditions, timings, and thermal evolution of the felsic volcanism are more prone to trigger and sustain high-temperature hydrothermal systems and, hence, VHMS formation, and/or to provide direct magmatic metal contributions.

1 Introduction

Heat is one of the most critical components of hydrothermal systems: it has a crucial role in controlling metal solubility, transport and metal deposition, and is paramount in the development of thermal gradients, which are the effective drivers of sustained crustal-scale fluid flow processes responsible for the formation of mineral deposits, such as volcanic-hosted massive sulfide deposits (VHMS). These deposits are important base-metal sources that can be classified into five categories, based on the geodynamic setting and/or hosting lithostratigraphic sequence (e.g. Barrie and Hannington 1997). Nevertheless, the relation between these deposits and magmatism has been proved to be, in most cases, unquestionable. Magmatism provides not only the heat source to trigger and sustain hydrothermal circulation and ore forming processes but can also act as an important metal source (e.g. Huston et al. 2011).

One of the most important VHMS provinces worldwide is the Iberian Pyrite Belt (IPB), which hosts nearly 90 deposits, seven of them in operation, providing the most important EU base-metal supply. In this felsic-siliciclastic province, despite the variety of sulfide depositional environments recognized, with some deposits exhibiting hybrid genetic features between sediment-hosted and volcanic-hosted massive sulfides, the large majority are undoubtfully associated with felsic volcanic rocks (Tornos 2006), as in other felsic-siliciclastic VHMS provinces.

VHMS deposits exploration, at a regional and local scale, in the IPB and elsewhere, commonly relies in the use of geophysical methods and the detection of the typical hydrothermal alteration patterns related to mineralization. Nevertheless, in the IPB and other brownfield provinces, the rate of deposit discoveries is decreasing and, although these methodologies keep being of inestimable value, the challenge is to seek for new additional exploration tools able to find deeper orebodies. Thus, new exploration criteria need to be developed, in order to maintain or even increase the EU’s contribution of base-metals in the future.

This project aims to understand how magmatism and volcanism impact (temperature-wise) ore-forming systems and the formation of massive sulfide deposits. Its major goal is to establish a more complete relationship between the orebodies and their likely heat sources, and, ultimately, to develop new regional exploration criteria, able to distinguish productive from barren volcanic axes and cycles, by using the Neves-Corvo ore-forming system as a case-study.

2 Geological background

2.1 Iberian Pyrite Belt

The oblique collision between the South Portuguese Zone (SPZ) and the Ossa Morena Zone (OMZ) led to the closure of the Rheic ocean during the Variscan orogeny resulted in a local transtensive tectonic setting, generating a series of pull apart elongated basins infilled by a siliciclastic-dominated lithostratigraphic sequence (Tornos et al. 2005, 2006). This infill constitutes one of the most important tectonostratigraphic domains of the SPZ.

The most important lithostratigraphic unit is the Volcanic-Sedimentary Complex (VSC), characterized by a bimodal volcanic suite, which hosts all the VHMS orebodies. The VSC outcropping sequences suggest that
felsic volcanism largely dominates, but geophysical surveys indicate that mafic counterparts can be more significant at depth (Tornos et al. 2005).

The IPB deposits occur associated to felsic volcanic rocks (e.g. Tornos et al. 2006), and thus, this spatial and temporal association has long been interpreted as reflecting a genetic relationship with felsic magmatism and used in exploration. Nevertheless, no direct correlations between the metallogenetic and the petrogenetic constraints and signatures have been established so far.

2.2 The Neves-Corvo deposit

The Neves-Corvo deposit is one of the giant VHMS deposits in the IPB and one of the seven active mines in this district. It is composed of seven, unusually Cu-, Zn- and Sn-rich deposits found in the SE termination of the Rosário antiform. As in other sectors of the IPB, at the Neves-Corvo area the tectonically imbricated lithostratigraphic sequence includes (from bottom to top) i) the Phyllite Quartzite group (PQG), composed mostly of a more than two km thick sequence of metagraywacke and shale/schists, whose top is dated from the upper Famennian (base unknown); ii) the VSC, comprising a variably thick (usually less than 600m thick) metasedimentary-dominated sequence, with dark shales and other mudstone-siliciclastic rocks, ranging from the Upper Famennian up to the Visean, with two important sedimentary hiatuses – one corresponding to the Tournasian, and another one dated from the early Visean; iii) the synorogenic Baixo Alentejo Flysch Group (BAFG) composed of turbiditic and other gravity-driven deposits, often more than 2 km thick.

The orebodies are hosted by the lower VSC sequence, mostly comprising felsic explosive and effusive volcanic rocks and dark-shales dated from the upper Famennian (Oliveira et al. 2004, Rosa et al. 2008, Solá et al. 2015).

Although the gross metal budget of the Neves-Corvo orebodies formed as typical IPB VHMS ore-forming system, the unusually high tonnages, metal grades and ratios, and radiogenic signatures reflect a unique metallogenetic evolution, involving different metal and fluid sources, in time and space, including the typical IPB ore-fluid and metal sources, local magmatic-hydrothermal contributions and tectonometamorphic remobilisations (e.g. Relvas et al. 2001, 2006). Ore-forming systems must have been especially effective in this area, and abundant data has been gathered for the Neves-Corvo deposit (the best-known deposit in the IPB), making this deposit an excellent case-study to address the relationship between magmatism and metallogeny.

3 Petrogenesis of felsic volcanic rocks and VHMS exploration

Besides contributing with metals and fluids, magmatism plays a critical and more general role in the formation of VHMS deposits it acts as the heat source. Crustal thermal gradients, triggered by the shallow emplacement of crustal-derived felsic melts or mantle-derived mafic magmas, promote crustal-scale hydrothermal circulation and consequently the formation of massive sulfide deposits. Several authors have proposed that estimating melt temperatures using zircon saturation temperatures can provide important regional and/or local criteria for VHMS exploration, namely at the Abitibi and the IPB felsic-siliciclastic provinces (e.g. Barrie 1995; Codeço et al. 2018), where “higher-temperature” rhyolitic melts are more prone to trigger, sustain and host hydrothermal systems and VHMS deposits. Furthermore, lithogeochemistry data has been also proposed as regional criteria for VHMS exploration (e.g. Hart et al. 2004), focusing essentially on the petrogenetic processes and the classification of the felsic rocks that more often host VHMS deposits: FII, FIIia and FIIib rhyolites are more commonly the hosts of VHMS deposits and their petrogenetic processes considered ideal to trigger hydrothermal circulation and mineralization processes.

3.1 Neves-Corvo and other IPB sectors

Numerous studies have focused on the geochemistry and petrogenesis of the (sub)volcanic rocks in the IPB (e.g. Munhá 1983, Mitjavilla et al. 1997). Presently, it is widely accepted that mafic rocks are the result of partial melting of a heterogeneous mantle source and their emplacement at shallow (upper-crustal) depths triggered crustal melting and the formation of felsic melts from which the calc-alkaline felsic volcanic suites derive. These suites range from dacites to (high-silica) rhyolites, interpreted as the result of differential partial melting rates (Mitjavilla et al. 1997). Minor intermediate rocks (andesitic-like) are also recognized in the IPB, resulting from the mixture between felsic and mafic melts.

A compiled local (Neves-Corvo) and regional (mineralized and apparently barren IPB sectors) lithogeochemistry database (n=99 and 334, respectively; references of the regional data in Codeço et al. 2018) show that both the hanging-wall and footwall felsic volcanic rocks in the Neves-Corvo area are altogether similar to those commonly found throughout the IPB, classified as FII and minor FIIia rhyolites to dacites (Fig. 1A). Moreover, when inspecting the calculated zircon saturation temperatures (T SatZirc; Fig. 2) for the various mineralized (e.g. Neves-Corvo, Aljustrel, Rio Tinto) and barren sectors (e.g. Ervidel-Roxo), it is clear that: 1) the temperature range for the IPB is similar to those of the Abitibi greenstone belt (Barrie 1995); and, 2) although several “groups” can be divided considering their median and average T SatZirc temperatures, some mineralized sectors are clearly characterized by lower T SatZirc temperatures than some barren sectors, and vice-versa.

Furthermore, the samples do not show geochemical evidences of intense hydrothermal and/or regional alteration. Hence, significant mass-changes are not expected and absolute Zr contents (for T SatZirc calculations) should not be biased (Fig. 1B).

Another noteworthy feature is the discrepancy between calculated T SatZirc temperatures and the so far published Ti-in-zircon temperatures in the IPB, which are significantly higher (for detailed comparison see Codeço et al. 2018).
4 Zircon saturation temperature – is it a real geothermometer?

The development and review of zircon saturation models (Watson and Harrison, 1983, Boehnke et al. 2013) had tremendous impact in the understanding of magmatic systems. Recent reviews (e.g. Siégel et al. 2018) have shown that, although these models have been widely interpreted as real “geothermometers”, the calculated temperature data must be carefully interpreted. Once the estimation of the M factor and Zr contents are based in the whole-rock geochemical composition, the calculated $T_{\text{SatZirc}}$ values only represent the temperature at which a specific melt, with a specific composition (the lithogeochemical input data), starts to precipitate zircon. Hence, $T_{\text{SatZirc}}$ should not be considered a magmatic geothermometer but a theoretical variable intrinsic to the magmatic evolution process (see Siégel et al. 2018). For $T_{\text{SatZirc}}$ data to be reliable as a geothermometer for volcanic rocks, it should be applied to rocks with bulk-rock compositions similar to the melts from which zircon grew, and, ideally, glassy (if altered, alteration must be accounted) and almost phenocryst-free rocks, with autocrystic zircon grains (Hanchar and Watson 2003). Furthermore, for correctly interpreting such temperatures, a detailed geochronological characterization is required examining the relative amount of autocrystic, antecrystic and xenocrystic zircon. This is not the case for the previously mentioned works, and hence, the proposals assume that all Zr contents derive from autocrystic zircon, precipitated from melts with a similar composition to that of the volcanic rock, surely biasing and overestimating temperatures.

Thus, if $T_{\text{SatZirc}}$ does not prove to be a reliable magmatic geothermometer, it should not be considered a useful criterion for VHMS exploration, and other methodologies for studying the thermal evolution of these crustal melts must be envisaged.

5 Thermal evolution of felsic melts: future approaches and possible implications for VHMS mineral exploration

The fact that zircon saturation temperatures alone should not be used as valid criteria for calculating the temperature evolution of specific volcanic suites, hence assessing the productivity of specific melts as favourable heat sources for triggering and sustaining hydrothermal systems, does not imply that considering the overall petrogenetic processes and thermal evolution of crustal melts for the development of VHMS exploration criteria cannot be considered. When combined geochronology, other zircon- and other mineral-based data (e.g. rutile, quartz) can be used to better constrain the petrogenesis and thermal evolution of volcanic rocks.

A possible approach is to use Ti-in-zircon (Watson et al. 2006; Ferry and Watson 2007) to constrain the melt temperature during zircon crystallization. This approach is even enhanced when combined with U-Pb data, tracking temperature evolution within the magmatic system and the life-span of felsic plutonic to subvolcanic systems. This data integration must be made carefully, as zircon-based temperatures give only information regarding crystallization temperatures, and so, information regarding subsequent temperature changes...
can only be inferred interpolating the obtained data from different time intervals. Even when state-of-the-art equipment or analytical techniques are used, the combination of geochronology and Ti-in-zircon data does not provide distinction between continuous long-lived magmatic systems and episodic, multi-staged short-pulses of melts, as analytical uncertainties (in dating) are usually too big (Kent and Cooper 2018). This has critical implications for the understanding of thermal evolution of igneous systems and, hence, for the heat supply in oro-forming hydrothermal systems, sometimes providing reliable information, useful for mineral exploration. Other geothermometers that allow to constrain temperature evolution in magmatic systems are the Zr-in-rutile (Watson et al. 2006) and/or Ti-in-quartz (Wark and Watson 2007). The latter is often used for the interpretation of the time-scale and temperature estimation of magmatic and hydrothermal systems (e.g. Audétat 2013, Codeço et al. 2017), and can prove to be useful as quartz phenocrysts are relatively common in felsic volcanic rocks, possibly offering a way of estimating temperatures and/or pressures in subvolcanic settings.

The variety of volcanic rocks in the Neves-Corvo area (and in the IPB) must reflect different petrogenetic processes. Thus, a comprehensive and complete petrogenetic model for the volcanic rocks of Neves-Corvo, integrating geochronology and thermochronology, is envisaged as a possible major contribution to a better understanding of the metallogenesis of this fascinating deposit and outstanding province. Different thermal evolutions should be assessed and since these magmatic events were conceivably largely responsible for the heat supply, they should be related with the corresponding metallogenic processes. In this sense, this project aims to develop new mineralogical, geochemical and isotopic exploration criteria, relating heat sources, hydrothermal systems and formation of VHMS deposits in the IPB.

Acknowledgements

A. Cravinho has been awarded with a PhD scholarship funded by Fundação para a Ciência e Tecnologia (FCT) (PD/BD/142784/2018), under the scope of the Earth Systems Doctoral Program - Instituto Dom Luiz (IDL). The research project is funded by SOMINCOR-LUNDIN Mining. Publication supported by FCT-project UID/GEO/50019/2019 - Instituto Dom Luiz, and EXPLORA/Op.ALT20-03-0145-FEDER-000025 Project, funded by Alentejo2020/Portugal2020 + European Regional Development Fund/ERDF.

References

Unravelling the geochemistry of dark-grey to black metapelites in the Iberian Pyrite Belt (Portugal): the relation to massive sulphide ores

Filipa Luz & António Mateus
Dep. Geologia & IDL, Faculdade de Ciências, Univ. de Lisboa, Lisboa, Portugal

Abstract. Volcanogenic massive sulphide deposits in the Iberian Pyrite Belt can be linked with the deposition and evolution of fine-grained siliciclastic sediments represented by dark-grey to black metapelites. We present a lithogeochemical study of 60 samples from the Aljustrel and Neves Corvo mines and exploration drill holes in the Portuguese IPB segment. Geochemical fingerprinting of these dark-grey to black metapelites allow us to discriminate barren from altered/mineralized samples using the ratios Al2O3/(Al2O3+Fe2O3+MnO), Fe2O3/TiO2, (As+Sb)/Sc, (Cu+Zn+Pb)/Sc, and 5×[(Fe2O3+MgO+MnO)/Al2O3]. Geochemical data indicate that sulphide mineralization in dark-grey to black metapelites does not necessarily imply that early sediments were deposited in anoxic (to euxinic) environmental conditions.

1 Introduction

Massive sulphide ores of the Iberian Pyrite Belt (IPB) are mostly hosted in volcanic-sedimentary rocks of uppermost Devonian age [Late Strunian, miospore biozone LN, 360.7 ± 0.7 Ma - 362 Ma] to Early Carboniferous (e.g. Carvalho et al. 1999; Barrie et al. 2002; Pereira et al. 2007; Oliveira et al. 2013). These ore bodies do not show simple relationships with volcanic piles and some of them occur near the top of sequences that mark the waning stages of volcanic cycles. Here they show clear connections with the deposition of fine-grained siliciclastic sediments now represented by black metapelites (Sáez et al. 1999, 2011). There are also examples where the association of sulphide ores with volcanic rocks is not supported by firm evidence of any kind (e.g. Tornos et al. 1998). Therefore, additional data are needed to improve the characterization of specific geological settings where sulphide ore formation may have occurred.

2 Geological Background

The IPB is a fundamental unit of the South Portuguese Zone (SPZ) of the SW Variscides. Its stratigraphy includes, from bottom to top, the Phyllite-Quartzite Group (PQG), the Volcano-Sedimentary Complex (VSC) and part of the Baixo Alentejo Flysch Group (BAFG), also known as Culm Group (e.g. van den Boogard 1963; Oliveira 1990). The Middle to Upper Devonian PQG consists of a siliciclastic succession composed of dark-grey to black metapelites, quartzites and meta-quartzwackes. The VSC (Upper Fammenian to Upper Visean) comprises different volcanic suites inter-fingered or interbedded with a variety of metasedimentary rocks, including dark-grey to black metapelites and meta-siliciclastics, locally accompanied by meta-quartzwackes. The upper sections of VSC are dominated by siliceous, green and purple metapelites often coming along with meta-jaspers (or meta-cherts). The basal sequence of BAFG (Mértola Fm.) is a typical flysch sequence that contains intercalations of variable thickness of prevalent meta-greywackes and metapelites.

Variscan deformation is intense, documenting the progression of strain accommodation triggered by the oblique continental collision during Carboniferous. The resultant south-verging thin-skinned thrust-fold belt (e.g. Silva et al. 1990; Quesada, 1998) is concurrent of synorogenic metamorphic re-crystallization from the prehnite-pumpellyite to greenschist facies conditions (e.g. Munhá et al. 1983 a, b; Abad et al. 2001).

The sulphide ore-forming systems related to the large massive bodies are usually rooted in stockwork hosted in hydrothermally altered volcanic and metasedimentary sequences (e.g. Barriga et al. 1997, Tornos et al. 2000, Sáez et al. 2011). Evidence of synorogenic ore remobilization (during metamorphism and tectonic stacking) is common, further complemented by late-Variscan hydrothermal activity related to the propagation and reactivation of several strike-slip fault zones (e.g. Quesada 1998; Castroviejo et al. 2011; Luz et al. 2014).

3 Sampling

A geochemical sampling program was performed in the Portuguese segment of IPB, being oriented to (mineralized or non-mineralized) dark-grey or black metapelites included in several PQG and VSC sections. At the Aljustrel and Neves Corvo mining centres, samples were collected from different orebodies. Additional samples were obtained from drillcore of exploration surveys, including the recent massive sulphide intersection (hosted in black metapelites) of Sesmarias.

According to the compiled information (Pereira et al. 2007; Oliveira et al. 2013; unpublished technical reports), samples gathered in PQG sections (n=14) range from AD to LN miospore biozones (Givetian-Strunian). The VSC samples are distributed into three subsets: i) Lower VSC (n=15), spreading from VCo to LN miospore biozones (Upper Fammenian); ii) Intermediate VSC (n=8), between LN and CM miospore biozones (= Lower Tournasian); and iii) Upper VSC (n=23) ranging from CM to NL miospore biozones (= Upper Visean).
4 Main features of dark-grey to black metapelites

Metapelites show lepidoblastic textures and many microstructures that document heterogeneous strain accommodation. Irrespectively of the lithostratigraphic unit or their sub-divisions, all metapelites are variably enriched in non- or poorly ordered organic matter and the prevailing mineral assemblage comprises fine-grained white mica (± chlorite) and quartz, along with other accessory minerals, such as zircon, rutile, apatite and tourmaline. Considering the relative abundance of the major mineral phases, many of the sampled metapelites from PQG and Lower VSC comprise a significant component of sandy-derived (sub-millimetre sized) quartz. When enriched in sulphides, the relative abundance of chlorite and siderite (± dolomite/ankerite) increases.

Botryoidal and euhedral pyrite are common, often coupled with very fine-grained disseminations of chalcopyrite, pyrrhotite, sphalerite and galena. Early-fracture fillings (folded and affected by schistosity) are frequent and comprise siderite/dolomite/ankerite + pyrite ± pyrrhotite (± chalcopyrite ± sphalerite). At Aljustrel and Neves Corvo, many of these early-fracture infillings also contain Co-Ni- and Ni-Sb-bearing sulphides along with As-Co-Ni- and As-Ni(-Sb)-bearing sulfosalts.

5 Geochemical fingerprinting

According to the available whole-rock geochemical data, no significant differences exist in major element abundances for samples from PQG, Lower/Intermediate and Upper VSC. However, when samples are sorted as mineralized and non-mineralized according to their petrographic features, it is clear that: (i) higher median abundances of SiO$_2$, Fe$_2$O$_3$, MgO and MnO characterize mineralized samples in Neves Corvo, Aljustrel, Lousal and Sesmarias; and (ii) higher median abundances of Al$_2$O$_3$, CaO and Na$_2$O typify non-mineralized metapelites in all the sampled sections. The K$_2$O, P$_2$O$_5$ and TiO$_2$ abundances are not significantly different for the two groups of samples.

Abundances of minor and trace elements normalized to the Average Shale Composition (AS; Wedepohl, 1991) generate patterns that are similar for PQG and VSC metapelites. Systematic As and Sb positive anomalies (up to 5×, sometimes 10×AS) are observed when metapelites do not comprise sulphides. These As and Sb anomalies increase to 50×AS (at times 100×AS), when the samples are mineralized. In these cases, positive anomalies in Co, Ni and Cu (5× to 30×AS) ± Zn ± Pb (5×AS) are also seen. Locally stronger (above ×100AS) positive anomalies in Zn and Pb typify metapelites from Lower VSC of Neves Corvo and Upper VSC of Moinho orebody (Aljustrel mine) and of Monte das Mesas (mineral exploration drilling). Samples from Neves Corvo also show consistent depletions in Cu, Rb and Ba (<0.05 to 1×AS). One sample from Moinho orebody (Aljustrel mine) displays a positive anomaly in Ba (×10AS). The remaining elements tend to be close to the standard AS contents.

Patterns of REE abundances normalized to AS are flat, excepting those of mineralized samples from Neves Corvo which show slightly positive anomalies in Eu.

5.1 Provenance analysis

Considering the Zr/Sc (5.82-29.66), Th/Sc (0.56-2.06) and Eu/Eu* (0.31-1.90) elemental ratios, an evolved felsic source might be inferred for the prevalent siliciclastic component forming the examined dark-grey to black metapelites from PQG or VSC (for reference values see, e.g., Middelburg et al. 1998, McLennan et al. 1993; Slack et al. 2004). This conclusion is also consistent with results reported in many other studies (e.g. Jorge et al. 2006; Luz et al. 2019), indicating that the chemically alike PQG and VSC metapelites derive from the same continental source.

5.2 Alteration/Mineralization Indexes

The Al$_2$O$_3$/[(Al$_2$O$_3$+Fe$_2$O$_3$+MnO) and Fe$_2$O$_3$/TiO$_2$ ratios can be used to assess overprints of hydrothermal processes acting over a prevalent siliciclastic component (e.g. Marchig et al. 1982; Goodfellow et al. 2003). For IPB metasedimentary rocks, the overprinting is evident for Al$_2$O$_3$/[(Al$_2$O$_3$+Fe$_2$O$_3$+MnO) < ≈0.6 and Fe$_2$O$_3$/TiO$_2$ > 10 (see also, Luz et al. 2019; Fig.1).

Figure 1. Fe$_2$O$_3$/TiO$_2$ vs. Al$_2$O$_3$/[(Al$_2$O$_3$+Fe$_2$O$_3$+MnO) diagram illustrating a possible mixing strip between a “terrigenous” end-member (samples clustering) and a conceptual “exhalative-hydrothermal” term represented by the East Pacific Rise and/or the Red Sea brine pool compositions (e.g. Marchig et al. 1982; Goodfellow et al. 2003). Black borders indicate mineralized samples. Average values for felsic metavolcanic rocks of IPB are shown, using the dataset in Codeço et al. 2018.
The $5\times \left[ (\text{Fe}_2\text{O}_3 + \text{MgO} + \text{MnO})/\text{Al}_2\text{O}_3 \right]$, $(\text{Cu} + \text{Zn} + \text{Pb})/\text{Sc}$ and $(\text{As} + \text{Sb})/\text{Sc}$ ratios, when above 10, can also be used to separate barren from altered/mineralized dark grey to black metapelites (Fig. 2), in agreement with previous results gathered for other metasedimentary sequences in IPB (Luz et al. 2019).

5.3 Redox Conditions

Environmental redox conditions are critical to evaluate the degree of oxygen and hydrogen sulphide available in bottom-waters in equilibrium with sediments; and these may be determinant for the accumulation of shale-hosted massive sulphide ores (e.g. Sáez et al. 2011; Velasco-Acebes et al. 2018). Redox conditions can be inferred from a combined interpretation of some elemental abundances (e.g. S, Fe, Mn and Co) along with several element ratios (e.g. V/Cr, V/(V+Ni), U/Th) previously validated in a large variety of sedimentary settings (e.g. Wignall & Myers, 1988; Jones and Manning, 1994; Wignall & Twichett, 1996). However, as briefly documented above, some of these elements (S, Fe, Mn, Ni and Co) are included in mineral fingerprints of hydrothermal alteration and mineralization processes. In addition, U/Th ratios tend also to increase during fluid flow related to the formation of massive sulphide ores (Luz et al. 2019; Piercey & Kamber 2019). Thus, abundances of redox sensitive elements are disturbed in mineralized samples, which should be discarded of the intended assessment.

Most of our dataset display V/Cr ratios below 2 and 0.6 $< V/(V+Ni) < 0.9$; the correspondent S/Fe ratios are lower than 0.52. Deviations from these trends are recorded for some mineralized samples of Aljustrel and Neves Corvo, documenting the hydrothermal alteration and mineralization progression. The U/Th ratios range mostly from 0.14 to 0.70; samples from Neves Corvo, Albernoa, Pincaros and part of Aljustrel are mostly below 0.5, but mineralized samples of Aljustrel show U/Th ratios above 0.5, reaching 2.94 (Fig. 3 and 4). Considering only the non-mineralized samples from all sectors, parental sediments of the dark-grey to black metapelites were mainly deposited under oxygenated environments (sometimes transitional to suboxic conditions). At Aljustrel and Neves Corvo, many of these samples represent stratigraphic levels laterally equivalent to those that are mineralized. So, as far as can be extrapolated from the available information, sulphide mineralization in dark-grey to black metapelites does not implies necessarily that early sediments were deposited in anoxic (to euxinic) settings.

6 Final Remarks

The main highlights from our results can be summarized as follows:

- Early-developed (prior to Variscan metamorphism and deformation) hydrothermal overprinting over a prevalent siliciclastic composition lead to Fe$_2$O$_3$/TiO$_2$ ratios $\geq 10$ and Al$_2$O$_3/(Al$_2$O$_3$+Fe$_2$O$_3$+MnO) ratios $\leq 0.6$;
Proximity to hydrothermal discharges potentially associated with massive sulfide mineralization is indicated by (As+Sb)/Sc, (Cu+Zn+Pb)/Sc and 5·[(Fe₂O₃+MgO+MnO)/Al₂O₃] ratios ≥ 10; and

The development of sulphide mineralization in dark-grey to black metapelites does not imply necessarily that early sediments were deposited in anoxic (to euxinic) environmental conditions.

Acknowledgements

Filipa Luz acknowledges the support of Fundação para a Ciência e Tecnologia (FCT; PD/BD/114485/2016 grant). Publication support by FCT project – UID/GEO/50019/2019 – Instituto Dom Luiz. Support provided by EPOS S.A., Lundin Mining, ALMINA, EDM, ESAN and AVRUPA Minerals to the performed sampling surveys is warmly acknowledged.

References

Diagenetic evaluation of a possible redbed source for anomalous Cu in the Paleozoic-hosted Cornwallis Zn district, NU

Mathieu, J., Turner, E.C
Laurentian University

Abstract. The Storm Cu deposit in Arctic Canada overlies a Proterozoic red sandstone unit (Aston Formation), which may have had a role in mineralisation. Petrographic analysis of red and grey/white samples of the Aston Formation reveal multiple hematite cement phases, including an early and a late stage. Early hematite is identified by the presence of hematite-coated Aston Formation grains in Mesoproterozoic strata. Late hematite is identified by relationships indicating that it post-dated chemical compaction during maximum burial. Bleaching removed hematite cement locally and is associated with higher amounts of quartz cement and maximum burial. Bleaching implies the circulation of a reduced fluid, whereas oxidised fluid circulation is implied by the presence of hematite post-dating bleaching. The timing relationship of a reduced fluid mobilised during early to maximum burial followed by the circulation of oxidised fluids is similar to that recorded at the Storm Cu deposit. This suggests that the Proterozoic Aston Formation red sandstone may have been a source for metals for the Paleozoic Storm Cu deposit, and that several prolonged episodes of fluid circulation took place.

1 Introduction

Sedimentary-rock-hosted Cu deposits are commonly attributed to metals sourced from adjacent red-bed units (Hitzman et al. 2005), but diagenetic studies of the redbeds invoked are generally lacking, Walker et al. (1984) and Zelinski et al. (1987) concluded that red-bed source rocks were not deposited red, but were reddened during early diagenesis over several millions of years. It is this oxidising process is what liberates and transports the Cu to the site of mineralisation Brown (2005; 2009). In the Cornwallis Zn-Pb district of Arctic Canada (Dewing et al. 2009), an anomalous Cu deposit (Storm copper) is exposed in the southern part of the district on Somerset Island. Storm copper is a carbonate-hosted Cu deposit that overlies Mesoproterozoic red-beds of the Aston Formation, an inferred source of metal for Storm copper (Mathieu et al. 2018). The present study involves a petrographic analysis of the Aston Formation red-beds in order to determine its diagenetic history and evaluate whether it was a metal source for the Storm copper deposit.

2 Geologic history

The stratigraphy on Somerset Island is a succession of Paleozoic carbonate rocks unconformably overlying Mesoproterozoic clastic (Aston Formation) and carbonate (Hunting Formation) units, both of which are cross-cut by Proterozoic dykes and sills (Tuke et al. 1966).

The Aston Formation is an 800-m-thick succession of red, purple, grey, brown, and white terrigenous clastic sandstone, conglomerate, and siltstone/shale (Tuke et al. 1966). The Hunting Formation is a 1.3-km-thick carbonate succession (Dixon et al. 1971).

The Devonian-Carboniferous Ellesmerian orogeny was the main tectonic event that affected the Cornwallis district and resulted in a clastic wedge up to 6 km thick (Embry 1991). This event is also thought to be the main fluid mobilisation event responsible for mineralisation in the district (Dewing et al. 2007).

3 Materials and methods

Samples collected along a transect through the Aston Formation, which include both red and white (bleached) sandstone (Fig. 1), were used for this study. Samples were prepared as polished thin sections for petrographic and SEM analysis at Laurentian University, Sudbury Ontario. Petrography was done on standard petrographic microscope using transmitted, reflected, and oblique incident light. Abundance of grains, cement, and porosity was estimated visually.

4 Results

Sandstone samples are composed of 75-85% framework grains, with 10-20% cement, and approximately 5% porosity. Framework grains are predominantly fractured quartz (80%) and feldspar (20%), with rare Ti-Fe grains. Grain-to-grain contacts are predominantly long concavo-convex surfaces with subordinate sutured and point contacts (Fig. 1). Quartz cement is the dominant pore-filling phase, with lower amounts of feldspar. Hematite is present primarily as grain-coating cement (providing the red colour of the formation).

Hematite cement is typically overlain by other cements, but is also present as overgrowths on other cements. It is less abundant in bleached samples and apparently absent at pressure-solved contacts, but present around pressure-solved grains (Fig. 1). Some bleached samples have grains that are partially coated with hematite. Muscovite is primarily pore-filling but is also present in bleached samples coating grains and altering feldspars.
5 Interpretation

In order to determine the timing of fluid circulation and the possibility that the Aston Formation was the metal source for the Storm copper deposit, the paragenesis of diagenetic events is presented in Figure 2 and discussed below.

The presence of hematite both underlying and overlying other cements indicates that at least two episodes of hematite precipitation took place (reddening events). The first reddening is represented by hematite underlying later cements; the timing of this cement is constrained by the presence of hematite-coated Aston Formation grains in Hunting Formation (Mesoproterozoic) rocks, which indicates an early diagenetic event. The absence of hematite at pressure-solved grain contacts, but its presence around such grains, indicates that a second hematite-precipitating event post-dated (maximum) burial. This timing then provides a youngest time constraint on the timing of the bleaching event, which predated hematite in order to not have hematite at pressure-solved grain contacts.

Partly hematite-coated grains that are overgrown by quartz cement suggest that bleaching occurred prior to or at the same time as quartz cementation. The abundance of fractures in framework grains, but their absence in cement, suggests that cementation took place during (near-)maximum burial, and may be related to pressure-solution. This provides an additional timing constraint sandstone bleaching which had to take place at burial depths where pressure-solution is the dominant compaction process (i.e., deeper than 2 km; von Noort et al. 2008). Because The Hunting Formation is only approximately 1 km thick, it may not have been thick enough to cause chemical compaction of Aston Formation sandstone; therefore burial must have been related to the accumulation of Paleozoic passive-margin strata and/or the clastic wedge of the Ellesmerian orogeny.

6 Discussion

The majority of diagenetic events recorded by the Aston Formation took place during the middle Paleozoic (Fig. 2). The initial reddening processes may have prepared the rocks for a later fluid that transported Cu. Bleaching of the red sandstone indicates a reduced fluid, which removed the hematite at around the time of the Ellesmerian orogeny, which was probably the driving force behind fluid circulation. This condition is in agreement with the fluid history of pre-ore mineralisation at the Storm copper deposit, which involved a reduced, basement-equilibrated fluid (Mathieu et al. 2018). Following bleaching and maximum burial, the Paleozoic reddening process most probably indicates the circulation of a meteoric-sourced, oxidised fluid that would have transported Cu (Brown, 2005; 2009). The shift from a reduced basin-equilibrated fluid to an oxidised meteoric fluid as indicated here is in agreement with the change from pre-ore to main-stage ore at Storm copper, which was precipitated by a meteoric-sourced fluid that acquired Cl by dissolving evaporites and equilibrated at depth (with the Aston Formation), bringing Cu to a site of reduction (Mathieu et al. 2018). Therefore, it is probable that the Aston Formation red-beds were the metal source for the Storm copper deposit.
Figure 2. Paragenetic interpretation of diagenetic phases and the proposed timing relative to fluid circulation and burial history.

Acknowledgements

Financial support for analytical work supplied by Geological Survey of Canada GEM-II program; field support and logistics through NSERC-Discovery Grant to E. Turner and Polar Continental Shelf Project (NRCan).

References


Hot, deep-sourced, hydrothermal Cu-Ag-Au-PGE-polymetallic deposits of Zechstein Kupferschiefer age

Volker Spieth, Hans-Joachim Massonne  
*University Stuttgart, Germany, Institute for Mineralogy and Crystalchemistry*

Jürgen C. Kopp  
*JCK Consulting, Seddiner See, Germany*

Tillmann Viehaus  
*AViSpectro TGU, Stuttgart, Germany*

Michael Trinkler  
*Erz und Stein, Bobritzsch, Germany*

Heinz-Jürgen Bernhardt  
*University Bochum, Mineralogical Institute*

Stanley B. Keith, Jan C. Rasmussen  
*MagmaChem, Sonoita, Arizona, USA*

**Abstract.** Cu-Ag-Au ore grade mineralization of hot hydrothermal origin has been discovered in the Zechstein Kupferschiefer deposit in Spremberg, Lausitz, Germany. The uppermost Permian aged, 15 by 5 km deposit is hosted in Weissliegend silica extrudite, Kupferschiefer *sensu stricto* Mg-Ca-Si-rich chemical mud and Mg-Ca-rich Zechstein dolostone.

Multi-phase mineralogical investigations based on a large number of new exploration drill samples have revealed hydrocarbon-rich and co-existing metallic mineralization with depositional temperatures of >350°C. The dominant metallic mineral assemblage is chalcocite, digenite, bornite, chalcopyrite, electrum and disseminated silver and gold. Microscopic, electron microprobe, Raman and Sulfur isotope studies indicate an origin of deep-sourced basic-ultrabasic brines of serpentinitic-lherzolitic geochemistry in the continent sized European-Copper-Belt extending over more than 750 km with a width of 5 to 20 km. The Polish Lubin district mines produce more than 500,000 t of Cu metal annually (Zientek et al. 2015).

Change is happening in the understanding of the high grade Zechstein Kupferschiefer paragenesis. For decades the depositional model was synsedimentary-sapropelic, replacement, low-temperature mineralization in the context of an euxinic Kupferschiefer sea (Köbel 1958; Richter 1941; Rentzsch 1965; Borg at al. 2012). Recent publications have indicated the novel possibility of Permian to Triassic era rift-related, multi-phase, hydrothermal geological models (Blundell et al. 2001; Blundell et al. 2003; Kopp and Spieth et al. 2012; Spieth et al. 2014) causing the abandonment of the “obsolete” syn-sedimentary (Borg 2017) model. Though most paragenetic observations are shared, the interpretation of the origins is leading to a contentious scientific discourse. Here, the current research results favor the high energy, hot hydrothermal, deep sourced models.

2 Geological setting and age of the deposits

The European Copper Belt of Permian Kupferschiefer deposits stretches from the Rhoen-Richelsdorf mountains in the west of Germany via the Spremberg to the Sudetic Forelands in the east of Poland over a distance of more than 750 km. The individual deposits are about 5 to 20 km wide, 2 to 40 meters thick, outcropping sometimes, but are mostly at a depth from 300 to 2,500 m. The Polish Lubin district mines produce more than 500,000 t of Cu metal annually (Zientek et al. 2015).

The Kupferschiefer sea transgression covered more than 600,000 km² of upper Permian penneplain from Greenland to eastern Poland. The calcareous shale may carry some iron sulfides and rarely reaches a thickness of more than a few centimeters. The southern margin of the Kupferschiefer sea covered the west-east striking continent size lineaments on top of the buried Variscan massifs with a perpendicular tectonic faulting pattern. These basement deep lineaments and faults have been active pre- and post-Permian. They can be traced by 3-D seismic geophysical and residual anomalous heat.
A great deal of individual micro-layers in the Kupferschiefer sensu stricto was analyzed (Von Bubnoff 1950) and calculated regarding the time needed for the deposition with the result of not more than 10,000 years. This does not contradict the accepted depositional age of the Zechstein Kupferschiefer black shale sensu stricto to be from 247 to 257 Ma, based on Re-Os dates (Mikulski et al. 2017). Also reported is a whole-rock and mineral-separate isochron from several samples from the Sangerhausen, Germany, Kupferschiefer sensu stricto deposit with a Re-Os date of 257±1.6 Ma. This represents a depositional age for the base of the Zechstein Group. Six samples of non-mineralized black shale from a Kupferschiefer section in the northern part of the Polish Zechstein Basin yield a Re-Os date of 247±20 Ma (Pašava et al. 2010). The paleo-magnetic dating of the alteration phase “Rote Fäule” hematite yielded dates of 255 to 245 Ma (Nawrocki 2000). Eight high-quality illite samples (Bechtel et al. 1999) yielded an average age for the Kupferschiefer sensu stricto of 252.5 ± 4.5 Ma (Keith and Spieth et al. 2018). These illite samples occur in the high energy / high early copper / Rote Fäule illite-hematite core zones of the Cu-Ag-Au-polymetallic high grade Kupferschiefer system. The complex age history centered on 252.5 Ma with a range of plus/minus 5 Ma indicates the multi-phase origin and consequent alteration of the high grade Kupferschiefer deposits.

3 Spremberg, Lausitz, Germany, Zechstein Kupferschiefer deposit

The Spremberg-Graustein-Schleife Zechstein Kupferschiefer deposit is representative for the mineralization along the Permian-Triassic age European Copper Belt. In each of these deposits, the geometallurgy of the Kupferschiefer related high-grade, copper-polymetallic-precious-metal, hydrocarbon mineralization is present. Chalcocite and digenite are common occurrences. Bornite often carries disseminated silver and exsolutions of electrum. Base-metal-bearing selenides (klockmannite [CuSe] and krutaite [CuSe2]) coexist with covellite and digenite, which form at high temperatures (384-343°C). The Kupferschiefer sensu stricto facies contains exotic elements such as PGE, Co, Ni, Cr, V, Se, Re, Os, that suggest Kupferschiefer copper-silver mineralization fractionated from deep-sourced, high-temperature, hydrothermal fluids, possibly mantle-sourced ultra-mafic rocks. The new high energy hot hydrothermal Kupferschiefer deposit model is a paradigm change to the “obsolete” (Borg 2017) syn-sedimentary to epigenetic model.

3.1 Zechstein Weissliegend sand injectite/extrudite silica slurry

A principal geological parameter for the recognition of the dynamic emplacement model are the observations and geological mappings in Sangerhausen-Wettelrode and Spremberg, Germany, and the Lubin-Rudna district, Poland, that shows: (1) The Weissliegend sand is an injectite/extrudite, silica slurry of Zechstein age that mostly rests on top of the Permian Rotliegend peneplain and is covered in an undulating manner by Kupferschiefer sensu stricto. (2) The Weissliegend sands are cut by veins and veinlets of sulfides and hydrocarbon and Kupferschiefer-like black mud rock that may represent the feeder veins of an open, hot-hydrothermal vent. (3) The Weissliegend sand hosts by far the majority in quality and quantity of the Kupferschiefer-type, mineable copper resources, measured in 100s of millions of tons. The recognition of sand injectites/extrudites is a paradigm change in evaluation of the Zechstein Weissliegend sands and sandstone sedimentary structures globally (Hurst et al. 2006; Hurst et al. 2011).

3.2 Hot hydrothermal metallic and hydrocarbon mineralization

Mineralogical results obtained from the Spremberg-Graustein-Schleife and other European Cu-Ag-Au-polymetallic high grade deposits through microscopy, electron microprobe, Raman spectroscopy, geochemistry and δ34S sulfur isotope analysis show that: (1) The Kupferschiefer deposit type mineralization in its vast majority is somewhat monotonous, as it is made up in Spremberg and the European Copper Belt of chalccocite (Cu2S), digenite (Cu1.75S2), covellite (CuS), bornite (Cu9FeS4) and chalcopyrite (CuFeS2), plus a high (up to 24 wt. % Corg or nearly 50 % by volume) hydrocarbon content, which is significant as it occurs over a distance of more than 750 km in length. (2) Much of the copper minerals are of non-stoichiometric composition and unusual association. Bornite, chalcocite, chalcopyrite and pyrite occur as spherules, immiscible metallic drops in the slurry mud. Bornite of the Kupferschiefer sensu stricto T-1 layer often shows exsolutions of electrum (AuAg) and other solid state copper-copper exsolutions with chalcopyrite and covellite, indicating pre-mixture in the rising metal-hydrocarbon mud slurry and rapid cooling after extrusion on the sea floor surface. (3) The microprobe element analysis of sulfide phases that are widespread in natural ores of the Kupferschiefer Cu-Ag deposits plot in a phase field that includes chalcocite, digenite, djurleiite, anilite, yarrowite (“blaubleibender” covellite), klockmannite and krutaite. Klockmannite (CuSe) and krutaite (CuSe2) have a stability field of about 343°C and 384°C and thus document the high-temperature, hydrothermal nature of the mineral deposition (Kopp and Spieth et al. 2012; Viehhaus and Spieth et al. 2013). The calculations were undertaken with the MINCALC program (Bernhardt et al. 1995; Bernhardt 2010).

3.3 δ34 Sulfur stable isotopes analysis

The δ34 Sulfur stable isotopes are a unique feature to the Kupferschiefer sensu stricto and at Spremberg have a similar composition as those of the copper mineralization of the other deposits of the European Copper Belt. The δ34 Sulfur stable isotopes are light to very light with values...
ranging from –15‰ to –31‰ to –42‰ in chalcocite -
Guzmer et al. 2018) sensu stricto
that influences the beneficiation of the Kupferschiefer
Corg) hydrocarbon chemical mud, a mineralogical factum
with the contemporaneously deposited (up to 24 wt. %
and scientific data proves the genetic association of the
remnants.

sulfide mineralization has been oxidized leaving hematitic
and precious metals are enriched to a higher grade while
independent new deposits. The advancing “Rote Fäule”
which one might have added gold to the system, forming
places, the “Rote Fäule” may have two distinct phases, of
Zechstein-Kupferschiefer pervasive alteration event. In
developed during the recent PhD study by Spieth (2019).

3.4 Geochemistry and geometallurgy
Geochemical, major and trace element compositions are
anomalous and much enhanced compared to average
global black shale. The Kupferschiefer sensu stricto
analysis and geostatistical comparison diagrams demonstrate the interdependence of the base, precious
and polymetallic mineralization with the hydrocarbon
deposition in the Zechstein rocks.

Geometallurgical analysis of the available operational
and scientific data proves the genetic association of the
enriched exotic elements PGE, Co, Ni, Cr, V, Se, Re, Os
with the contemporaneously deposited (up to 24 wt. %
Corg) hydrocarbon chemical mud, a mineralogical factum
that influences the beneficiation of the Kupferschiefer sensu stricto ore greatly. (Guzmer 2014; Rahfeld and
Guzmer et al. 2018)

3.5 Rote Fäule hematitic alteration
Geological observation and mineralogical analyses demonstrate that the hematitic “Rote Fäule” is a post-
Zechstein-Kupferschiefer pervasive alteration event. In
places, the “Rote Fäule” may have two distinct phases, of
which one might have added gold to the system, forming
independent new deposits. The advancing “Rote Fäule”
front creates a “TZ Transition Zone” where existing base
and precious metals are enriched to a higher grade while
in the vast areas covered by pervasive “Rote Fäule” all
sulfide mineralization has been oxidized leaving hematitic
remnants.

4 The new hot, deep-sourced, hydrothermal
Cu-Ag-Au-PGE-polymetallic deposit model
The new hot hydrothermal deposit model documented by
geochemical, mineralogical, sulfur isotope measurements in tables and diagrams has been developed during the recent PhD study by Spieth (2019).

The new model for the Zechstein Kupferschiefer
depositions postulates a high-energy, hot hydrothermal,
extrusive environment that is somewhat similar to
submarine “black smoker” and volcanogenic, submarine,
metal-brine deposits. The metal-rich fluids ascended
through deep-reaching faults and erupted as slurries in
low-relief, mud volcanism above fractures in an open,
shallow, inland sea. Metal sulfide deposition is
systematically accompanied by the precipitation of silica,
dolomitic carbonate, and illite, as well as primary copper
chlorides (such as atacamite CuCl₂) and other brine
minerals, such as anhydrite and sylvite.

Large, deep-reaching, continent-size, rifting
lineaments are known in the Zechstein mineralized area
of the European Copper Belt. These NW-SE lineaments
are disrupted by NE-SW faults. This tectonic pattern is
common in all Kupferschiefer districts and has been
demonstrated with a seismic exploration program at
Spremberg

The ultimate brine source is interpreted to be
serpentinitized peridotite in the lower crust near the Moho
transition to the mantle. Dehydration of the serpentinite
source to talc (steatization) by mantle heat during failed,
inhacontinental rifting of the Pangaea supercontinent at
the end of Permian time released vast amounts of
 element-laden, high-density brines into deep basement
fractures, depositing them above the continental flysch
sediments of the Rotliegend sandstone and
conglomerate penplain in the shallow Kupferschiefer
sea, which is analogous to the modern northern Caspian
Sea and the Salton Sea of southern California, USA.

5 Outlook
The paradigm change (Spieth 2018) in the geologic and
paragenetic Kupferschiefer deposit model has consequences for exploration and mining in the European
Copper Belt. The Cu-Ag-Au-PGM-polymetallic
“undiscovered Kupferschiefer resources” (Zientek and
Spieth et al. 2015) may be hosted by (1) the
underexplored footwall Zechstein Weissliegend
injecte/extrudite hot hydrothermal primary silica slurry
metallic mud strata; (2) the primary native gold deposits
(Piezownka et al. 2008); and (3) the Cu-Ag-Au-PGM-
metallic enriched “TZ” Transition Zone in front of the
vast advancing “Rote Fäule” hematitic alteration
(Oszczepalski et al. 2017).

Two thirds of the European Copper Belt is
underexplored. The new model, based on the
underground mining and geological knowledge from the
Polish operations and the Spremberg deposit, indicates
that the guides to locate new Zechstein Kupferschiefer
resources are (1) large tectonic lineaments; (2)
Weissliegend “sand bars” in the sulfide mineralized
areas; (3) the up to several kilometer wide fringes of the
“TZ” Transition Zone in front of the “Rote Fäule”
alteration; and (4) the large “sand bars” possibly
mineralized with primary native gold within the “Rote
Fäule” alteration zone that was previously considered
barren. This exploration model has been successfully
tested at the Spremberg-Graustein-Schleife deposit that
contains in an area of about 20 km by 5 km an
underground resource of 3 Mt copper plus associated
metals (Spieth 2016).

Acknowledgements
This research was carried out with the support of the
Mineralogical Institute of the University Stuttgart under
the leadership of Prof. Dr. Massonne, and at the
Mineralogical Institutes at Tuebingen, Bochum, Aachen
and Freiberg, Germany, whose technical and knowledge
support is gratefully acknowledged. Much appreciation is expressed for the generous assistance provided by many research colleagues, geologists and engineers in the Spremberg project, Germany, the Gliwice Instytut Metalu Niezelianzych, Poland, and Kupferschiefer exploration projects, mines and plants that were visited and studied.

References


Permeability network, alteration and mineralization of the Spitfire basement-hosted uranium prospect, Western Athabasca, Canada.

Maher Abdelrazek¹, Antonio Benedicto¹, Mostafa Fayek², Cameron Mackay³, Darren Slugoški³, Olivier Gerbeaud⁴, Patrick Ledru⁵
¹Université Paris-Sud, UMR GEOPS, Orsay, France
²University of Manitoba, Department of Geological Sciences, Winnipeg, Canada
³Purepoint Uranium Group, Saskatoon, Canada
⁴Orano, Paris, France
⁵Orano Canada, Saskatoon, France

Abstract. The spatial distribution of uranium and associated hydrothermal alteration within the structural network is a key feature for basement-hosted mineralization of the Athabasca metallogenic province. Uranium oxides precipitated within steeply dipping fault systems and zones of strong rheological contrasts. Microscopic observations focused on micro-textures and mineral assemblages to characterize the permeability network and the alteration. Isotopic analysis (SIMS) on sulfides investigated possible connections between the different parts of the orebody. This study shows that the permeability of the pre-existing ductile fault zone has been enhanced by dilatational micro-brecciation followed by strong dissolution, thereby reactivating and creating a new permeability network.

The main mineralizing event is followed by an oxidizing ore remobilization event at the top of the prospect, just below the unconformity. Sulfur δ34S isotopic values range from -40 to +40 ‰, showing a complex geochemical evolution of the deposit through time.

1 Introduction

In the Athabasca Basin, most of uranium high-grade mineralization is localized at the unconformity between Paleoproterozoic and Archean basement rocks and the Helikian Athabasca sandstone (Kyser and Cuney 2005). Unconformity-type deposits are commonly associated with the presence of graphite-rich basement shear zones, which are inherited from basement structures formed during the Trans-Hudson orogeny, and which were reactivated during or after the deposition of the Athabasca basin in the upper crust brittle domain (Jefferson et al. 2007). Mineralized orebodies form lenses either within the basement (Eagle Point), at the unconformity (Cigar Lake) or sometimes both (Key Lake; Harvey and Bethune 2007). Two sub-types of the unconformity-type model have been characterized (Hoëve and Quirt 1984): (i) the Egress model involving uranium-bearing fluids flowing through the basement via permeable structures, uranium precipitating at the unconformity; (ii) the Ingress model involving basinal fluids flowing from the bottom of the basin into the basement through basement reactivated structures, that act both as trap and fluid pathway. Recent numerical modeling showed that the two processes can coexist in the meantime and be actives in the same area (Li et al. 2018). Most of known economic uranium concentration is known to be located in the Eastern part of the Athabasca basin, lying over a unique domain in the basement, called the Wollaston-Mudjatik Transition Zone (WMTZ). However, significant uranium high-grade concentrations were found in the Western part (Maybelle River, Shea Creek, Beaverlodge district), and some of these have been mined in the past (Cluff Lake).

Since 2012, discoveries of high-grade uranium mineralization along the Patterson Lake Corridor have caught the attention of many companies. These discoveries are exclusively basement-hosted, and may be deeply rooted below unconformity (900 meters for Arrow), with little to none of Athabasca basin formations preserved on top (these areas are located outside the actual southern limit of the basin). Card and Noll (2016) carried out new definition for basement geology of the West-Athabasca basement, corresponding to Talston domain (Card et al. 2014), as it is dominated by altered orthogneiss, instead of metapelites, which are known to be prominent in the WMTZ. The Hook Lake project hosts the Spitfire deposit, which is presumed to be located in the geological continuity of large known deposits along the Patterson Corridor (Arrow, Triple R). Few structural studies has been carried out in the patterson Lake Corridor, and few have been presented (Benedicto et al. 2017; Hillacre et al. 2017).

These studies established some links between the basement structures and high-grade uranium mineralization. Regarding Spitfire, but there is still a doubt on the nature of the permeability network through which uranium-bearing fluids percolated to form the known mineralization, as well as the mechanisms responsible for the enhancement of permeability in basement rocks. The origin of fluids, the number of mineralizing events and the chronology of events are still open questions. This study couples macro- and micro-structural observations made on samples from newly drilled uranium-rich cores with petrography and secondary ion mass spectrometry. The results allow to define a structurally-driven paragenetic sequence for Spitfire, and to establish which were the mechanisms responsible for permeability enhancement.

2 Deposit architecture
The Spitfire discovery is located in a bend of a graphitic conductor, generally striking N-E that locally turns towards N015 (Benedicto et al. 2017). This change in strike is interpreted to have induced local trans-tensional conditions, resulting in the creation of dilational-jog structures through reverse-sinistral reactivation of prior structures.

Geological cross-sections across the Spitfire orebody (Figure 1) suggest the existence of a network of anastomosing graphitic shear zones, eventually stacked together, encompassed within non-graphitic silicified lithological units (silicified gneiss) or quartz veins. Shear zones are affected by extensive alteration, characterized by quartz depletion, chlorite and locally graphite enrichment. Upper contacts of the shear zones with silicified units are preferentially intruded by mafic dykes, which show different degrees of deformation and alteration, ranging from fresh-undeformed to foliated and completely chloritized. In the upper basement (just below the unconformity), secondary oxidation has affected the overall basement lithology.

Mineralization occurs along zones of strong rheological contrast between the upper shear zone and the silicified gneiss, as well as on the contact between shear zones and overlying silicified pyritic-rich gneisses. Upper contacts are both intruded by dykes set in place before mineralization.

The composite orebody is made up of three major sigmoidal lenses, whose shapes are guided by the orthogneiss foliation. Figure 2 shows the mineralized envelopes (with a cut off defined at 500cps) and their projection on the cross section. In the upper part, the mineralization spreads laterally along the shear zone, which seems mostly to occur within the oxidation zone. The mineralization exhibits a gradual change in texture and width from distal oxidized zones to the center of the orebody.

2.1 Upper mineralization – Yellow and purple lenses

The shear zone interval is composed of mylonitic rocks with S-C fabric indicating dextral shear. Folds develop toward depth without preferential orientation. The rocks are chloritized and phyllosilicates are the dominant minerals. Locally, some redox fronts overprint the ductile fabric, especially closer to the unconformity. The shear zone can be locally affected by a later brittle deformation stage. Small breccias can develop in the vicinity of mafic to ultramafic dyke intrusions crosscutting the shear zone. Breccias are identified by rotated clasts of mylonite. These intrusive orebodies seem to use rheological contact between the footwall of the shear zone and the hanging wall of the underlying orthogneiss as weakness plane.

Outside the oxidized zone, mineralization is mostly disseminated and higher grade near the top of the shear zone, at the interface with the silicified gneiss. Grade tends to be lower with increased fold intensity. Uranium oxide veins display a variable orientation ranging from foliation-parallel to oblique to foliation. The density and width of veins tends to increase toward the center of the shear zone and with depth. In the oxidized zone, mineralization is remobilized to form botryoidal uraninite. A metamorphic foliation formed by elongated quartz is seen in the gneiss. Breccias can be observed at the contact with the dyke, showing clasts of the gneiss within an argillitic dyke matrix. Several fracture sets develop in the gneiss, crosscutting the foliation at different orientations. Small veins less than millimeter width of chlorite, clays and iron-oxides postdate the previous ductile and brittle structures, as well as uranium mineralization.

Mineralization in the gneiss is visible as uranium oxide veins similar to the veins in the shear zone, up to centimeters in width, and also as micro veins crosscutting quartz with mineralization spreading from the vein into the foliation in a “Christmas tree” pattern. Mineralization appears to be of higher grade in the sheared interval than in the orthogneiss.
2.2 Lower mineralization – Green lens

Mineralization is hosted at the contact between a pyrite-rich silicified gneiss and a chloritized mafic dyke at its footwall. The dyke is emplaced between the gneiss and the graphitic shear zone below. Strong alteration overprints the dyke. Textures show white clasts of argillitic material within a matrix of dark-green chlorite. Chlorite grains are well developed and oriented in the same direction. Edges of the clasts show dissolution textures. The first steps of the dissolution process are visible in the less altered part of the dyke. Chlorite veins develop in small fractures and spread to replace the host rock. The pyrite-rich silicified gneiss also shows strong dissolution in the vicinity of the dyke. The dissolution affects both quartz and pyrite, and seems to be driven by fractures crosscutting the foliation.

Mineralization in both the silicified gneiss and the dyke is disseminated in the phyllosilicates, in association with pyrite. Compared to the upper part of the orebody, grade of the mineralization is lower.

3 Textural relations and observations of alteration and mineralization

Observations at macro-scale were reinforced by micro-structural observations in order to characterize alteration textures related to uranium mineralization, and the eventual associated permeability network. This will be here presented in a separated way for each main lithological group.

3.1 Shear zone

The shear zone mineralogy is dominated by phyllosilicates. Disseminated mineralization coats the grain surfaces and fills porosity between grains, forming patches of mineralized phyllosilicates. Uranium oxides are not homogeneously distributed at the micro-scale. Locally, the intensity of mineralization can totally overprint the clays (Figure 3).

3.3 Pyritic silicified gneiss and chloritized intrusive

The gneiss is strongly affected by silicification. The mineralogy is composed of quartz, dark-green chlorites and sulfides (large pyrites overgrown by quartz and micro-pyrite/chalcopyrite disseminated into the chlorite). Samples from the mineralized area highlight first a strong dissolution affecting both quartz and the large pyrite...
grains, in zones where dark green chlorite is visible. The main pathway localizing the dissolution seems to be fractures, as shown by few peripheral fractures in quartz, showing dissolution textures on their edges. The chlorite fills spaces left by the dissolution and hosts the mineralization. Mineralization that coats grain surfaces, fills intra-grain porosity, forms veins in quartz, and replaces micro-pyrites and parts of large pyrite grains.

4 Isotopic analysis

Four texturally different pyrite generations are observed: (i) anhedral pyrite interpreted as the oldest generation and of metamorphic origin, often associated with a second generation of pyrite overgrowths, and showing dissolution textures; (ii) pyrite overgrowths on the first generation; (iii) disseminated pyrite in hydrothermal chlorite and associated with chalcopyrite; and (iv) framboidal pyrite.

Large pyrite grains (i) have δ34S values ~0‰, consistent with the interpretation of metamorphic origin. Pyrite overgrowths (ii), and the framboidal pyrite (iv) have low δ34S values of -30 ‰, interpreted as forming from bacterial sulfate reduction. Uranium mineralization replaces both framboids and the phyllosilicates filling fractures with the large pyrite grains. Pyrite associated with chalcopyrite in chlorite (iii) has a mean δ34S value of -2.6 ‰, consistent with the supposed hydrothermal origin of the chlorite. Some subeuhedral pyrites in clays from both lower and upper mineralization also have δ34S values of up to +40 ‰. Pyrites with these high isotopic values can be interpreted to have formed from sulfate from Athabasca basinal brines or from a closed S isotopic system where biogenic sulfate reduction depleted the S reservoir of δ32S and continued sulfate reduction formed pyrite enriched in δ34S.

Uranium mineralization postdates all pyrite generations.

5 Discussion

Permeability enhancement in the basement rocks in the Patterson Lake corridor results of a long and complex geological history starting with the high grade metamorphism.

Gneissification in the upper amphibolite to granulite facies formed strong rheological contacts between lithological units. Micro structural analyses on different cores suggest that basement was deformed in pure shear. Within this structural frame, corridors of higher strain developed mylonitic rocks along with fluid circulation, transforming the protolithe into pseudo-pelite.

Micro-fracturation developed in quartz, cross-cutting dynamic recrystallization textures. This event seems to take place in a tensile regime, creating space lately filled with phyllosilicates. This brittle event is well developed in rocks in the vicinity of the orebody but really discrete in rocks outside. As no major fault linked to the mineralization has been intersected in drillhole, the Spitfire area can be seen as a damaged zone, with fracturation acting as conduit for fluid circulation (Caine et al. 1996).

The permeability network hosting uranium-rich mineralization in the basement rocks is interpreted to develop through a combination of physico-chemical mechanisms overprinting the inherited ductile fabric and further deformation in the form of micro-fracturing and associated dissolution processes. Micro-scale observations emphasize that a single event is responsible for the majority of mineralization observed in the Spitfire orebody, which was later on remobilized by an oxidizing event. Most of the mineralization is texturally associated with pyrite. Sulfur isotope results from four different pyrite textures confirm that pyrite precipitation happened in different contexts: metamorphic, hydrothermal, and biological processes. The high δ34S values at the upper mineralization from sample showing a redox front could be linked to basinal brines circulation. Textural evidences show that mineralization post-dates the different textures and uses sulfides as one of the main chemical trap. The presence of chalcopyrite in pyrite and in uranium-oxide-enriched zones raises the question about the potential of copper in the system as a potential tracer.

Acknowledgements

This study was funded by Orano. Purepoint Uranium Group is acknowledged for all the resources provided during this work.

References


The Mineral System concept applied to unconformity-related uranium deposits of the Athabasca Basin (Canada)

Patrick Ledru
Orano Canada Inc., Canada

Abstract. The concept of Mineral Systems (McCuaig and Hronsky 2014) is applied to the formation of unconformity-related uranium deposits in Athabasca Basin (Canada). Critical elements defining such systems are identified in terms of (i) crustal architecture of this part of Laurentia, (ii) transient geodynamics as characterized by the progressive evolution of the structures, their interaction with thermal convection and deformation driven fluid circulation and (iii) fertility of the lithologies. The unconformity at the base of the Athabasca Basin acts as a major interface in which fluid flow has transported and precipitated high-grade uranium deposits, in particular at the intersection with basement hosted graphitic bearing steeply dipping fault systems.

The application of the Mineral Systems concept provides a baseline to reassess strategies and to identify/prioritize the most appropriate technologies at different stages and scales of exploration, from the early regional assessment to resource estimates. Changes in paradigms may be necessary to include not only information collected from drill core but also the architecture of the main structures at regional scales and their ability during successive reactivations to enhance permeability of the systems through organized and focused fluid-flux.

The role and mode of reactivation of these basement faults in connection with the formation of unconformity-related uranium deposits is emphasized and an analogy with Enhanced Geothermal Systems is proposed. In both cases a pre-existing permeability network is stimulated, whether by forceful injection of fluids or by tectonic processes, enabling the creation and maintaining fluid convection at least at the scale of the upper crust, down to the brittle-ductile transition.

1 Defining the critical elements of the unconformity-related uranium deposits of the Athabasca Basin

The Trans-Hudson orogen (THO, 1.84 - 1.78 Ga, Hoffman 1988; Alexandre et al. 2009; Jeanneret et al. 2017) and the Taltson/Thelon orogen (1.9 – 1.8 Ga, Card et al. 2014) are the main Paleoproterozoic orogens that contributed to the assembly of the Canadian Shield, a part of Laurentia, between 2.0 and 1.8 Ga (Hoffman 1988; Eglington et al. 2013) marking the collision between the Superior Province to the east and the Hearne Province and Slave craton to the west (Fig. 1). The Hearne Craton is mainly constituted by the Mudjatik domain, composed of Archean granulitic tonalitic-trondhjemitic gneiss domes and the Paleoproterozoic meta-sedimentary gneisses of the Wollaston domain (Annesley et al. 2015). These domains were strongly imbricated during orogenic processes marked by vertically-accretive growth histories and the development of steeply dipping anastomosed shear zones that extend over several hundred kilometers along strike, mainly the Wollaston-Mudjatik transition Zone (Fig. 2) and the Snowbird Tectonic Zone/Virgin River shear zone (Fig. 1).

![Figure 1. Simplified geology of the Canadian Shield (Jefferson et al., 2017)](STZ: Snowbird tectonic Zone, VR: Virgin River Shear Zone)

This tectonic evolution has been sealed since 1.71Ga (maximum age) by the deposition of basins (Paleoproterozoic to Mesoproterozoic Athabasca, Thelon, Elu and Hornby Bay basins) mainly composed of detrital sediments that rest unconformable over these deeply eroded domains (Fig. 1). The architecture of the lithosphere in this part of Laurentia is characterized by the intersection of deeply rooted anastomosed shear zones, as defined by discrete geophysical signatures (Fig. 2). Transient geodynamics are marked by the polyphased tectonic evolution of these domain defining structures, prior and after the deposition of the detrital basins. Steeply dipping shear zone have undergone intense retroomorphic evolution synchronous of a greenschist metamorphic grade following the development of ductile to brittle reverse fault systems in zones of high rheological contrast and particularly in graphite-rich horizons. Hydrothermal alteration is present in zones of compression marked by significant dissolution, transport and precipitation of silica along with metalliferous elements.
The offset of the unconformity, up to several hundred meters along the Virgin River shear zone (Fig. 1) and the development of fault network within the Athabasca Basin show that these inherited structures have been reactivated several times and used as channels enabling mixing of fluids from basin and basement origin and leaching of metals (Martz et al. 2017, 2018). The dynamics of this system is considered as the main source for high-grade uranium deposits, so called in-gress and egress depending respectively of the downward and upward main flow of the fluids at the unconformity (Fig. 3) (Hoeve and Quirt 2007; Jefferson et al. 2007), as controlled by thermal convection and deformation-driven mechanisms (Li et al. 2017).

The lithologies and the tectonic evolution present favorable features in terms of mineral fertility. A large part of the graphite observed in the main basement fault systems of the Wollaston domain are derived from metal-enriched black shales and incipient melting is the source of uranium enrichment in anatectic melt (McKechnie et al. 2013; Mercadier et al. 2013). Moreover, at this period, the great oxidizing atmosphere event has been able for the first time in Earth history to mobilize uranium in an oxidized complex.

The architecture of part of the Laurentia centered within the footprint of the unconformity at the base of the Athabasca Basin along with the geodynamics and polyphased tectonic reactivation of deeply rooted structures and the fertility of the crust are considered as critical elements favorable for the formation of uranium ore deposits. The presence of low permeability zones within the basin above the unconformity due to clay-rich horizons or silicified zones (diagenetic or hydrothermal origin) and the clamped vertical permeability in the basement fault systems, have contributed to the preservation of primary mineralized zones.

In conclusion, the concept of Mineral Systems (McCuaig and Hronsky, 2014) can be applied to the formation of unconformity related deposits being a dynamic system exhibiting self-organized critical behaviours (Fig. 3).

**2 Implication of the Mineral System concept applied to the exploration of unconformity-related uranium deposits**

Exploration of unconformity-related uranium deposits mainly focuses on identification of lithological, geochemical and mineralogical footprints with an empirical approach that more footprints equals greater chances of finding a deposit. The information collected defines pathfinders that are priori vectors towards mineralization (Jefferson et al 2007; Lesher et al. 2017, IAEA 2018). Common practice for unconformity mineralization drilling programs is to target conductive horizons near the unconformity trying to quantify alteration haloes and geochemical pathfinders. Less focus is put on physical properties and characterization of permeability of structures and lithologies at varying scales.

Experience from historical discoveries, exploration of fertile trends (i.e. along conductors) and recent discoveries in non-conventional targets, like the
unconformity-related Centennial deposit (Reid et al. 2014) and basement-hosted Arrow deposit (Hillacre et al. 2017), provides opportunities to reassess some of the pre-conceived ideas and defined empirical models. Thus the application of the Mineral Systems concept provides a baseline to reassess strategies and to identify/prioritize the most appropriate technologies at different stages and scales of exploration. Changes in paradigms may be necessary to include not only information collected from drill core but also the architecture of the main structures at regional scales and their ability during successive reactivations to enhance permeability of the disposition systems through organized and focused fluid-flux. While footprints provide rather static observations that mainly illustrate the variety of ore deposit models, scientific and drilling targets should also focus on the characterization of the mineral systems, aiming to understanding the dynamics of paleo-hydrothermal systems and conditions for preservation of the deposits using modern geological analogs. In this perspective, the distribution of physical properties and characterization of the permeability of the systems are critical to constrain geophysical modeling and decrease the uncertainty of 3D geological models.

Multiple decades of exploration in Saskatchewan has allowed access to large datasets regarding geology (lithology, mineralogy, alteration, structure), geophysics (airborne, ground and downhole-probing magnetics, gravimetry, EM, MT) and geochemistry (major and trace elements, isotopic composition and geochronology), allowing for data mining, reprocessing and re-analysis. Data and knowledge-driven approaches lead regularly to the discovery of new deposits and even of new metallogenic provinces, like the Patterson Lake trend, hosting the Triple R and Arrow deposits and the Spitfire prospect. This recently discovered trend, displaying up to now only basement-hosted high-grade uranium mineralization, illustrates the need to change our scale of investigation and review our models. The main structural components and observed footprints must be evaluated with the consideration of geophysical imagery, multidisciplinary combined analysis and development of sound 3-D modelling to advance our knowledge of the geodynamics of these terranes. New capacities in artificial intelligence and machine learning are also opportunities to update the known footprint of the deposits based on physical and chemical properties of the lithologies and structures.

3 An analogy between Unconformity-related uranium deposits and Enhanced Geothermal Systems

The application of the Mineral System concept emphasized the role and mode of reactivation of the basement faults in connection with the formation of unconformity-related uranium deposits. Following a recent proposal for a shallow-burial mineralization system driven by magmatic heat sources at depth (Chi et al. 2018), an analogy is proposed with Enhanced Geothermal Systems.

The concept of Enhanced Geothermal Systems (EGS) was defined following experiences of reservoir stimulation in hot dry rocks (Elders 1981, Kelkar et al. 2016). Within regions of high geothermal gradients, temperature may reach more than 200°C at depth less than 5 km that can be attained by borehole doublets. Experiments have shown that the natural permeability network was able to be stimulated by mechanical and chemical processes, mainly through the injection of fluids at the base of an injector well. Structural and fluid flow analysis completed in these boreholes has demonstrated that the stimulation of the permeability was mainly related to the development of fracture systems tightly controlled by inherited reactivated structures within mainly altered lithologies and emphasized the connection between basin and basement-hosted fluid reservoirs (Cathelineau and Boiron, 2010; Geraud et al. 2010; Sausse et al. 2010; Vidal et al. 2017; Vidal and Genter 2018). This EGS is then used for initiating and maintaining a loop enabling injected fluid to exchange heat with the reservoir and transfer it to the surface to produce electricity. This concept has also been applied to active geothermal field as it has been proven that reinjection of fluid in the reservoir was a condition for maintaining a sustainable exploitation of the vapor.

A comparison between the Athabasca Basin and the Rhine Graben, where the borehole triplet of the Soultz EGS project has reached fractured Variscan granite at 5000 m depth, below the unconformity at the base of the Mesozoic sequence, shows striking similarities (Fig. 4).

Figure 4. Comparison between the Rhine Graben and the Athabasca Basin and main fluid flow (Boiron et al. 2010; Cathelineau and Boiron 2010).

The role of the basement fault system, heat convection and deformation driven mechanisms for fluid flow modeling are very comparable. In both cases a preexisting permeability network is stimulated, whether by forceful injection of fluids or by tectonic processes,
enabling the creation and maintaining fluid convection at the scale at least of the upper crust. The temperature range to which this stimulation occurs is around 200°C for both environments and fluid rock interactions are observed, marked by the leaching of large volume of rocks and progressive enrichment in metals. It is considered that the knowledge gained during several decades of EGS experiments can be applied to a paleo-enhanced geothermal system: the unconformity-related uranium deposits of the Athabasca Basin.

References


Cathelineau M, Boiron MC (2010). Downward penetration and mixing of sedimentary brines and dilute hot waters at 5 km depth in the granite basement at Soultz-sous-Forets (Rhine graben, France). C. R. Geoscience 342, 560–565


Tran HT, Kevin A, Bethune KM, Ashton K, Hamilton MA. (2008), Provenance and tectonic setting of Paleoproterozoic metasedimentary rocks along the eastern margin of Hearne craton: Constraints from SHRIMP geochronology, Wollaston Group, Saskatchewan, Canada. Precambrian Res 167:171-185


Mineral Systems to Exploration Systems to Research Roadmaps

T. Campbell McCuaig,
*BHP Geoscience Centre of Excellence, Perth, Western Australia*

Stephen Busuttil
*BHP Copper Exploration, South Australia*

Keenan Jennings, Elizabeth R. Sharman, Jean des Rivières
*BHP Copper Exploration, Santiago, Chile*

Abstract. A systems approach to understanding how earth processes combine across spatial and temporal scales to form economic concentrations of mineralisation has been progressively adopted over the last 40+ years. More recently, the marriage of the mineral system to the exploration process has been more effectively established. What remains to be realised is the use of a systems approach to guide research roadmaps. When applying a mineral systems analysis to exploration decisions, we note that large value decisions can hinge upon highly uncertain knowledge. We consider these gaps opportunities for focused fundamental geoscience research. We propose that using a mineral systems approach to highlight high-value fundamental research questions is an effective way to align research institutions and industry, and to better focus research investment on improving exploration success.

1 The Adoption of Mineral Systems

Over the past 40 years there has been a progressive adoption of a ‘systems’ approach to understanding the genesis of various styles of mineralisation. Prior to adopting mineral and petroleum systems, the economic accumulation of mineralisation was largely classified taxonomically by analogue deposit model descriptions. A systems approach is fundamentally different in that it focuses on understanding the fundamental earth processes that must align to form economic concentrations of mineral and petroleum resources. First formally postulated for the petroleum industry in the 1970’s (Dow, 1974) and then effectively translated into practice in the 1990’s (Magoon and Dow, 1994; Magoon and Beaumont, 1999), it was adopted in the minerals industry in the 1990’s (Wyborn et al., 1994) and translated into practice in the 2000’s and 2010’s (e.g. Kreuzer et al., 2008; 2010; McCuaig et al., 2010; 2018; McCuaig and Sherlock, 2017).

The progressive adoption of a systems approach to mineralisation can be illustrated in the economic geology community’s progressive understanding of porphyry copper deposits (PCD). Originally found by prospecting, PCD were observed to be associated with intrusive rocks. A landmark body of research in the 1960’s led to the recognition of remarkably similar zonation of minerals around PCD (Lowell and Guilbert, 1970), which reflected the interaction of heat and fluids from the mineralising system with the surrounding host rocks at the site of metal deposition. This analogue model was then successfully applied to vector into partially covered systems to aid discovery. The concurrent growing understanding of plate tectonics provided a framework within which PCD were recognised as forming in volcanic arcs at destructive plate boundaries. The genesis of these deposits was largely seen as controlled by what happens in the upper 8km of the crust, and much research focused on understanding this part of the system.

Fast forward to the present day, and PCD are now more commonly viewed in a multi-scale process-based systems framework. It is now recognised that PCD form in brief geological periods in the history of a volcanic arc, within which fertility is interpreted to be controlled by geodynamics and processes deep in the crust that produce high volumes of hydrous, oxidised melt (e.g. Richards, 2011; Loucks, 2014). Whether or not economic concentrations of metal form within these fertile time periods and arc segments is controlled by conditions of emplacement in the upper crust. This multi-scale approach, through both space and time, to understanding PCD mineral systems is now impacting on exploration strategies for this important deposit type.

2 The Application of the Mineral System Concept in Exploration

The key to application of mineral systems in exploration is to marry the geological understanding of the mineralisation across spatial scales to natural decision points in the business. These decisions can be grouped as (McCuaig and Sherlock, 2017; McCuaig et al., 2018):

- Regional scale targeting – what basin/belt/arc/district has the potential of hosting a substantial mineral system?
- Camp scale targeting – where within the basin/belt/arc/district could a number of deposits be clustered?
- Prospect-Deposit scale targeting – where is there an orebody of sufficient quality within the camp or cluster of deposits?

Figure 1 illustrates this subdivision of the mineral system conceptually. At each scale, one can identify the relevant critical processes that are interpreted to operate...
in the system, the geology that is interpreted to represent the operation of those processes, and the spatial datasets or synthesis knowledge products that can be used to make the area selection decision. The coloured boxes show the areas of emphasis at each scale, from large scale processes that establish the potential for a large mineral system at the regional scale down to specific processes of deposition/accumulation and the preservation of a high-quality resource accumulation at the deposit scale.

3 Creation of Research Roadmaps from Mineral System Maps

Applied correctly, a systems approach to guiding exploration targeting also reveals gaps in understanding of the mineralising process across the range of scales of exploration decisions. Where do we not understand the process? Where are we unable to link geological expression to process? Where are we using datasets, or interpretations that are not necessarily representative of the critical process or geological elements being targeted? If major exploration decisions are being pinned on any of these aspects that have a high uncertainty, then these aspects become potentially high-value avenues for fundamental geoscience and technology research to develop appropriate tools and mappable spatial proxies.

In sediment-hosted systems, for example, a systems review of conventional and unconventional petroleum, sedimentary rock-hosted copper, lead-zinc and uranium revealed some common gaps in understanding (McCuaig et al., 2018):

- Basin hydrodynamics – what are the mechanisms of brine and petroleum expulsion from, and migration through, basins?
- Timing of fluid movement – what are the timescales of brine and petroleum movement through basins (e.g. the timing controversy over the genesis of sedimentary rock-hosted copper and lead-zinc systems; how do some reservoirs seem to fill faster than petroleum should theoretically migrate in some young petroleum systems?)
- Specific to metals: what are the dynamic physics and the interplay between solubility and transient permeability under varying stress fields in leaching of metal by a brine in source rock regions?

Moreover, such fundamental knowledge gaps in the mineral system can be mapped to appropriate scale of influence on the exploration targeting process. For example, Figure 2 shows some of the large outstanding questions in the genesis of high quality hypogene PCD systems.

Of note is our lack of understanding of the physical (c.f. chemical) controls on mineral systems. Over the past 20 years, ever more precise geochronological constraints on mineral deposits has shown that mineralisation processes can happen very fast. Much of our understanding is built on the forensic dissection of mineral deposits and their larger geological context by careful documentation of geological relationships, their multiscale (nano- to regional scale) chemistry, mineralogy, and structural geology. However, much of the mineralising process appears to occur on timescales that cannot be resolved by traditional radiometric geochronological techniques. A more fundamental understanding of the dynamic physics of the systems may be required for us to generate a step change in our ability to understand the genesis of high quality mineralisation and thereby better predict its location under cover.

Researchers are, in the context of tightening research budgets, increasingly seeking areas to apply fundamental research to industry challenges. By using a mineral systems approach applied to exploration decisions, identification of high-value research initiatives can be achieved that not only better align exciting and innovative fundamental geoscience research efforts to application in industry, but better direct the limited resources towards this goal.

Figure 1. Diagram summarising the mineral system application of conceptual targeting across spatial scales. Top: relative inputs of prediction versus detection and discrimination technology from broad regional scale at left to prospect scale at right. Also shown are relative trends in flexibility of exploration programs, direct costs versus opportunity costs, and uncertainty. Middle: diagram summarising mineral systems translated to the three scales of exploration decision – regional terrane selection, camp-scale targeting, and prospect delineation. Bottom: key activities of area selection, data gathering (precompetitive vs. new proprietary), strategic versus tactical response, and exit decisions across scales. See text for discussion. Modified from McCuaig and Sherlock (2017) and McCuaig et al. (2018).

Figure 2. Research roadmap showing major areas of uncertainty in the PCD mineral system, expressed across scale and exploration decision as depicted in Figure 1.
Acknowledgements

The authors acknowledge discussions with numerous geoscience colleagues in BHP who have contributed to the thoughts expressed in this abstract.

References


Evaluating the role of the mantle as a source of metals for magmatic-hydrothermal ores in arc systems

José María González Jiménez, Fernando Gervilla, Claudio Marchesi & Juan José Rovira
Departamento de Mineralogía y Petrología, Universidad de Granada, Facultad de Ciencias, Granada, Spain.

Fernando Tornos
Instituto de Geociencias, Consejo Superior de Investigaciones Científicas-Universidad Complutense de Madrid (CSIC-UCM), Spain.

Rubén Piña
Departamento de Mineralogía y Petrología, Facultad de Ciencias Geológicas, Universidad Complutense de Madrid, Spain

Vanessa Colás
Departamento de Procesos Litosféricos, Instituto de Geología, Universidad Nacional Autónoma de México, Ciudad Universitaria, México

Edward Saunders
Division of Earth Sciences, School of Environmental and Rural Science, University of New England, Australia

Graham C. Begg
Minerals Targeting International PL, Australia

Abstract. This communication reviews geochemical data on the sub-arc mantle underlying ore-productive arc crust. We highlight that re-fertilization of the subcontinental lithospheric mantle by subduction-related fluids might be a key factor in forming metal-rich domains that contribute to the formation of parental magmas able to generate large metallogenic provinces in the Earth’s crust. As noted in several other previous works, the optimal alignment of factors to produce these types of deposits embraces three common features: a mantle source region that has been previously enriched in metals (e.g., Au and Cu), trans-lithospheric faults and a tectonic, possible thermal trigger. The results and interpretations we provide here are a complementary view to current crust-related enrichment models.

1 Introduction

Our current view of the Earth’s interior dynamics envisions repeated cycles of melt extraction from a convecting fertile mantle, producing a mafic crust (which could differentiate to form continental crust) and a complementary residual depleted mantle (DM). Each crust-formation/depletion episode is followed by a period of recycling, during which the mafic crust is partially or totally mixed back into the convecting mantle or stored deep in the Earth. This scenario, usually taking place during an orogeny, is very favorable for the chemical exchange between different Earth’s layers, and therefore for the formation of large ore deposits. These deposits host some of the major mineral wealth in the Earth and provide the largest world resources of copper and gold, plus a significant source of other base (zinc, lead, iron, silver) and critical metals hosted in different styles of the mineralization.

Geoscientists have turned to a number of proxies in an effort to answer questions such as: when did recycling start, did these cycles operate continually or episodically through time, and how efficient is the convective recycling, particularly at the time to generate those metal-enriched melts. Most of the proxies involved the chemical and isotopic analysis of the ore deposits. However, this only provides an indirect view on the foundational controls able to generate these metal-rich magmas in the convecting mantle. Indeed, the best approach is to study samples representative of the mantle. These samples are nowadays accessible in tectonically uplifted slices and in xenoliths from volcanic rocks.

Perhaps, the highly siderophile elements (including PGE and Au) are the most robust of the geochemical proxies for the study of these metal-rich magmas in the upper mantle. These highly siderophile elements (HSE) have stronger affinity for metal than the chalcophile Se, Se, Te and Cu [Luguet and Reisberg 2016]. In the Earth’s mantle they are mainly hosted within accessory base-metal minerals (BMM, including sulfides, arsenides and sulfarsenides; [Luguet and Reisberg 2016]) and refractory platinum-group minerals (PGM; [O’Driscoll and González-Jiménez 2016]). Magmatic processes such as partial melting, crystallisation and melt-rock interaction can strongly fractionate HSE, S, Se, Te and Cu. As a result of moderate degrees of mantle melting, the most refractory PGE (IPGE: Os, Ir, Ru) behave as compatible elements, while the less refractory PGE (PPGE: Pt and Pd), Au, Re, S, Se, Te and Cu are more incompatible [Luguet and Reisberg 2016]. Hence, the HSE and chalcophile elements can be used along with lithophile elements to unravel the multistage magmatic history of a mantle domain, and therefore mechanism of mass transference of metals between the different layers of the Earth.

Of particular interest is the potential use of the PGE
and Au as tracers of mantle processes able to generate metal-rich magmas that are eventually involved in the ore forming magmatic-hydrothermal systems in the arc crust. It is well accepted that in arc settings, the oxidation state of primitive melts is directly correlated with the amount of fluids released from the dehydration of the subducting slab (Kelley and Cottrell 2009). At fO2 conditions typical of an oxidized mantle wedge (FMQ+1 to +3), the dominant sulfur species is S+6, and thus sulfur solubility increases significantly from typical mantle concentrations of ~200 ppm (at FMQ<1) to S contents in excess of 1 wt% (Jugo et al. 2010). Empirical and experimental works indicate that S is supplied to the migrating hydrous-oxidizing silicate melts after the removal or pre-existing trace sulfides resident in the peridotites (Hattori et al. 2002). As noted above, these sulfides, together less abundant alloy phases, control the budget of metals such as Au and Cu in the mantle (Luguet and Reisberg 2016). Therefore, the degree of enrichment of metals in S-rich melts in the mantle is associated with the degree of partial melting of the mantle source and its previous history of depletion or re-fertilization. In particular, regional-scale re-fertilization processes by oxidizing subduction-related fluids may have enhance dissolution of sulfides at deep mantle sources and their later precipitation along sizeable (> 100 km) domains at shallower upper mantle. These metasomatic sulfides can be significantly charged in Au, Cu, Co, and other incompatible chalcophile elements (e.g., Wang et al. 2009; Lorand et al. 2013; Hughes et al. 2017; Tassara et al. 2017, 2018).

2 Transfer of metals from subducting slabs to sub-arc mantle

2.1 Dehydration of subduction channel serpentinites

Subduction zones not only return oceanic lithosphere into the mantle but are also sites where water and other components are transferred from the subducting plate back to the lower/upper crust. During subduction, downgoing oceanic crust that has an important volume of sediments may dehydrate releasing hydrothermal fluids enriched in in fluid-mobile elements (e.g., As, Sb, Cs, Pb, Li or Ba). The main dewatering takes place at temperatures between 300 and 600 °C and pressures lower than 15 kb. The upward percolation of these fluids may induce hydration of the overlying peridotite wedge beneath the crust of continental or oceanic arcs. Hydration may produce the partial or total transformation of the peridotite to serpentinites, which act as sponges for a wide suite of elements such as semi-metals (As, Sb, Se), and base (Fe, Zn, Cu) and precious metals (Au, Pd, Pt). The study of some subduction channel serpentinites seems to indicate that anomalously high contents of metals are directly associated with the formation of Ni-As-Sb-S rich minerals, including sulfides, arsenides and sulfarsenides. Particular enrichment of these minerals is observed in serpentinite shear zones, which are interpreted as a preferential pathway for fluid movement [González-Jiménez et al. 2016]. Continued movement downward of the already hydrated sub-arc lithosphere promotes burial of these serpentinites while they are progressively heated (i.e., prograde metamorphism). As result minerals carrying the metals are destabilized while liberating metal-leaden fluids that infiltrate deeper regions of the sub-arc mantle. The subduction channel serpentinite from the Cerro del Almirez in south Spain are good examples of this process of dehydration involving the releasing of metal-rich fluids. Here, antigorite serpentinites of oceanic origin are dehydrated to secondary chlorite harzburgite and both these rock-types crop out in the massif. This is the unique example in the world where the isograd of antigorite breakdown crops out in the Earth’s surface. Our systematic study of the bulk-rock abundances of highly siderophile elements (Ir, Ru, Rh, Pt, Pd, Au) in these rocks show significant partitioning of gold towards the fluids released by the dehydration of serpentinites, confirming previous observations subduction-related melts may promote Au enrichment of specific portion of upper mantle (Saunders et al. 2018). Interestingly, the crustal section overlying this portion of mantle infiltrated by these subduction-related fluids charged in Au and other noble metals contain various districts of Au-Ag epithermal deposits.

2.2 Mobility of metal-rich serpentinite-related fluids within the sub-arc mantle

As associated with corner flow may produce the downward movement of the hydrated sub-arc peridotitic rocks. Once heated, these rocks may release fluids enriched in metals. The upward percolation of these fluids through the overlying mantle wedge may produce metasomatism while dissolving pre-existing metal-rich minerals. For example, Hattori et al. (2002) noted that sulfides in peridotite mantle xenoliths that sampled the sub-arc mantle from the Ichinomegata in Japan and Nunivak Island in Alaska have lower contents of As and Sb than sulfides from the primitive mantle. Hattori and co-workers concluded that these lower contents of As and Sb reflect the removal of metasomatic sulfides residing in the mantle during partial melting, consistently with high values in some mantle wedge xenoliths attributed to fluid transport of these elements during mantle metamorphism. Lower contents of As and Sb may also reflect a quick transference of elements by aqueous fluids from the subducting slab/mantle wedge serpentinite to arc magmas without residing long in the mantle. These authors also noted that high abundances of As, Sb and S in arc magmas generally could reflect their enrichment in mantle wedges, although they did not find any evidence of such enrichment in mantle wedges. This suggests that these semimetals were removed from mantle wedges by hydrated arc magmas.

3 The metasomatized mantle as a source for the parental melts of Au-rich magmatic-hydrothermal deposits

New discoveries – new views: Advances in the Science of Mineral Exploration 1187
3.1 Porphyry copper deposits (PCD)

The infiltration of these metal-rich fluids through specific regions of the sub-arc mantle may not only produce dissolution of pre-existing metal-bearing minerals but also deposition of assemblages, giving rise to metal-fertile domains. The size of these domains may range from microns to terranes and are relatively durable until the metal-rich minerals are removed, thus contributing to the formation of metal-rich magmas (e.g., Griffin et al. 2013).

Mantle xenoliths rapidly brought to the surface by volcanism have provided valuable information about the nature and evolution of this type of processes, particularly in those sections of the upper mantle beneath arc crusts hosting Au-rich porphyry and epithermal deposits. For example, xenoliths of arc-related mantle from near the giant Lihir gold deposit in Melanesia show metasomatic enrichment in Cu and Au. McInnes et al. (1999) reported that the Au ores of this deposit exhibit Os isotopic compositions identical to the metal-enriched peridotite xenoliths. Furthermore, there is a direct relationship between high Cu tonnages in Chilean PCD and their low initial Os ratios (Mathur et al. 2000), suggesting the input of mantle-derived melt. Similarly, xenoliths that have sampled the SCLM beneath the edge of the South China Craton also exhibit anomalously high values of Au in whole rock (14 ppb) and sulfide minerals (5 ppm). These values of gold in the SCLM beneath ore productive crusts are relatively higher than those of both the asthenospheric (about 1 ppb Au) and the non-re-fertilized lherzospheric mantle [Griffin et al. 2013 and references therein]. Additionally, Hanley et al. (2010) have documented PGE incorporation into pyrite coincident with Co-Ni enrichment during high-temperature hydrothermal events pre-dating Cu and Au precipitation in porphyry deposits from British Columbia. The formation of these ore deposits is linked with alkaline arc magmas derived probably from an enriched (metasomatized) mantle source.

The enrichment in gold (and other noble and base metals such as PGE and Cu) observed in the SCLM underlying arc crusts hosting PCD could be associated with preferential channeling of primitive mantle melts through zones of weakness that exist between buoyant domains of ancient SCLM [c.f. association of Ni-Cu-PGE deposits with craton margins (Begg et al. 2010, 2017)]. Such enrichment in metals in the SCLM beneath ore-productive crust seems to be associated with modal metasomatism due to migration of melts at decreasing melt-rock ratios, which may result in the modification of the bulk PGE and Au contents of the peridotite via the precipitation/dissolution of PGE- and Au-bearing Ni-Cu-rich sulfides and/or Pt-Pd-rich PMGs. The domains of the SCLM enriched in these precious metals may range from microns to kilometers and the mobility of the precious metals can take place in the form of sulfide melts [Tassara et al. 2018], solid metal alloys [O’Driscoll and González-Jiménez 2016] or (supercritical) oxidizing, volatile-rich (C-O-H-S±Cl) fluids of carbonate-like affinity [Hughes et al. 2017; Tassara et al. 2018]. Griffin et al. (2013) have suggested that such domains of metasomatized SCLM are relatively durable and may store metals (e.g., Cu and Au) until a later melting event is triggered, leading to episodic formation of ore deposit. Repeated events of melt migration during one or more orogenic cycles may promote multiple episodes of mineralization in the overlying crust.

3.2 Epithermal Au–Ag deposits

The ultramafic xenoliths hosted in the alkali basalts from volcanic fields in the back-arc of the Andes and the neighboring Patagonian realm (i.e., Deseado and North Patagonian Massifs) preserve the record of a protracted history of melt depletion and re-fertilization of the SCLM beneath South America. The styles of metasomatism include silicate, silicate-carbonatite and pure carbonatite-like affinities, which have been in some cases attributed to dehydration of subducting slabs. The recent work by Tassara et al. (2017) has revealed the presence of gold minerals in the portion of SCLM beneath the auriferous province of the Desado Massif in the Argentinian Patagonia. This area hosts several Au–Ag epithermal deposits including low and intermediate sulfidation veins associated with calc-alkaline rhyolites, basaltic andesites and basalts from the Chon Aike silicic large igneous province (CA-SLIP) related with the break-up of Gondwana and the subsequent separation of South America and Africa. These results provide the first evidence that link the formation of Au-epithermal deposits in the crust with a mantle source enriched in Au. Tassara and co-workers have suggested that a precursor stage of mantle re-fertilization by plume-derived melts generated a gold-rich mantle source during the Early Jurassic when the aperture of the Atlantic sea separated South American from Africa. The interplay of the enriched mantle domain and subduction-related fluids released during the Middle-Late Jurassic resulted in optimal conditions to produce the ore-forming magmas.

Our preliminary results on the study of mantle xenoliths that have sampled the SCLM beneath the Mesa Central in Mexico also show the presence of several nano-to-micron size particles of gold in metasomatic glasses. This volume of the SCLM enriched in gold is also underlying a back-arc crust with epithermal Au deposits. In this case, metasomatism of the SLCM is related with the infiltration of dehydration fluids released from the subducting Pacific plate.

Acknowledgements

This research was financially supported by FEDER Funds through the project RTI2018-099157-A-I00 and CGL2015-65824-P granted by the “Ministerio de Ciencia, Innovación y Universidades” J.M.G.J. acknowledges financial support of the Ramón y Cajal Fellowship RYC-2015-17596 granted by the Spanish MINECO.

References

Begg GC, Hronsky JAM, Arndt NT, Griffin WL, O’Reilly SY, Hayward N, (2010). Lithospheric, cratonic, and geodynamic setting of Ni-
The metal budget above subduction zones: evidence from pyroxenite xenoliths

Hannah S. R. Hughes¹, Magdalena M. Matusiak-Małek², Iain McDonald³
¹Camborne School of Mines, University of Exeter, Cornwall, UK
²University of Wrocław, Wrocław, Poland
³School of Earth and Ocean Sciences, Cardiff University, Cardiff, UK

Abstract. Highly siderophile elements (HSE) which, in the absence of a metallic liquid, may behave in a chalcophile manner, are largely hosted by base metal sulphide (BMS) minerals in the peridotitic asthenospheric mantle. Such elements including Cu, Au, Mo, platinum-group elements (PGE) and Co have an affinity for S. Therefore, during partial melting of mantle peridotites, their BMS and metal budget is released into the magma generated. This classic model underpins metallogenesis and the concept of ‘fertility’ of a magma in certain tectonic environments – for example, above subduction zones. But what proportion of these metals become trapped in the lithospheric mantle and lower crust during magma ascent? We use Scottish and Swedish pyroxenite xenoliths to assess the palaeo-tectonomagmatic environment of the Grampian event (during which there was active oceanic subduction) of the Caledonian orogeny.

1 Caledonian pyroxenite xenoliths

Pyroxenite xenoliths are characterized by cumulus textures. They may be of upper mantle or lower crustal origin. On the basis of trace element geochemistry for Scottish and Swedish pyroxenite xenoliths (and other global examples), these rocks have been interpreted as fragments of crystalized basaltic (alkaline and tholeiitic) magma underplating the continental crust (e.g., Downes et al., 2007). Pyroxenite xenoliths are therefore directly analogous to material from the melting, assimilation, storage and homogenization (‘MASH’) zone overlying subduction environments (Hildreth & Moorbath, 1988; Richards, 2003 and references therein), and hence provide a unique insight into the magma and metallogenic processes operating below porphyry mineralising systems.

Scotland has experienced multiple tectono-magmatic events and provides an ideal framework to test the metallogenic record of the lithospheric mantle and lowermost crust (or MASH zone). In situ BMS analysis of
Scottish peridotite xenoliths has already shown that there are detectable regional trends in metal content. Caledonian basement forms the southern terranes of Scotland, south of the Great Glen Fault (GGF) and provides a direct comparison between on- and off-craton lithospheric mantle and lower crust geochemistry. Cobalt is consistently elevated in peridotite xenolith BMS from south of the GGF (> 2.9 wt.% Co) but is found to be considerably lower in BMS of peridotite xenoliths north of the GGF (< 0.36 wt.% Co). The cause for this persistent Co enrichment south of the GGF remains unclear – Hughes et al. (2016) suggested that the subduction of the Iapetus during the Caledonian Orogeny was critical to this process. But is this Co enrichment echoed in the equivalent pyroxenite xenoliths from these terranes? Are there distinct differences between the HSE and chalcophile element characteristics of peridotite and pyroxenite suites per terrane?

2 Methods

In situ mineralogical and geochemical analyses of BMS within pyroxenite xenoliths are used to measure the metal budget of the MASH zone and gain an insight into the mobility of HSE and chalcophile elements in a suprasubduction mantle wedge.

Major element abundances (S, Fe, Ni, Cu, Co) of the BMS were measured by electron microprobe. Laser ablation ICP-MS was then conducted at Cardiff University and performed on each BMS in a single pyroxenite xenolith. Both line and spot analyses are used depending on the size of each BMS. The full suite of minor and trace elements analysed include and Co, As, Se, Ru, Rh, Pd, Ag, Cd, Sb, Te, Re, Os, Ir, Pt, Au, Bi, Pb and Mo.

Using these data, married to the textural characteristics of each BMS and its petrographic siting (e.g., interstitial vs included) within each xenolith, we ask: (1) What were the parental melts (and/or metasomatic characteristics) of these cumulates? And (2) what is the pyroxenitic metal budget in the context of the mineralization potential of the region (in this case, Caledonian)?

3 A role for volatiles and semi-metals?

Previous studies of peridotite and eclogite-hosted BMS in mantle xenoliths and inclusions in diamonds have displayed ambiguous trends in semi-metal concentration, despite clear differences in their precious metal abundance (e.g., McDonald et al., 2017). Yet the role of semi-metals, such as Se, Te, As and Bi, in affecting the partitioning of chalcophile elements in BMS fractionation during cooling is relatively well documented (for example, in PGE mineralizing systems – e.g., Holwell & McDonald, 2010). Further, populations of BMS associated with carbonate and phosphate minerals in mantle peridotite xenoliths have unexpectedly rich precious metal contents (particularly Ir-group IPGE) and Ni abundances (Hughes et al., 2017). This could be indicative of an efficient volatile-rich ‘fluxing’ of BMS and their metal budget, bypassing the traditional partial melting scenario of mantle sulphides and temporally linked to carbonatitic magmatism. These semi-metal and volatile-based controls on BMS mobility, preservation and metal budget may have significant implications for metallogenesis, not least in the volatile-rich subduction zone environments underlying and feeding porphyry systems.

In this study, we aim to ascertain the underlying controls on subduction-related metallogeny. We seek to understand the efficiency of metal budget migration during partial melting and magma ascent in suprasubduction zones and assess how much melt becomes trapped within the MASH zone.

Acknowledgements

This project is funded by the Polish National Science Centre grant no. UMO-2016/23/B/ST10/01905.

References


Crustal-scale controls on zinc-lead-silver deposits of the North Australian Zinc Belt: evidence from lead isotope geochemistry and surface wave tomography

David L Huston, David C Champion, Karol Czarnota, George M Gibson
Geoscience Australia
Mark Hoggard, Fred Richards
Harvard University
Bryant Ware, Svetlana Tessalina
Curtin University
Graham Carr
Commonwealth Scientific and Industrial Research Organisation

Abstract. The North Australian Zinc Belt is the largest Zn-Pb province in the world, containing three of the ten largest individual deposits known. Despite this pedigree, exploration in this province over the last two decades has not been particularly successful, yielding only one significant deposit (Teena). One of the most important aspects of exploration is to choose regions or provinces that have greatest potential for discovery. New results from the North Australian Zinc Belt highlight previously unused datasets that may assist area selection and targeting at the craton- to district-scale.

Lead isotope mapping in the North Australian Zinc Belt using analyses of mineralized material has identified a gradient in \( \mu^{238U/204Pb} \) that coincides closely with many major deposits. Similarly, the locations of these deposits also coincide with gradient in the depth of the lithosphere-asthenosphere boundary as determined from surface wave tomography. The change from thicker to thinner lithosphere is interpreted to localize prospective basins for Zn-Pb and Cu-Co mineralization, a change that is also thought to control the gradient in lead isotope data.

1 Introduction

Sediment-dominated basins are by far the largest global source of zinc and lead, containing 54% and 68% (D Huston, B Eglington, S Pehrsson and S Peircey, unpublished data), respectively, of the world's pre-mining resources of these metals. Because of the giant size of these deposits, they are attractive exploration targets but difficult to find owing to their rarity in comparison to other zinc-lead deposits such as volcanic-hosted massive sulfide deposits.

Despite their attractiveness, very few major deposits have been discovered in the last two decades. One of the reasons for this has been a poor understanding of fundamental, large-scale controls on mineralization: given that there are hundreds of basins present in the world, are there ways to screen prospective from un-prospective basins?

The North Australian Zinc Belt, which is hosted by the Paleo- to Mesoproterozoic North Australian Basin System (Southgate et al. 2000, 2013), is the richest zinc province in the world, containing a total pre-mining resource of 89 Mt Zn and 41 Mt Pb, or 10% and 13% of global pre-mining resources of these metals. As part of its Exploring for the Future program, Geoscience Australia is acquiring new and reprocessing old data sets to provide industry with new exploration tools for iron-oxide copper-gold and basin-hosted Zn-Pb and Cu-Co deposits. As part of this program we have been assessing a range of criteria to distinguish fertile mineral provinces, including spatial variations in lead isotope and surface wave tomographic data. This re-assessment has led to some surprising relationships between these two datasets and the distribution of basin-hosted Zn-Pb deposits. This contribution presents the evidence for these relationships and then speculates as to possible reasons for the relationships.

2 The North Australian Zinc Belt

The North Australian Zinc Belt (Fig. 1) contains three of the ten largest Zn-Pb deposits in the world (McArthur River (Hyc), Hilton-George Fisher and Mount Isa) as well as several other smaller, but still important deposits (Century, Dugald River, Teena, Lady Loretta and Cannington). Of these, only Teena is a recent (2013) discovery. In addition, significant Cu-Co, as well as Zn-Pb resources, are being defined at the Walford Creek deposit.

Figure 1 shows the surface geology of the North Australian Zinc Belt and the location of sediment-hosted Zn-Pb and Cu-Co deposits as well as iron-oxide copper gold and orogenic gold deposits. The North Australian Basin System, which hosts the North Australian Zinc Belt,
has been subdivided into three superbasins, the 1780-1740 Ma Leichhardt, the 1730-1640 Ma Calvert and the 1640-1595 Ma Isa superbasins (Gibson et al. 2016). A continental extensional setting for formation of the Leichhardt and Calvert superbasins is widely assumed. The Leichhardt Superbasin consists of a rift filled with continental tholeiites, fluviatile to lacustrine siliciclastic and minor carbonate rocks (Jackson et al. 2000). The Calvert Superbasin consists of shallow marine siliciclastic and carbonate rocks in the west, but deeper marine siliciclastic rocks in the east that mostly lack carbonates but contain coeval mafic sills and possible lavas (Jackson et al. 2000; Southgate et al. 2013). Deposition of the siliciclastic dominated succession in the east coincides with erosion and development of an unconformity and emplacement of granites to the west (Neumann et al. 2009). The uppermost Isa Superbasin consists of fluvial to deep marine sandstone, siltstone and dolostone (Southgate et al. 2000).

The North Australian Basin System has been compartmentalized into third and fourth order sub-basins by long-lived north-northeast- and northwest-trending faults (Fig. 1). The former are steep to subvertical and thought to have been inherited from the underlying ≥1840 Ma crystalline basement. The northwest-trending faults are mainly of Calvert age and form a right-stepping en echelon array of crustal-scale normal faults along the western margin of the Lawn Hill and Mount Isa regions (Fig. 1) where the majority of Pb-Zn deposits are located. This array originated during northeast-southwest-directed extension and broadly marks the western limits of bimodal magmatism and lithospheric thinning during Calvert (and earlier) time (possibly indicating a craton edge). Along with the older basement faults, these Calvert-age faults were reactivated during later basin-forming events and strongly influenced the location and distribution of younger, more easterly-trending sub-basins making up the Isa Superbasin. Calvert-age faulting and rift-related basaltic magmatism concluded at or before 1655 Ma, to be followed by thermal subsidence, basin inversion and orogenesis from 1650-1640 Ma (Riversleigh Event). Subsequent to this event, extension resumed in a north-south-directed orientation and continued through until ca. 1620 Ma when terminated by onset of the Isan Orogeny. Orogenesis and sedimentation in the Isa Superbasin came to a close around 1575 Ma. No basaltic rocks are present in this basin which, with the exception of a few tuff horizons and late ~1620 Ma rhyolite sills, was largely amagmatic in character.

The sediment-hosted Zn-Pb deposits are hosted by the Calvert and Isa superbasins. The oldest deposits, which include the Cannington and Pegmont deposits, formed at ~1680 Ma in the eastern, siliciclastic-dominated, part of the Calvert Superbasin (hereafter siliciclastic-mafic deposits). The upper part of the Calvert Superbasin hosts the ~1665-1645 Ma Dugald River, Mt Isa, Hilton-George Fisher and Lady Loretta deposits, whereas the Isa Superbasin hosts the ~1640 Ma McArthur River and Teena deposits as well as the ~1575 Ma Century deposits further to the north and west. These deposits (hereafter siliciclastic-carbonate deposits) are hosted in dolomitic and carbonaceous siltstone units within successions that contain abundant carbonate but lack significant volcanic rocks. In contrast, the succession that hosts the Cannington and Pegmont deposits lack carbonate but contain abundant shallow-level mafic sills. Importantly, many of the deposits are hosted by carbonate-rich sediments.

3 Variations in lead isotope data

Previous studies (Huston et al. 2014, 2016) have indicated variations in parameters such as $\mu$ ($^{238}$U/$^{204}$Pb), as determined from lead isotope data, can indicate the spatial distribution and fertility of mineral provinces. Figure 2 shows spatial variations in $\mu$ (calculated using the Stacey and Karmer (1975) lead isotope evolution model) in the North Australian Zinc Belt as determined mostly from analyses of ore-related galena and Pb-rich pyrite from deposits and prospects. $\mu$ increases from northeast to southwest, and most siliciclastic-carbonate Zn-Pb and the Tick Hill orogenic gold deposits are localized along a north-northwest-trending break in $\mu$ values. Interestingly, these deposits have a relatively consistent spacing of about 140 km along this break. Iron-oxide-copper-gold and siliciclastic-mafic Zn-Pb deposits are located to the east of this break. Other parameters determined from lead isotope data, including $\kappa$ ($^{235}$Th/$^{238}$U) and $\omega$ ($^{232}$Th/$^{208}$Pb), also define a similar break.

In detail, the break in $\mu$ appears to be en echelon, broadly following the trend of the northwest-trending Calvert-age structures with individual offsets or steps determined by the position of the underlying north-northeast basement structures. As both sets of structures are thought to have been active during formation of the Calvert and Isa superbasins and their sub-basins, it
would appear that variations in $\mu$ mimic development of these sub-basins along the isotopic break.

4 Lithosphere-asthenosphere boundary as defined by surface wave tomography

Figure 3 shows that the locations of major deposits coincide with the edge of thick lithosphere, as defined from surface wave tomography (Fishwick and Rawlinson 2012) using the 170 km thickness contour. All deposits in the North Australian Zinc Belt, including Zn-Pb deposits hosted by carbonate-rich and siliciclastic-dominated succession and iron-oxide copper-gold deposits are within 200 km of the 170 km thickness contour; outside of this corridor major deposits are unknown even though the North Australian Basin System extends well beyond this corridor. Like the lead isotope pattern, the edge of thick lithosphere cuts across the local geological grain (compare Fig. 3 with Fig. 1), suggesting a more fundamental, deep-seated control on mineralization.

5 Discussion and exploration implications

The association of basin-hosted Zn-Pb deposits in the North Australian Zinc Belt with gradients in $\mu$ (and with $\kappa$ and $\omega$) and a rapid thickness or depth change in the lithospheric-asthenospheric boundary suggest a fundamental lithospheric-scale control on these deposits. Compartmentalization of spatial variations in $\mu$, however, suggests a second order control related to the development of sub-basins and their bounding structures along this deep-seated feature.

The North Australian Basin System formed as a stacked series of rift-sag basins with extension oriented northeast-southwest (Calvert Superbasin) and north-south (Isa Superbasin). We suggest that the edge of thick lithosphere, which represents a fundamental zone of weakness, had a strong control on the overall geometry of the basin system. Failure across this zone of weakness determined the location of the transition from the western, generally shallow-water part to the eastern, deeper water part of the Calvert Superbasin. This defined the localized lithological make-up and, therefore, the style of mineralization. The broad scale boundary observed in the lead isotope data reflects different lead sources from the western and eastern parts of the Calvert Superbasin. In detail, the en echelon character of the lead isotope distribution pattern possibly relates to the localized development of sub-basins in response to the overall stress patterns prevalent during evolution of the North Australian Basin System.

We have observed similar relationships in other sediment-hosted base metal provinces around the world (Czarnota et al. in review), which suggests that the relationships observed in the North Australian Zinc Belt have more general applications. Based on these relationships we suggest that fertile basins for sediment-hosted zinc-lead mineralization coincide with zones of rapid changes in lithospheric thickness. Changes in basin...
architecture and make-up related to the interaction of the fundamental lithospheric control and stress patterns associated with basin formation control the lead isotope distribution patterns and, ultimately, the location of deposits. A combination of surface wave tomography and lead isotope mapping potentially can provide guidance in area selection and early-stage district-scale exploration, with specific targets then determined at later stages of exploration using local-scale geological, geophysical and geochemical data.

Acknowledgements

The results presented here are the result of regional-scale data collection in northern Australia as part of the Exploring for the Future program. The understanding of the results has benefited by researchers in the North Australian Zinc Belt past and present. This contribution has benefited from reviews by Michael Doublier and Steve Hollis, and is published with permission of the Chief Executive Officer of Geoscience Australia.

References


Mapping Pb isotope variations across Ireland: From terrane delineation to deposit-scale fluid flow

Steven P. Hollis  
_Geological Survey Ireland & University College Dublin_

Aileen L. Doran, Julian F. Menuge, J. Stephen Daly, John Güven  
iCRAG, University College Dublin

Stephen J. Piercey  
_Memorial University of Newfoundland_

Mark Cooper  
_Geological Survey of Northern Ireland_

Oakley Turner  
iCRAG, Trinity College Dublin

Richard Unitt  
iCRAG, University College Cork

Abstract. Carbonate-hosted Zn-Pb deposits have been the mainstay of metal mining in Ireland for decades, but only one mine is currently operational. The nature and extent of metal source rocks and the pathways along which leached metals were transferred to ore deposition sites are key questions, both of which may be addressed using Pb isotope ratios as tracers. Using Pb isotope data from galena we have mapped basement terranes across Ireland. Significant variations in \(^{206}\text{Pb}/^{204}\text{Pb},^{207}\text{Pb}/^{204}\text{Pb},^{208}\text{Pb}/^{204}\text{Pb}\), model age and \(\mu\) (source rock \(^{238}\text{U}/^{204}\text{Pb}\)) occur systematically across the island and steep gradients in all of these variables outline the Iapetus Suture Zone. In the Rathdowney Trend, subtle Pb isotope variations have been noted at the deposit scale in the Lisheen, Galmoy and Rapla deposits. At Lisheen, samples from the Lisduff oolite display the least radiogenic Pb isotope ratios along with areas adjacent to normal faults which acted as mineralized fluid conduits. All three Pb isotope ratios increase through the Main Zone, Derryville and Island Pod orebodies. Mineralization at Bog West, Bog East, Bawmmore, Templetuohy, Galmoy and Rapla (progressively farther NE) show systematically increasing ratios. Larger orebodies at Lisheen and Galmoy show the most significant amounts of isotopic variation.

1 Irish Zn-Pb deposits

In the last 50 years, five carbonate-hosted, Irish-type Zn-Pb orebodies have been mined, and over twenty sub-economic prospects have been discovered. However, since the closure of the Lisheen mine in 2015, only one mine is currently operational: the giant Navan deposit (110 Mt at 8.0% Zn and 2.0% Pb; Ashton et al. 2015). Finding more Irish-type orebodies requires a better understanding of the various processes required to form them, to inform mineral exploration strategy.

There is now a consensus that Irish-type Zn-Pb deposits are formed during early burial by the replacement of Lower Carboniferous limestones. Conditions required for their formation include dense networks of normal faults that allowed ascending, warm, metal-bearing fluids equilibrated with Lower Palaeozoic basement to mix with sinking, cooler, hypersaline brines (Wilkinson and Hitzman 2015). However, there is a lack of understanding of pre-Carboniferous geology in the Irish ore field, and particularly the pre-Silurian basement from which metals were most likely sourced. A key problem centres on the nature and spatial extent of metal source rocks and the pathways along which leached metals were transferred to sites of ore deposition. Both of these questions may be addressed using Pb isotope ratios as tracers.

The pre-Silurian Lower Palaeozoic basement of central Ireland is known from exposures of several Ordovician inliers, e.g., the Grangegeeth and Beeliewstown terranes south-east of Navan (e.g. McConnell et al. 2010, 2015), the Slieve Aughty inlier (Pracht et al. 2004) south-west of Tynagh within the Longford Down/ Central terrane as well as exposures of the Leinster-Lakesman terrane at Lambay-Portrane (Parkes and Harper 1996) and the Chair of Kildare (Parkes and Palmer 1994). Pre-Silurian basement is also known from from a handful of drillholes underneath the Navan Zn-Pb deposit (Ashton et al. 2015) and from deep crustal xenoliths (Daly et al. 2016). All major Zn-Pb deposits within the Irish ore field are located within 50 km of the likely position of the Iapetus Suture Zone, a relic of end-Silurian continent-continent collision (the Caledonian orogeny) between Laurentia and Gondwanan-affinity continental crust (Cooper et al. 2013). Deep-seated, NE-SW trending structures associated with orogenesis most likely provided suitable pathways for upwelling metal-rich hydrothermal fluids during the Carboniferous. Furthermore, the metallogenic variation of Irish Zn-Pb deposits may reflect the composition of the basement
from which metals were derived.

The U-Pb isotope system involves both the decay of $^{238}\text{U}$ to $^{206}\text{Pb}$ and $^{235}\text{U}$ to $^{207}\text{Pb}$, with respective half-lives of 4.47 Ga and 704 Ma (Champion and Huston 2016). Pb-rich minerals, such as galena, contain negligible U and retain their initial Pb isotopic ratios. These initial ratios may be used to reveal information on the nature of the Pb source reservoir at the time of extraction. Similar arguments apply to $^{206}\text{Pb}$, which accumulates from the decay of $^{232}\text{Th}$. Isotopic mapping of Pb isotopes may be achieved by measuring the mixing of Pb sources directly using $\mu$ (source rock $^{206}\text{U}/^{204}\text{Pb}$) (Huston et al. 2014), or indirectly by estimating mixing ratios of modelled endmember sources (Huston et al. 2016).

### 2 Pb isotope analysis

Compiled historical Pb isotope data from galena (n=504) have been combined with additional samples collected and analysed from across Ireland (e.g. The Burren, Shallee, Curraghnait, Rapla, Donegal, Copper Coast) to improve data coverage. To investigate the extent of deposit scale variation, galena was also sampled from a variety of ore textures in a grid-like fashion across the Lisheen deposit. Samples of galena were also analysed from available drillcore of the Rathowney Trend, including Bawnmore, Templetuohy, Rapla and Galmoy (G, R and K ore bodies).

Galena was extracted for analysis using a dentist drill. Approximately 5 mg to 10 mg of galena was dissolved by adding 2.5 ml of 6M HCl and 250 µl of 70 % HNO$_3$. The samples were dried down on a hotplate at ~120°C, and re-dissolved in 19 ml of deionised water and 1 ml of 70 % HNO$_3$. Subsequently, an aliquot of 10 µl was taken, centrifuged, diluted with 2.5 ml of 3% HNO$_3$, and spiked with 25 µl of thallium solution of known $^{203}\text{Tl}/^{205}\text{Tl}$ ratio to correct for mass bias fractionation. Sample solutions were analysed using a Thermo-Scientific Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the National Centre for Isotope Geochemistry, University College Dublin (UCD). The two year mean values of standard NIST NBS 981 (n=36) for this method at UCD is $^{206}\text{Pb}/^{204}\text{Pb}$ = 16.9350, $^{207}\text{Pb}/^{204}\text{Pb}$ = 15.4896 and $^{208}\text{Pb}/^{204}\text{Pb}$ = 36.6920. Data was corrected to the known Pb isotopic ratios for NIST NBS 981 as reported by Yuan et al. (2016). The two-year standard error (%) of NBS 981 for this method at UCD is $^{206}\text{Pb}/^{204}\text{Pb}$ = 0.0038%, $^{207}\text{Pb}/^{204}\text{Pb}$ = 0.0049% and $^{208}\text{Pb}/^{204}\text{Pb}$ = 0.0073%.

### 3 Terrane scale mapping

Several researchers have investigated Pb isotope variations of galena from mineral deposits across Ireland (e.g. Boast et al. 1981; O’Keefe 1986; LeHuray et al. 1987; Mills et al. 1987; Everett et al. 2003). In the past three decades it has become increasingly apparent that individual ore deposits display remarkably homogeneous Pb isotope compositions, but that there is large, systematic variation across Ireland. Ratios of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, calculated $\mu$ and model ages, can be contoured to reflect variations in basement sources from which metals were derived (O’Keefe 1986; Everett et al. 2003; Fig. 1).

![Diagram](https://via.placeholder.com/150?text=Diagram)
Incorporating our new analyses, a clear isotopic division is apparent crossing central Ireland from NE to SW (Fig. 1), which corresponds with the Iapetus Suture Zone. Whereas galena from Precambrian and Lower Palaeozoic mesothermal gold, VMS and SEDEX occurrences in NW Ireland are characterized by a µ value of 9.2 (reflecting Laurentian-affinity crust), similar Lower Palaeozoic hosted mineral occurrences in SE Ireland plot along a trend with a µ value of ~10 typical of Ganderian-Avalonian basement (O’Keefe 1986). The high $^{206}\text{Pb}/^{204}\text{Pb}$ values in the Longford-Down terrane suggests this Silurian accretionary prism, is underlain by the leading edge of Ganderia. The latter was most likely the dominant source of Pb in galena from the Irish-type Zn-Pb deposits. Older model ages in SE Ireland correspond to the boundary of the East Carlow Deformation Zone. In SW Ireland, future model ages correspond with high $^{206}\text{Pb}/^{204}\text{Pb}$ associated with the Munster Basin.

4 Variations along the Rathdowney Trend

Analysis of galena from across the Lisheen deposit (Fig. 2) reveals a remarkably homogeneous Pb isotopic signature (e.g. $^{206}\text{Pb}/^{204}\text{Pb} = 18.147-18.216$). However, subtle variations between ore lenses are now detectable with the improved precision of our new MC-ICP-MS analyses (Fig. 3). The Lisduff oolite (the proposed feeder zone) at Lisheen is characterized by the lowest $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios and µ values of 9.65 to 9.69, along with a number of analyses from the southern part of the Main Zone and Derryville orebodies. These areas are associated with early normal faults that facilitated mineralization, and with elevated levels of Cu and Ni (Torremans et al. 2018). The distal and high-grade Island Pod is characterized by slightly higher and very homogeneous ratios. Increased $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios occur progressively to the NE through Bog Zone W, Bog Zone E, Bawmmore and Templetoohy. This trend of increased ratios continues NE along the Rathdowney Trend through Galmoy (Fig. 3), Rapla, and Tonduff. Larger orebodies at Lisheen (Main Zone, Derryville) and Galmoy (G and K lenses) show the greatest isotopic variation.

5 Implications

Pb isotope analysis of galena from across Ireland has proven a valuable tool for characterizing metal sources within the lower crust and identifying potential terrane boundaries. With the improved precision of MC-ICP-MS analysis, subtle Pb isotope variations can be now delineated within mineral deposits. Although the Pb isotopic source of the Rathdowney Trend is remarkably homogeneous, small systematic differences between ore lenses indicate either: 1) minor variations occurred in the source region at depth and were preserved as fluids migrated upwards; or perhaps more likely 2) minor Pb was added to hydrothermal fluids on ascent (from metasedimentary rocks of the Down-Longford terrane). Systematic Pb isotope variations to the NE may simply reflect deep-seated crustal structures of the Rathdowney Trend associated with mineralization cutting across Ordovician-Silurian metasedimentary rocks of more evolved isotopic compositions.
Acknowledgements

Mick Murphy, David van Acken and Eszter Badenszki at University College Dublin are thanked for assistance with sample preparation and analysis. The authors would also like to thank the following people for providing samples - John Ashton, Rob Blakeman, Paul Henry, Koen Torremans, Roisin Kyne, Sean McClennaghan, Gavin Berkenheger, Raymond Keenan, Dermot Smyth, John Kelly, Orla McKenna, Matt Mawson, Jamie Wilkinson, Bart Jaworski and Gosia Horaj ska. This work has been funded by Geological Survey Ireland/DCCAE Postdoctoral Fellowship Programme, No. 2016-PD-003. Pb isotopic analyses were carried out at the National Centre for Isotope Geochemistry (NCIG), which is a joint venture of University College Dublin, Trinity College Dublin, University College Cork, and National University of Ireland Galway, funded mainly by Science Foundation Ireland, including grant 04/BR/ES0007/EC07 awarded to J.S. Daly.

References


Correlated petrographic and isotopic studies (S, Pb) of carbonate-hosted Zn-Pb mineralization: the formation of the high-grade Island Pod, Lisheen

Aileen L. Doran, Julian F. Menuge, John Güven
iCRAG & University College Dublin

Steven P. Hollis
Geological Survey Ireland & University College Dublin

Adrian J. Boyce
SUERC & University of Glasgow

Stephen J. Piercey
Memorial University of Newfoundland

Abstract. Irish Zn-Pb deposits are a type of carbonate-hosted mineralization, typically found adjacent to normal faults. Ore deposition occurred due to the replacement of Lower Carboniferous limestones, triggered primarily by fluid mixing. The Lisheen deposit (23 Mt at 13.3% Zn & 2.3% Pb) in the southern Irish orefield consists of several stratabound orebodies, which are strongly controlled by a left-stepping, ramp-relay fault array. The Island Pod (0.4 Mt at 20% Zn & 1.6% Pb) is a small high-grade orebody, found in the northern part of the Lisheen mine (Fig. 1). We present the first detailed petrographic and paragenetically constrained S-Pb isotopic study and mineral chemical analysis of the Island Pod mineralization. Homogenous Pb isotopic signatures in galena have been observed throughout the Island Pod, regardless of paragenetic stage. Sulfur isotope ratios vary but suggest a dominantly bacteriogenic source for S. Sulfide minerals have low trace element concentrations, below electron microprobe detection limits for most elements.

1 Introduction

Ireland has seen five carbonate-hosted zinc-lead (Zn-Pb) orebodies mined and over twenty sub-economic prospects discovered since the 1960s (Fig. 1). With the closure of the Lisheen mine in 2015, only the giant Navan mine remains operational. The exploration success rate for Irish Zn-Pb deposits may be improved by increasing current knowledge of deposit formation and their associated geochemical haloes.

Irish carbonate-hosted Zn-Pb sulfide deposits are structurally controlled and stratabound. They display intermediate characteristics between SEDEX- and MVT-style mineralization (Wilkinson 2014). Mineralization typically occurs adjacent to normal faults and formed from carbonate replacement of Lower Carboniferous limestone. This replacement was triggered by mixing of a metal-bearing, hydrothermal fluid (up to 280 °C) (Wilkinson 2010), which ascended along normal faults, and a sinking, cooler (<100 °C), hypersaline brine, carrying bacteriogenically reduced sulfur (Fallick et al. 2001; Wilkinson et al. 2005). In the southern Irish orefield, mineralization is typically hosted in hydrothermal breccia bodies found at the dolomitized base of the Waulsortian Limestone Formation, where it is in contact with the older Ballysteen Limestone Formation (Hitzman et al. 2002).

Figure 1. Simplified geological map of the southern Irish orefield with some of the main Zn-Pb deposits and prospects outlined. Geology adapted from the Geological Survey Ireland bedrock series.

While there is a good fundamental understanding of Irish Zn-Pb deposit formation, there are many aspects which are still poorly understood. Specifically, the reasons why high-grade bodies such as the Island Pod form are not known, and the sub-economic haloes around deposits have been little studied. A focused application of sulfur (S) and lead (Pb) isotope analyses, combined with other isotopic tracers and mineral chemical studies (electron probe microanalysis; EMPA) and relating to mineral texture and paragenesis, has the potential to illuminate the processes responsible for these features.

2 The Lisheen deposit and Island Pod orebody
The Lisheen deposit (23 Mt at 13.3% Zn & 2.3% Pb; Fig. 2) was discovered in 1990 and was the second biggest base-metal deposit mined in Ireland, closing in 2015. Lisheen is composed of several stratabound Zn-Pb orebodies which are controlled by an extensional, left-stepping, ramp-relay fault array (Torremans et al. 2018; Kyne et al. 2019). Six distinct orebodies were mined at Lisheen: Main Zone, Derryville, Bog Zone West, Bog Zone East, Bog Zone Central, and the Island Pod.

As Lisheen was active as a mine for over fifteen years, there is a wealth of information and drill core available. Thus, Lisheen offers the perfect testing ground for potential isotopic vectoring tools, as well as offering the opportunity to enhance our understanding of deposit, and especially halo, formation.

The Island Pod (0.4 Mt at 20% Zn & 1.6% Pb; Fig. 2) is a small, satellite orebody found approximately 900 m northeast of the Derryville orebody. It was first intersected by drilling in 2005 but only properly evaluated by drilling in 2011 and resulted in an additional two years of mine life.

When compared to other Lisheen orebodies, the Island Pod displays some key differences: there is weaker structural control on the best quality and thickest ore; mineralization in the Island Pod is located approximately 20 m above the Waulsortian Limestone Formation/Ballysteen Limestone Formation contact; there is little development of black matrix breccia surrounding ore, with white matrix breccia development more extensive than expected; and penalty elements are low.

We present the first detailed paragenetic study of the Island Pod orebody, incorporating detailed optical, SEM and cathodoluminescence work. Additionally, detailed isotopic (S, Pb) and mineral chemical investigations were performed on samples selected to be representative of all stages of the mineral paragenesis.

3 Petrography and paragenesis

Sphalerite, galena and pyrite are the main sulfide minerals in the Island Pod and its surrounding sub-economic halo, with multiple generations of each mineral present. Minor marcasite, arsenian Fe-sulfides and sulfosalts have also been identified. Several carbonate (calcite and dolomite) phases have been recorded, associated with each stage of mineralization (Fig. 3f). Summary textures from the study area are shown in Figure 3.

Textural studies of the Island Pod mineralization and its surrounding sub-economic halo have provided insights into the depositional environment during sulfide precipitation. Early sulfide textures, such as dendritic galena and pyrite (Fig. 3a), and colloform sphalerite (Fig. 3b), suggest rapid precipitation into open spaces, from a supersaturated fluid (Roedder 1968; Anderson et al. 1998; Atanassova and Bonev 2006; Gagnevin et al. 2014). These textures record the onset of fluid mixing in the mineralizing environment and mark the initiation of ore-stage sulfide deposition. Dendritic galena is interpreted to result from low temperature (100 - 200 ºC), supersaturated fluids (Atanassova and Bonev 2006). Dendritic galena acted as a nucleus for colloform sphalerite and associated bands of dolomite, similar to that reported from the Navan deposit (Anderson et al. 1998). As fluid mixing continued, sulfide textures evolved to coarser, non-colloform crystal habits (Fig. 3e), reflecting an environment closer to equilibrium. Zoned pyrite grains have also been noted from main ore stage mineralization, representing the introduction of new pulses of fluid into the depositional environment (Fig. 3c-d).

Figure 3. Summary sulfide and carbonate textures from the Island Pod. (a) Dendritic pyrite (Py) being replaced by galena (Gn); UCD SEM image. (b) A clast of colloform sphalerite (Sp), surrounded by later, non-colloform Sp; UCD transmitted light image. (c) Brecciated zoned Py, with later infilling Sp; MUN SEM image. (d) Zoned Py grain from the south of the Island Pod; MUN reflected light image.
The final stage of sulfide mineralization in the Island Pod consists of disseminated sulfides (pyrite, sphalerite), often associated with late stage carbonates. The observed sulfides and carbonates identified from the Island Pod orebody and its surrounding sub-economic mineralization have been used to create the paragenesis shown in Figure 4. The paragenesis has been divided into Pre-, Main- and Post-ore stages.

Figure 4. Island Pod paragenesis, showing key sulfide and carbonate phases.

4 Isotopic analyses

4.1 Pb isotope analysis

A spatially representative suite of samples (n = 23) from across the Island Pod orebody and its sub-economic halo were analyzed for Pb isotopes at the National Centre for Isotope Geochemistry (NCIG), University College Dublin (UCD). Analysis was carried out for 206Pb/204Pb, 207Pb/204Pb, 208Pb/204Pb ratios, using the Thermo-Scientific Neptune multi-collector inductively coupled plasma mass spectrometer. Further details are provided in Hollis et al. (this volume). The results from this study display an extremely homogeneous Pb isotopic signature, suggesting that Pb in the Island Pod originated from a single source, or by prior thorough mixing of fluids from several sources.

Further Pb isotopic analysis was performed using the Cameca IMS 4f SIMS at the MAF-IIC Microanalysis Facility of MUN, Canada, resulting in an additional 89 Pb isotope analyses. Crucially, the extra SIMS work allowed for analysis of small-scale sulphide textures, including those associated with the onset of fluid mixing, such as dendritic galena, which were not possible to measure at the NCIG. SIMS analysis also allowed us to collect multiple spatially associated data (< 1 mm), to test for Pb isotopic variation on a grain scale. Importantly, the SIMS Pb isotopic analysis did not reveal any variation related to texture, suggesting a continuous source of Pb from the pre-ore to post-ore stages.

4.2 S isotope analysis

In-situ laser ablation of sulphide minerals from the Island Pod was initially carried out at SUERC, Glasgow, resulting in 148 data points. Further analysis was performed at MUN using the SIMS facilities outlined in Section 4.1, resulting in an additional 118 data points. As for SIMS Pb isotope analysis, multiple data points were collected on a small-scale (< 1 mm), to test for δ34S variation on a grain scale. In addition, textures which were too small for in-situ laser ablation (< 50 µm) were analysed.

Figure 5. δ34S data from the Island Pod, collected at MUN and SUERC.

Data from both MUN and SUERC (Fig. 5) reveal a dominantly bacteriogenic δ34S isotopic signature (negative δ34S) for the Island Pod. The Island Pod also shows a stronger bacteriogenic δ34S signature than other orebodies in Lisheen (Main Zone, Derryville, Bog; Wilkinson et al. 2005). However, the data suggests that there was a stronger hydrothermal (positive δ34S) sulfur influence in the southern part of the Island Pod, with δ34S values typically becoming lower (negative δ34S) northward. Pyrite δ34S values reveal a bimodal distribution, with each range representing a different paragenetic stage. Early, pre-ore pyrite falls into the range of -48 to -30 ‰, while main-ore stage typically shows values ranging from -30 to -15 ‰. However, sphalerite and galena are generally unimodal, with galena δ34S values typically displaying the heaviest δ34S values (maximum 18 ‰).

The stronger bacteriogenic component seen from all sulfides in the Island Pod fits well with the idea that it was deposited distal to the proposed main Lisheen feeder-fault system at the southern edge of the Main Zone and Derryville orebodies (Torremans et al. 2018). The feeder faults in the main part of Lisheen would have been responsible for the introduction of hydrothermal, metal-bearing fluids to the mineralizing system. Importantly, no δ34S variation was observed between the Island Pod orebody and its surrounding sub-economic halo.

5 Electron probe microanalysis (EPMA)

Electron probe microanalysis was carried out at NHM, London, and MUN, Canada, resulting in a total of 672 data points from the major sulphide phases. While the elements Fe, Mn, Co, Ni, Cu, Zn, Sb, As, Pb, Bi, Mo, Ag, Cd, In, Ti, S, Si, Au and Se were analysed for, only Fe, Mn, Co, Ni, Zn, As, Pb, Ti and S exceeded detection...
limits.

Low trace element values were recorded in all sulfides, with only Fe detected in sphalerite, consistent with the proposed distal position of the Island Pod from feeder faults to the south; undetected Cd has been linked to a dominant hydrothermal S source (Barrie et al. 2009). Pyrites showed the greatest variation, with pyrite grains in the southern part of the deposit often showing As-Co zonation.

6 Conclusions

Petrographic studies of the Island Pod have revealed a dynamic mineralizing environment, that changed from a rapid precipitation, depositional setting, to a slower, more equilibrated one as time progressed. The changes in depositional environment are recorded well by the sulfide textures observed in the Island Pod. Sulfur isotope analysis has revealed a dominantly bacteriogenic sulfur source, consistent with a distal position from feeder faults of the orebody, and Pb isotope analysis suggests a well-mixed Pb source for the entire Island Pod, regardless of paragenetic stage. Sulfide mineral chemistry reveals low trace element abundances, again consistent with the distal position of the orebody from the feeder faults of the main mineralization at Lisheen. Textural, mineral chemistry and isotopic analysis from the south of the Island Pod mineralization reveal slight differences to those found in the northern section. Features characteristic of hydrothermally influenced ore precipitation (e.g. trace elements carried via hydrothermal fluids, zoned pyrites, heavier δ34S values) are more commonly observed from the south. However, no variations in texture, isotope or mineral composition have been identified between the orebody and its surrounding sub-economic halo.

Acknowledgements

Vedanta Resources are thanked for access to drill core from Lisheen mine. This publication has emanated from research conducted with the financial support of Science Foundation Ireland (SFI) under Grant Number 13/RC/2092 and co-funded under the European Regional Development Fund. Extra funding was provided by a James M. Flaherty Research Scholarship from the Ireland Canada University Foundation, with the assistance of the Irish Government. Pb isotope analysis was funded by Geological Survey Ireland/DCCAE Postdoctoral Fellowship Programme, No. 2016-PD-003.

References

Preliminary results: the Tara Deep Zn-Pb deposit, Navan, Co. Meath, Ireland

Drummond, D. A., Boyce, A. J.
Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride, Scotland, UK

Yesares, L., Blakeman, R. J., Ashton, J. H.
Irish Centre for Research in Applied Geosciences, O’Brien Centre for Science (East), University College Dublin, Belfield Down, Dublin 4, Ireland.

Blakeman, R. J., Ashton, J. H.
Boliden Tara Mines, Exploration Department, Navan, County Meath, Ireland.

Abstract. Tara Deep is the latest major Zn-Pb discovery by the Boliden Tara Mines Exploration Department, which significantly adds to the world-renowned Navan-cluster of deposits. Tara Deep has a current Inferred Resource of 18.2 Mt grading at 7.6% Zn and 1.6% Pb (Ashton 2019).

Mineralisation occurs primarily in two Lower Carboniferous lithologies: 1) Micrite and associated calcarenite units within the Pale Beds sequence. 2) Pale Bed-rich conglomerates in the hanging walls of two key faults (G and S faults).

Sphalerite and galena dominate in a >5:1 ratio. Massive, brecciated, veining and collomorphic/cavity lining mineralisation textures are the most abundant. These textures speak of complex episodic mineralisation events that display considerable reworking, fracturing, dolomitization, open space infill and selective replacement.

S isotope analyses outline a bimodal distribution, revealing both bacteriogenic and hydrothermal sulfur sources (n=117), -14 to -4 ‰ and +4 to +15 ‰, respectively – broadly similar to the Main Mine at Navan and a vital requirement for producing world-class Zn-Pb orebodies in Ireland. Both textural and sulfur isotope data reveal the dynamic nature of mineralisation at Tara Deep and infer fluid mixing. Tara Deep has the potential to extend mine life at Navan into the 2030s.

Introduction

Ireland hosts the greatest concentration of zinc per square kilometre in the world (Singer 1995). The Navan deposit alone is the largest zinc producer in Europe and one of the largest underground zinc mines in the world, with total production and in situ resources at end 2018 amounting to over 135Mt @ 7.7% Zn and 1.8% Pb (Ashton 2019). Tara Deep is the latest major Zn+Pb discovery (announced in 2017) by Boliden Tara Mines Exploration Department. Hosted in Lower Carboniferous carbonates at a depth of 1.2-1.9 km, this new discovery is providing a significant addition to the world-renowned Navan-cluster of deposits and sits 3 km SE of the Main Mine.

This study reviews the discovery and presents initial results from the Tara Deep deposit to begin constraining the depositional and tectonic processes that led to its formation.

Figure 1. Simplified geological map of Ireland highlighting the location of the main Zn-Pb orebodies.

2 History of Successful Discovery

Development of the Navan orebody began in 1974, with first production occurring in 1977. Located ~30 km NW of Dublin (Fig. 1), this stratabound orebody was initially discovered by Tara Prospecting through drilling a shallow soil Zn-Pb anomaly (O’Brien and Romer 1971). In the 1990s, further exploration drilling resulted in the discovery of the Southwest Extension (SWEX; Fig. 2), adding 30 Mt to the resource base (Ashton et al. 2003). A full review of the main phases of exploration can be viewed in Ashton et al. (2015). From 2000 to 2010, annual resource additions from underground and surface exploration and delineation drilling averaged 1.1 Mt. Despite these gains,
mine depletion was occurring at 2.6 Mt per annum, inevitably leading to potential mine closure before 2020. Furthermore, drilling down dip from the SWEX had failed to intercept new resources, meaning that further ore discovery was vital to the survival of Boliden Tara Mines.

Following on from an Experts Meeting in 2010, two significant aims were developed; 1) It was hypothesised that the area to the south of the Navan deposit would contain an undiscovered major normal fault that likely controlled the development of extensional structures in the Navan area, and potentially provide a suitable conduit for metal-bearing fluids. 2) Seismic data acquisition had the potential to locate these structures. By late 2012, seven 2D seismic surveys (totalling 101 km), had been acquired, processed, and initially interpreted. Hosted in the footwall of a large south-dipping basin margin fault, Tara Deep was discovered. See Ashton et al. (2018).

3 Regional Setting

Navan is located immediately south of the Longford Down Lower Palaeozoic inlier, adjacent to a major NE-trending fault zone forming the southern margin to the inlier. To the south and southwest platformal carbonates and calciturbidites of the developing Dublin Basin subcrop.

The Navan orebody is hosted by Lower Carboniferous carbonates. In Ireland, Zn-Pb mineralisation is largely restricted to Lower Carboniferous marine sequences of Tourmaisian and Visean age. In southern and central Ireland the Waulsortian Limestone Formation is host to many Irish Zn-Pb deposits in central Ireland, they are poorly developed and generally unmineralised in the Navan area.

Figure 2. Map modified from Ashton et al. (2015) summarizing the main phases in the exploration and development of Boliden Tara Mines.

Navan is spatially associated with several east-northeast-trending Courceyan/Chadian extensional faults and low angle slides associated with the developing basin margin. Rheno-Hercynian compression led to inversion on several of these structures, and a regional dip of 15-20° was also probably imparted at this time. A detailed synopsis of the timing and genesis of faulting is reviewed in Ashton et al. (2015).

4 Local Geology

At Tara Deep, mineralisation occurs primarily in two lower Carboniferous hosts: 1) Micrite and associated calcarenite units within the Pale Bed sequence, which display variable dolomitization, and host ~90% of the total resource 2) Polymict clasts of conglomerates hosted in the hanging walls of the G and S faults in the NW Zone (Ashton et al. 2018; Yesares et al. submitted).

The micrite-hosted mineralisation occurs in a series of fault-bounded slides with shallow dips southeast toward the Navan Fault. Associated with a quiescent depositional environment, the basal units of the Pale Beds at Tara Deep are typically 50m thick. Characteristic features of this interval are blue-dark grey micrites with abundant bird’s eye textures. The two micrite units are separated by dolomitized siltstones. The lower micritic is the main host to mineralisation at Tara Deep with the upper micrite showing variable grades. Mineralisation occurring within the dolomitized horizons is typically associated with hydrofracturing. Mineralisation within the micrites shows clear evidence of multiple phases of deposition, disruption and reworking.

The polymict conglomerates contain detrital clasts of sulphide as well as intervals of replacive mineralisation. Thus, demonstrating that the mineralising event straddled the formation of these debris flows. Similar features within the Boulder Conglomerate of the Navan deposit constrain
an Arundian (~345Ma) age for mineralisation.

Understanding the Tara Deep geology is still at an early stage. Nevertheless, several important differences to the established stratigraphy of the Navan deposit are recognized. Figure 3 shows the development of a massive calcarenite overlying the basal micrite sequences. In parts, this calcarenite demonstrates disruption represented by Healed Conglomerates, as described by Philcox (1991) in relation to the nearby Clogherboy mineralisation. The matrix of these Healed Conglomerates contains complex detrital apatites, jadeites, zircons and albites and is dolomitized. Above the erosion surface, several debris flows are hosted within the Thin Bedded Unit (Yesares et al. in this issue). This differs from the single Boulder Conglomerate observed at the Navan deposit. At several intervals, tuffs are preserved within the sequence. These are missing at Navan, having probably been removed during the formation of the Boulder Conglomerate. The Thin Bedded Unit thickens dramatically in the hanging-wall of the G Fault and has been termed the New Thin Bedded Unit.

5 Mineralogy and Associated Textures

Sphalerite and galena dominate the mineralisation at a ratio of >5:1. Gangue consists of calcite, dolomite, pyrite, marcasite and barite, in decreasing order of abundance. Antimony and copper sulfosalts exsolutions are common in galena, especially in those samples demonstrating a positive $\delta^{34}$S value. Multiple phases of mineralisation have led to a diverse array of complex textures (Fig. 4), dominated by collomorphic/cavity infill, brecciated, massive and veined mineralisation (Fig. 5).

6 S Isotope Results

$\delta^{34}$S in sulfides (n=117) show two main populations of -14 to -4 % and +4 to +15 % (Fig. 6). The lightest subgroup arises from bacterial reduction of Lower Carboniferous seawater sulphate (Falllick et al. 2001). The heavier
values represent hydrothermal sulfide which entered the deposit in mineralising brines (Boyce et al. 1993). Barite $\delta^{34}$S is indicative of Lower Carboniferous seawater sulphate (22.2 ‰) (Anderson et al. 1998). Mineralised textures outline a close interplay between bacteriogenic and hydrothermal sources and infer that fluid mixing was likely a dominant process.

Figure 6. $\delta^{34}$SCDT (‰) S isotope analyses of base metal sulfides from Tara Deep outlining a bimodal bacteriogenic and hydrothermal sulfur source.

7 Conclusions

The Tara Deep deposit is comparable to the Main Navan Orebody in terms of the stratigraphy, hosting lithologies and major mineralogy. Relative to the stratigraphy, Tara Deep appears to be the same age as Navan. Although the structural setting differs from the Navan system, the bimodal S source is pre-requisite of producing world-class Zn-Pb deposits, like the Navan Main Mine. Mineralisation displays multiple phases of reworking, fracturing, dolomitization, open space infill, and selective replacement, leading to a complex array of textures. These textures highlight a bimodal S isotope signature and reveal a close relationship between hydrothermal and bacteriogenic conditions. Tara Deep is beginning to show the vital signs that will allow Boliden Tara Mines to retain its pre-eminence as a major Zn-Pb producer.

Acknowledgements

We thank everyone at Boliden Tara Mines Exploration Department, whose hard work continues to facilitate this research.

References


Structural modification and associated remobilization of the San Vicente MVT deposit during the Andean Orogeny

Helen B. McFarlane, Steffen Hagemann
Centre for Exploration Targeting, School of Earth Sciences, University of Western Australia

Jorge Palacios, Nancy Tuanama, Carlos Flores
Compañía Minera San Ignacio de Morococha S.A.A. (SIMSA)

Abstract. The genesis of Mississippi Valley-Type Zn-Pb deposits is widely accepted to occur during expulsion of basinal brines during the maturation of sedimentary basins. Whilst the role of basement and basin-forming faults in MVT deposit formation is well documented, the role of contraction deformation and structural modification with associated remobilization during orogenesis remains relatively under-researched. Here we present a new interpretation of the structural framework of the San Vicente Zn-Pb deposit of central Peru, which exhibits both archetypal MVT mineralization characteristics and structural controls attributed to Andean deformation. Early deformation is characterized by folding and thrusting with subsequent brittle deformation associated with the most significant modification of orebody geometries and remobilization, spatially restricted to the southern half of the deposit.

1 Introduction

The genesis of carbonate-hosted Mississippi Valley-type (MVT) Zn-Pb deposits is commonly attributed to processes associated with sedimentary basin evolution (Anderson and Macqueen 1982). Fluid flow responsible for the transportation and deposition of metals occurs during basin formation, with brine fluid expulsion driven by diagenesis or changes to overburden, local geothermal gradients, topographic relief and deformation (Leach et al. 1995). Although the extent of influence of the tectonic setting for MVT deposits has been a previous source of discussion (Bradley and Leach 2003), the role of contractional deformation during their genesis and subsequent remobilization remains underexplored.

The San Vicente MVT Zn-Pb deposit is located within the eastern foothills of the Andes, 300km east of Lima, Peru, in tropical rainforest. Historically, it was one of Peru’s largest Zn producers with calculated reserves of 20 Mt at 11 wt% Zn and 0.8 wt% Pb (Fontboté et al. 1995). The San Vicente mine is situated in the footwall of the Utcuyatu Thrust Fault, responsible for the uplift and over-thrusting of the 240x4 Ma Tarma Granodiorite (Gunnesh et al. 1990) and Precambrian Basement in the hanging wall to the west. The tectonic contact is interpreted as late Miocene deformation during the Quehua 3 phase of the Andean Orogeny (Mégard 1984). The NNW-striking deposit is hosted within platform carbonate rocks of the Pucará Group. The group comprises alternating sequences of limestone and dolostone, the latter of which hosts mineralization, deposited on the margin of the Brazilian Shield in the Upper Triassic to Lower Jurassic.

Mississippi Valley-type Zn-Pb deposits are typically characterized by epigenetic stratabound, tabular ore bodies, or mantos, hosted within dolostone units with simple ore mineralogy of sphalerite-galena ± marcasite ± pyrite (Dörling et al. 1998). Mineralization is commonly characterized by replacement textures or rhythmically banded, zebra texture ore associated with low temperature, saline fluids. The regional geological setting typical of MVT districts includes rift-related intracontinental basins, with mineralization localized along basin margins, or foreland thrust belts (Leach et al. 1995; Sangster and Leach 1995).

The San Vicente deposit shares a number of these characteristics including variably stratabound, rhythmically banded ore and associated dark replacement dolomite (DRD) and white sparry dolomite (WSD) hosted in dolostone units within a platform carbonate sequence. Fluid inclusions studies of ore-related WSD indicate warm, saline fluids (115–162 °C and 9.5–26 wt% NaCl equiv.) (Moritz et al. 1996). However, the deposit also displays evidence of structural modification associated with Andean deformation, which prompted Badoux et al. (2001) to hypothesize a syn-tectonic origin for mineralization at San Vicente. Here we present a preliminary new structural framework for the San Vicente deposit derived from detailed underground and meso-scale mapping, drill core observations and ore shoot geometries. We discuss the framework within the context of contrasting paragenetic models for MVT deposits and explore the influence of structural modification and remobilization within the overriding tectonic context of the Andean Orogeny.

2 Regional Geological setting

2.1 Andean context

Stretching down the western margin of South America, the Andes are divided into five structural zones, defined as the Western Cordillera (WC), the Eastern Cordillera (EC), the intra-Andean Zone (IAZ), the sub-Andean zone (SAZ) and the Andean Plateau (Fig. 1). They predominantly comprise inverted pre-Andean sedimentary basins and Mesozoic to Cenozoic subduction-related continental magmatic arcs (Mégard 1984). The San Vicente mine area is located near the EC-SAZ boundary within the NNW-striking Pucará Basin,
which has been entrained in thin-skinned Andean tectonics since ~ 40 Ma (McQuarrie et al. 2008).

Figure 1. Simplified map of the central Andes. SAZ: sub-Andean Zone; EC: Eastern Cordillera; IAZ: inter-Andean Zone; WC: Western Cordillera; pC: pre-Cordillera. Red rectangle shows approximate location of Fig. 2.

2.2 Local stratigraphy

Sequences exposed in the San Vicente mine area include Lower to Middle Permian black shales and limestones of the Tarma-Copacabana Formation, deposited during fault-controlled subsidence (Sempere et al. 2002). These are overlain by terrigenous clastic molasse sequences of red sandstone, conglomerates and felsic volcanics, forming the rift-related Triassic Mitu Group (McLaughlin 1924; Rosas et al. 2007). Deposition of the Pucará Group shallow-water platform carbonate sequences is attributed to post-rifting subsidence and marine transgression. These units are in tectonic contact with the 240±4 Ma Tarma Granodiorite and the 255±4 Ma San Ramon Granite (Gunnesch et al. 1990), juxtaposed during Miocene Andean deformation.

3 San Vicente deposit geology

In the San Vicente district (Fig. 2), primary basin faults and structures are largely obscured by subsequent alteration and deformation. Rift-related redbeds of the Mitu Group are over lain by the Pucará Group, which is tectonic contact with the Tarma Granodiorite along the Utcuyatu thrust fault (Dávila et al. 2000). Discrete lithological units in the mine area comprise (from oldest to youngest): the Basal Unit (UB), which consists of intercalated limestone and minor clastic and dolostone units. The upper horizon of UB is characterized as a porous limestone unit (Caliza Porosa Basal – CPB) that partially preserves a primary oolitic texture. The overlying medium to coarse-grained San Judas Dolostone (DSJ) is the lower most ore-bearing unit. The fine-grained, partially dolomitized Neptuno Limestone separates DSJ from the main ore-bearing unit, the San Vicente Dolostone (DSV). The DSV is characterized by medium to coarse-grained dolostone with minor intercalations of organic rich material (Dávila et al. 2000; Fontboté and Gorzawski 1990). The overlying bituminous, silty Uncush Limestone is finely laminated with high total organic carbon content (Spangenberg and Macko 1998). The uppermost carbonate units comprise the Alfonso and Colca dolostones, which bear compositional and textural similarities to DSJ and DSV.

Host dolostone units (DSJ, DSV and DA) contain two distinct types of dolomite, fine to medium-grained dark replacement dolomite (DRD) and medium to coarse-grained white (to pale grey) sparry dolomite (WSD). Original sedimentary components, such as ooids, crinoid fragments and pellets have undergone extensive dolomitization and are rarely preserved. Mineralization within the dolostone units occurs predominantly in west dipping (~15-47°) sheet-like geometries (mantos). The main ore minerals are sphalerite and galena. Dolostone units feature both barren and mineralized zebra textures. The first paragenetic position of sphalerite (Sp1) is as fine-grained, anhedral grey-brown replacement textures intercalated with DRD. The second sphalerite generation (Sp2) is coarser-grained, brown sphalerite associated with WSD replacing DRD (Fig. 3). The third generation occurs as coarse-grained, orange sphalerite (Sp3) with euhedral galena in void-filling dolomite-calcite in a mineral-matrix breccia (Spangenberg and Macko 1998).
Structural framework for San Vicente deposit

Extensive underground mapping and core logging was conducted at the San Vicente mine in December 2018. Observations of mine stratigraphy, orebody geometries, microstructures and their relationship with different fault families were used to develop a new interpretation of the structural framework of the deposit.

The earliest compressional deformation event (D1) has a range of expressions depending on lithological composition. In limestone units, E-W shortening and brittle-ductile deformation are accommodated by east verging, inclined to recumbent tight folds (2 cm to ~5 m wavelength). F1 folds are observed both underground and in drillcore, with fold closures determined from alternating S1/S0 vergence. The D1 S-C fabric is characterized by deformation of primary lamination in limestone units (S) along low angle shear planes (C) in the limestone units, with dissolution developing along the C plane. The average S1 measurement has a strike of NW-SE to NE-SW, dipping 25–57° W. In addition, coeval bedding-parallel to subparallel thrust faults accommodate non-coaxial strain. Steeply east-dipping, bedding-normal en échelon extensional calcite veins in limestone beds indicate flexural slip during progressive deformation.

Within dolostone units, bedding relationships are largely obscured by dolomitization and replacement textures. Where observed, rhythmically banded ore is parallel to subparallel to bedding. Dolomite within the banded ore display high-angle undulose extinction and tapered edge twins (Fig. 4a) and finely recrystallized dolomite at the dolomite-sphalerite contact, indicative of accommodation of shearing within zebra textures.

The deposit is subsequently affected by three generations of brittle faulting, associated with the generation of hydraulic and mechanical breccias, partial remobilization of metals and structural modification of ore bodies. The second phase of deformation (D2) is characterized by ENE-WSW to NE-SW striking faults, dipping moderately NW (27-62°). Slickenfibres and slickenlines indicate that the brittle E-W D2 deformation was predominantly accommodated by dextral movement, evidenced, for example, in the displacement and truncation of mantos in the Nuevo Usa ore shoot. The third generation of faults is responsible for the strong structural modification of ore shoots in the southern half of the San Vicente deposit, and associated remobilization of sphalerite ore (Fig. 4).

Figure 3. Field photographs of San Vicente ore textures. A) Zebra textures of medium-grained sphalerite (Sp2) separated by syntaxial, coarse-grained, White Sparry Dolomite (WSD) and grey sparry dolomite, adjacent to Dark Replacement Dolomite (DRD) with bituminous seam. Red arrows indicate brittle displacement of ore textures. B) Coarse-grained orange sphalerite in white sparry dolomite and calcite in mineral-matrix breccia. Sp2/3: sphalerite generation 2/3.

Figure 4. A) W-E oriented 200 m thick cross section from the mine Leapfrog model displaying W-dipping units. Nuevo Rhamys mineralized corridor plunges shallowly to NW (into page) hosted in DSJ and DSV. b) Schematic sketch of a) illustrating east-verging D1 folds and thrust faults relative to mineralization (yellow). Refer to text for additional unit name abbreviations.
breccia, coarse-grained, orange sphalerite (Sp3) is deposited. Minor structural modification and metre scale displacement of ore bodies is attributed to N-S extension and normal movement along shallowly N- and S-dipping, E-W faults during D2.

5 Relative timing of deformation and mineralization

Previous studies of the San Vicente deposit have thoroughly documented the epigenetic replacement textures of the first generation of sphalerite and the dark replacement sphalerite (Fontboté and Gorzawski 1990; Kilian 2005). Microstructural evidence from this study suggest Sp2 was pre- to syn-D1, with non-coaxial shearing localized along WSD bands and minor sphalerite recrystallization. D2 ENE-WSW dextral faults resulted in the structural modification of mantos yet were associated with little remobilization. In contrast, D3 NW-striking dextral-normal faults cause prominent NW-elongation of pre-existing mantos and the generation of alternating NW-striking corridors of ore-bearing mineral matrix breccias and rock matrix breccias, coupled with elevated galena concentrations. More precise geochronological constraints yielded by different generations of calcite veins in limestone units and gangue dolomite-calcite intergrowths in breccia cement will be the focus of future studies.

6 Discussion and preliminary conclusions

The San Vicente Zn-Pb deposit displays paragenetic origins akin to most MVT deposits, however, structural controls on remobilization and the translation of ore body geometries suggest it may be partially analogous to MVT deposits in the Ozarks (USA), which were entrained in the Ouachita fold belt during Permain orogenesis (Leach and Rowan 1986). Where included in genetic models, research into the influence of strain on MVT deposits primarily focuses on the host-basin evolution. However, few studies have examined the direct impact of deformation within such deposits, including the potential for strain-driven remobilization. San Vicente displays evidence of early folding and thrusting followed by brittle faulting. The NW-striking structural controls on large-scale brecciation and their relative timing remains a source of interest, including the extent of remobilization and new ore formation versus dilution. It is important to note that this brecciation and associated fluid ingestion is spatially limited to the southern half of the deposit. Ongoing research aims to explore deformation processes within the mine and surrounding areas to better elucidate the 4D evolution of the San Vicente deposit, including primary ore body geometries. This will be of significance in identifying structurally modified, concealed ore shoots within the mine and region.

Acknowledgements

We gratefully acknowledge the financial support of Compañía Minera San Ignacio de Morococha S.A.A. (SIMSA), and to Alejandro Millership for aiding the conception of the project. Special thanks to the geologists at San Vicente who assisted during fieldwork.

References

Pre-metamorphic oxidation of the Broken Hill deposit at Aggeneys (South Africa) revealed by Cu isotopes

Stefan Höhn, Hartwig E. Frimmel
Bavarian Georesources Centre (BGC), Institute of Geography & Geology, University of Würzburg, Germany

Vinciane Debaille
Laboratoire G-Time, Université libre de Bruxelles, Belgium

Abstract. The Broken Hill deposit is part of the Aggeneys-Gamsberg ore district in northwestern South Africa. Although often portrayed as metamorphosed SEDEX mineralization, the ore district shows unusual mineralogical and geochemical features, like a distinct Mn-halo and nearby peraluminous rocks that cannot be explained by a simple SEDEX model. Here we present the first Cu isotope data for chalcopyrite from the Broken Hill deposit, which are interpreted as reflecting an oxidation event in the pre-metamorphic history of the deposit. The oxidation of sulfides was caused most probably by intense chemical weathering and led to enrichment in elements that are immobile under near-surface conditions. New trace element data for different sulfide generations from Broken Hill reflect such weathering-induced change in element abundances.

Weathering-induced oxidation of the ore prior to metamorphism would have led to a spatial redistribution of base metals, which is in accordance with observed metal zonation in the ore district. Our new data suggest that Cu isotopes can help in deciphering such a process and thus can be of significant assistance in further base metal exploration in this as well as other, genetically related, ore districts.

2 Geological setting

The Aggeneys-Gamsberg ore district is part of the volcano-sedimentary successions of the Bushmanland Terrane. The eponymous Bushmanland Group consist of ferruginous quartzite, shale, calc-silicate rocks, amphibolite and the ore schist formation, which hosts the ore exposed at the various deposits (Bailie et al. 2007). In the area around Aggeneys, peraluminous sillimanite and sillimanite-corundum rocks occur as scattered but strata-bound layers (Willner et al. 1990). Isoclinal folding and structural duplication are ubiquitous evidence of the intense deformation of this area (Colliston et al. 2012).
Broken Hill is the southernmost deposit of the ore district (Fig. 1) and shows many similarities with the famous Broken Hill deposit in Australia. It consists of multiple deformed and metamorphosed stratiform, strata-bound ore lenses of magnetite and sulfide, rich in Fe, Pb, Mn, Zn, Cu and Ba and in places with Cd, Co, Bi, Sb and traces of gold (McClung and Viljoen 2011). The sulfide mineralogy consists of chalcopyrite, galena, sphalerite, pyrite and pyrrhotite (Ryan at al. 1986; Bailie et al. 2007).

3 Results

3.1 Trace elements in sulfides

Trace element concentrations were measured on a total of 70 sulfide grains from the Broken Hill deposit using an Agilent 7500i ICP-MS with a 266-nm UP193FX New Wave Research laser at the GeoForschungszentrum Nordbayern, Erlangen, Germany.

Pyrrhotite
Twenty analyses were conducted on texturally late pyrrhotite from Broken Hill. These results confirmed the generally trace element-poor character of pyrrhotite. The averages for Ru, Rh, Pd, Au, Ga, As, In, Sn and Bi are below 1 ppm, whereas the values of Ge, Ag, Sb and Pb are lower than 10 ppm. Mn, Cu and Zn revealed slightly elevated concentrations (55 ppm, 260 ppm and 195 ppm) in combination with high standard deviations, which is a strong indicator for them being related to micro-inclusion within pyrrhotite. Co and Ni concentrations (1278 ± 827 ppm; 460 ± 433 ppm) show strong variations but generally constant Co:Ni ratios between 2.2 and 4.4 (σ = 3.6). All results can be described by a trend with a strong correlation coefficient of 0.90, which speaks for only one pyrrhotite generation (Fig. 2).

Sphalerite
A total of 29 sphalerite grains were analysed. The results indicate the existence of two distinct types of sphalerite, the first one (Sp1) occurring as small inclusions within gangue minerals. In open pore-space this sphalerite type shows advanced replacement by other sulfides like chalcocypnite, for which it is regarded as relictic. This sphalerite type yielded elevated Co (σ = 6100 ppm) and Mn (σ = 4790 ppm) contents. In contrast, Ni is very low with an average of 7.0 ppm. The very heterogenous Cu concentrations (σ = 13400; σ = 8340) are in good agreement with the microscopic observation of “chalcopyrite-disease” within sphalerite. The measurements further yielded mean Cd and In concentrations of 1890 ppm and 45.8 ppm, respectively. The other sphalerite type (Sp2) is spatially associated with volumetrically larger amounts of sulfides like chalcocyprite, galena and pyrrhotite. Sphalerite of the type Sp2 often appears as meniscus cement, indicating that it belongs to a texturally late sulfide generation. Compared with Sp1 this sphalerite type is richer in Zn (σ = 57.8 ppm; σ = 0.96) and Mn (σ = 21500; σ = 5900) (Fig. 3). The Cd contents are quite constant in all analyses with an average of 2050 ppm and a standard deviation of only 115 ppm. One of the biggest differences to Sp1 is the average Co value of 395 ppm, which is on average more than 15 times lower than in Sp1. Both sphalerite types have similar low Ni concentrations. With 9.6 ppm the average In content is significantly lower than in Sp1.

Chalcocyprite
Chalcocyprite is enriched in Ag (σ = 4070 ppm) and Mn (σ = 1640 ppm). In comparison with Co (σ = 14.8 ppm) the Ni values are distinctly elevated (σ = 311 ppm) but show a strong variation with σ = 1190 ppm. The concentrations of Ru, Pd, Au, Ga, As, Sn, and Bi were all found to be below the lower limit of detection of 1 ppm.
3.2 Copper isotopes

Chalcopyrite of eight samples from the Broken Hill deposit yielded a $\delta^{65}$Cu range from 1.20 to 1.68 ‰ with a mean value of 1.42 ‰. A comparison with Cu isotope values for other sulfide mineralizations from all over the world (Fig. 4) shows that the Cu isotope values from the Broken Hill deposit are significantly out of the range typical of high-temperature hydrothermal chalcopyrite ($\delta^{65}$Cu = -0.6 to +0.4) as defined by Ikehata et al. (2011).

Fig. 4. $\delta^{65}$Cu values of chalcopyrite from the Broken Hill deposit (this study) compared to continental high-temperature hydrothermal chalcopyrite (grey bar), Besshi-type deposits and supergene ores worldwide (Ikehata et al. 2011). Ccp = chalcopyrite.

4 Interpretation and discussion

The $\delta^{65}$Cu values of chalcopyrite from the Broken Hill deposit, with an average of 1.42 ‰, differ significantly from those of hydrothermal chalcopyrite that could be expected in an exhalative deposit. Chalcopyrite from Rammelsberg, for example, has an average $\delta^{65}$Cu of -0.54 ‰ (Höhn et al. unpubl. data). Because of the inability of the Cu isotopic system to fractionate at high temperatures, the metamorphic overprint cannot account for such a strong fractionation in a world-class sized orebody. The study of Pekala et al. (2011) suggested that an additional hydrothermal input and thus sulfide precipitation on pre-existing sulfides would cause a lowering of the $\delta^{65}$Cu values of the ore lenses. The only known process that could explain sulfide enrichment coupled with $\delta^{65}$Cu fractionation of as much as +1 ‰ to +3 ‰ is supergene oxidation of sulfides (Mathur and Fantle 2015). Fractionation of Cu isotopes is strongly temperature dependent. Consequently, resulfidation during high-grade metamorphic overprint would not be able to fully undo this low-temperature fractionation because of the high temperatures at the time of metamorphism.

For the Aggeneys-Gamsberg ore district, we therefore propose a pre-metamorphic oxidation event similar to that in many non-sulfide zinc deposits all over the world (e.g. Borg 2015). Regardless of the exact timing, oxidation of sulfide-rich sediments or sedimentary rocks would explain the observed fractionation of Cu isotopes, a decay of feldspar and mica and a loss of all elements mobile under acidic surface to near-surface conditions. The product of this process would be a laterite-like accumulation of quartz, base metal-rich clay minerals like saucnite (Balassone et al. 2017), Fe- and Mn-oxides/hydroxides and in case of a high content of organic materials phosphates. At the metamorphic event between 1350 and 1100 Ma, the close spatial association of all these geochemical anomalies could have been the base for the characteristic suite of metamorphic minerals found around Aggeneys.

Pre-metamorphic oxidation would be also in good agreement with the trace element contents of the sulfides from the Broken Hill deposit. They have high Mn contents in common, which is most probably due to a high Mn activity in the environment they crystallized in. Nevertheless, the two observed sphalerite types yielded significant differences in Mn, Co and In, which speaks in favor of multi-stage re-sulfidation. Furthermore, a multi-stage hydrothermal sulfur input, possibly from different source areas, could explain the different $\delta^{34}$S values observed in the different deposits of the Aggeneys-Gamsberg ore district (McClung et al. 2007).

In places where the metamorphic sulfur input was not sufficient for the genesis of sulfides, the elevated temperature and pressure caused silicates with high contents of Fe, Mn and base metals. This is in perfect concordance with the worldwide highest Mn contents in gahnite from the vicinity of the Broken Hill deposit in South Africa (O’Brien at al. 2015). New phases of sulfur input under higher metamorphic conditions could also trigger the variously observed replacement reactions of gahnite by sphalerite (Spry 1987).

The introduction of an early oxidation event in the complex metallogenic history might help to solve various geochemical and mineralogical peculiarities in and around Aggeneys. For example, Stalder and Rozendaal (2005) recognized a negative Eu-anomaly in massive barite from Gamsberg, which is unusual for hydrothermal barite. However, weathering-induced barite formation would happen under oxic conditions in which Eu$^{3+}$ lacks the necessary similarity with Sr$^{2+}$ to form such an anomaly. The Sr isotope ratios of barite (McClung et al. 2007) further indicate an evolved continental crustal source. In their study Stalder and Rozendaal (2004)
pointed out that the intimate association of apatite with the sulfides could be used as an exploration guide. However, a spatial association would only make sense if both are connected by a common enrichment process independent from basin conditions. In laterite, as a product of intense chemical weathering, high phosphorus contents are not uncommon (Economou-Eliopoulos 2003). Maybe, fluorapatite, which is abundant in the Aggeneys-Gamsberg ore district, has a similar origin.

All in all, the available geochemical and mineralogical evidence, now supplemented by new Cu isotope data, point to derivation of the sulfide ore bodies in the Aggeneys-Gamsberg ore district from syn-sedimentary sulfide concentrations that had been variably oxidized prior to metamorphism.

Acknowledgements

We thank H. Brätz for the assistance with the ICP-MS analyses. We also thank S. Cauchies and J. De Jong for valuable help in the clean lab and for keeping the Nu-Plasma 2 in good shape at ULB. Financial support was provided by the Philosophical Faculty of the University of Würzburg. VD thanks the FRS-FNRS and ERC StG ISoSyc for funding.

References


GIS-based mineral system approach for prospectivity mapping of iron-oxide apatite-bearing mineralisation in Bergslagen, Sweden

Martiya Sadeghi 1, Mehrdad Bastani 1,2, Stefan Luth1,2, Alireza Malehmir2, Emma Bäckström3, Paul Marsden3
1Department of Mineral Resources, Geological Survey of Sweden, Uppsala, Sweden
2Uppsala University, Dept. of Earth Sciences, Uppsala, Sweden
3NIO (Nordic Iron Ore AB), Sweden

Abstract. Bergslagen is one of the richest mineral districts in Sweden for base and precious/critical minerals and metals. In this work a mineral system approach for targeting of iron-oxide apatite-bearing mineralisation has been developed. GIS-based mapping of prospectivity for this type of mineralisation has been carried out with a focus on Ludvika mining area from Blötberget to Håksberg with known and high-quality iron-oxide deposits. According to spatial analysis on mappable criteria’s, strong positive airborne magnetic anomalies, density of structures and the contact between felsic volcanic rocks and granites are crucial for this type of mineralisation in the study area. This GIS-based model will also be used in targeting of iron-oxide deposits at depth in the Blötberget area. However, the mineral systems approach considers the origin of deposits in the framework of lithospheric-scale processes from the time-honored aspects of the source, fluids, transport and physical and/or thermo-dynamical traps. Applied to exploration strategy, this approach allows for more predictive models. Rather than matching patterns, knowledge of the underlying geological processes and tectonic-structural setting can be used for identifying areas with higher probability of finding deposits of interest. Furthermore, this method can broaden the scope of prospectivity indicators and allows for earlier and more efficient fertility assessments.

1 Introduction

Iron-oxide (also sometimes apatite-bearing) deposits, in Sweden are today are mainly known from Kiruna and Malmberget mines in the north. However, iron-oxide deposits of similar quality and to a disputed origin can also be found in central Sweden in the so-called Bergslagen ore province/district. The largest of these being Grängesberg, Blötberget and Idkerberget mined for their quality iron ore until the 20th century some of which for over a few hundreds of years. Based on their overall mineralogy, geochemistry, geometry and relationships with the host rocks, these Bergslagen deposits are suggested to have Kiruna-type origin i.e., high temperature to magmatic origin (e.g. Jonsson et al., 2010). This type of mineralization locally may show some differences between style of mineralization, associated alteration and texture. Beside, iron in the form of magnetite and hematite, fluorapatite and associated rare earth-bearing phosphates and silicates in these ores may represent a significant potential reserve of REEs as well as of phosphorus (Sadeghi et al., 2019) requiring an elevated and renewed attention (Malehmir et al., 2017).

McCuaig et al. (2010) describe a four-step procedure for linking the mineral system with data available for practical exploration targeting. These steps include translation from (1) critical processes of the mineral system, to (2) constituent processes of the mineral system, to (3) targeting elements reflected in geology, and (4) targeting criteria used to detect the targeting elements directly or by proxy. This procedure is today used, implicitly or explicitly, in all mineral prospectivity modelling studies.

There is some restriction that prospectivity models are dependent on the input exploration data, and any targeting criteria that are not mappable in the available exploration data cannot be incorporated in modeling.

In this study, we focus to present a mineral system model for iron-oxide apatite ores in the Bergslagen from mining camp scale and imply the concept in the deposit scale (Blötberget) in the Ludvika mining area. The result of this model will be employed for 3D prospectivity modeling in the Blötberget and surrounding areas in follow up studies within the trans-European H2020-funded Smart Exploration project.

2 Study area

The study area is situated in the historical mineral district of Bergslagen in south-central Sweden extending from Grängesberg in the south Håksberg in the north (Fig. 1). The mineralisation in Bergslagen comprises of banded iron formation (BIF), skarn-type iron-oxide deposits and apatite-rich iron-oxide deposits, with the latter deposits accounting for more than 40% of the iron ore produced in Bergslagen (Magnusson, 1970, Stephens et al., 2000). The area of interest, Blötberget and areas north of it are
known for their iron-oxide apatite-bearing deposits. The mineralisation in Blöteberget is known to extend down to at least 800–850 m depth (Malehmir et al., 2017) in a moderately dipping (approximately 45-50 degree) manner.

Geologically, Bergslagen belongs to the Svecokarelian orogen in the Fennoscandian Shield. Metamorphosed volcano-sedimentary rocks of Palaeoproterozoic age (1.85-1.8 Ga) dominate the host rocks (Fig. 1). Metavolcanic rocks including feldspar porphyritic rocks show close spatial association with iron-apatite mineralisation. The rocks show metamorphic grades ranging from medium to upper amphibolite facies. Coeval dacitic, andesitic and basaltic dykes and subvolcanic intrusions, and synvolcanic, granitic to intermediate plutonic rocks cut the host rock and the mineralisation. Post-mineralisation intrusion of granite-aplite-pegmatite and metamorphism severely resulted in the deformation of these rocks (Allen et al., 1996; Ripa and Kübler, 2003). During their formation, the host rocks were variably hydrothermally altered. The origin of the apatite-rich iron-oxide deposits is considered to be synvolcanic, although this is disputed, with a new study favouring a magmatic-to-high-temperature hydrothermal origin (Jonsson et al., 2013).

3 Mineral systems approach target generation

In a data-driven mineral prospectivity model the model parameters are estimated based on statistical spatial relationships to a training dataset of the iron oxide apatite mineralisation in the study area (knox-Robinson and Wyborn, 1997). The data-driven weights of evidence method (WofE) have been used (Bonham-Carter et al., 1994), which is a statistical method for quantifying spatial association between mineral deposits and geological features. A weight of evidence is normally applied to exploration situations in which there is an adequate number of mineral deposits or occurrences already discovered (e.g., for brownfields). Simply, WofE is a data-driven method based on the Bayesian theory and its fundamental concept of prior and posterior probabilities.

Figure 1. Simplified geological map of the study area showing locations of major iron-oxide deposits in the Ludvika mining area from Grängesberg to Håksberg. Map courtesy of the Geological Survey of Sweden (SGU).

In Table 1, regional scale mineral systems models including the list of the targeting elements and relevant spatial proxies / predictor maps for IOA mineralisation are listed. Based on previous knowledge on IOA mineralisation in Sweden and particularly in the Bergslagen district, a generalised conceptual mineral systems model were developed for iron-oxide apatite-bearing mineralisation in the Bergslagen; a selection of relevant data used for the mineral prospectivity mapping in the area. In each case geological proxies for metal source, metal transport pathways and depositional were applied based on the known characteristics of deposits and interpreted geology.
Table 1. Regional-scale iron-oxide apatite-bearing mineral system models listing targeting elements and relevant spatial proxies/predictor maps for the targeted apatite iron-oxide mineralisation deposit.

<table>
<thead>
<tr>
<th>Processes</th>
<th>Sub processes</th>
<th>Mappable ingredient</th>
<th>Predictor maps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluids, Metals And ligands</td>
<td>Magmatic</td>
<td>Geochemistry of rocks</td>
<td>Proximity and elemental map</td>
</tr>
<tr>
<td></td>
<td>Magmatic</td>
<td>The presence of iron-rich intrusive/extrusive rocks</td>
<td>Proximity of granitoid/ryholitoid rocks</td>
</tr>
<tr>
<td>Country rocks</td>
<td>The presence of iron-rich metal sedimentary rocks</td>
<td>Proximity of limestone/sedimentary rocks</td>
<td></td>
</tr>
<tr>
<td>Energy</td>
<td>Invasive-volcanic complex</td>
<td>The presence of iron-rich intrusive/extrusive rocks</td>
<td>Proximity and airborne magnetic anomalies</td>
</tr>
<tr>
<td></td>
<td>Hydrostatic head for oxidised fluid</td>
<td>Geochemistry of felsic rocks</td>
<td>Elemental map /</td>
</tr>
<tr>
<td>Fluid pathway</td>
<td>District-scale fault network reactivated during mineralisation event</td>
<td>Regional scale structures (Geophysical data)</td>
<td>Intensity of structures</td>
</tr>
<tr>
<td></td>
<td>Porosity</td>
<td>Bedrock and alteration</td>
<td>Proximity</td>
</tr>
<tr>
<td>Depositional processes</td>
<td>Structural</td>
<td>Fault/ fold/breccia zones</td>
<td>Proximity</td>
</tr>
<tr>
<td></td>
<td>Chemical</td>
<td>Redox reaction between reduced rocks and oxidised fluid</td>
<td>Proximity to geophysical magnetic anomalies and lithogeochmistry</td>
</tr>
<tr>
<td></td>
<td>Mineralisation closely linked with emplacement of intrusive-volcanic complexes and brecciation</td>
<td>The presence of iron-rich intrusive/extrusive rocks</td>
<td>Proximity to volcanic/ intrusive rocks</td>
</tr>
</tbody>
</table>

Firstly, spatial association between training site (iron-oxide apatite-bearing mineralisation) and the mappable ingredient was calculated, secondly, evidential maps for prediction were optimised, and finally, predictor maps were combined based on mineral system approach to created favourability maps and target generated map produced.

Figure 2. Potential prospectivity map of iron-oxide apatite-bearing (IOA) mineralisation in the study area around Blötberget and Ludvika area. It is remarkable areas west of the city Ludvika with a strike SW-NE stands out as high probability.

4 3-D modeling of airborne magnetic data

In the summer of 2016-2017, the Geological Survey of Sweden (SGU) conducted a new airborne survey in the area along flight-lines of 200 m spacing with nominal flight-height of 60 m above the ground surface; an along flight-line sampling interval of 15 m was used. Different than earlier data from the 70s, this survey was designed to orthogonally (NW-SE directed) transverse the structures observed on earlier airborne data and surface geological mapping. The airborne magnetic data were modelled in 3D using the VOXI Earth modelling program developed by Geosoft®. The resulting model contains voxels each having the average susceptibility of material within the voxels’ volume. The voxels have horizontal dimensions of 250 m by 250 m and a vertical dimension that increases logarithmically with depth starting from 25 m at the surface. Figure 3 shows iso-susceptibility surfaces of 0.05 (SI) generated from the voxel susceptibility model. The modelled iso-surfaces coincide well with the locations of known iron-oxide mineralisation in the area (e.g. Blötberget and Håksberg). Use of borehole information in the modeling of magnetic data as constraints can improve the accuracy of the method specially with depth. Such a model can be utilised for a 3D perspectivity mapping in the future. Moreover, at areas covered by water (e.g. the lake north of Blötberget) the model can facilitate planning reconnaissance drillings.
5 Conclusions

Based on spatial association of mappable ingredient with the IOA mineralisation in the Ludvika mining area, the highest spatial association with mineralisation is related to (i) proximity to the positive airborne magnetic anomalies, (ii) intensity of the structure, (iii) proximity to the contact between volcanic and granitic rocks and (iv) proximity to the dacite-rhyolite volcanic rocks. The data-driven spatial analysis in the area with several data and active mining and exploration activities (e.g. brown field) may help to adding values on knowledge of geological processes on mineralisation in district-camp scale. All this information may reveal new mineral system model(s) for better evaluation of targets for mineral exploration.

There are other types of iron-oxide mineralisation in the study area (e.g. skarn type and BIF) and it is essential to remember that the common practice of incorporating proxies of all mineral systems components (source, pathways and traps) in a single prospectivity model may not yield a deposit type-specific prospectivity map. The output of 2D mineral prospectivity and mineral system model can be applied in the 3D for calculation of exploration criteria’s and proximity to the ore deposit (target) in the 3D (e.g. proximity to the magnetic anomalies in depth and proximity of known mineralisation with contact between dacite-rhyolite and granitic rocks.

Acknowledgements

This study was conducted within the Smart Exploration project. Smart Exploration has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 775971. Partial funding received from SGU from the Bergslagen project contributed to the modification of the database and geological-geophysical data used in this study.

References


Defining an alkaline igneous-associated REE-HFSE mineral system: a foundation to map plays, uncertainty and risks to project value

Graham J. Banks
Geological Survey of Denmark and Greenland

Benjamin F. Walter, Michael A.W. Marks
University of Tübingen

Pete R. Siegfried
GeoAfrica Prospecting Services

Abstract. REE-HFSE exploration and research projects tend to focus on describing deposit- to outcrop-scale mineralisation. Regional-scale frameworks, mineral system maps and predictive targeting capability are largely lacking. A contextual, probabilistic REE-HFSE mineral system approach is being developed by the authors to enable any REE-HFSE mineral system’s extent to be defined, mapped and ‘risked’ in 4D. This will enable systematic investigation of the crustal pathways and potential trap locations along which a mantle-derived REE-HFSE ‘batch’ may now be distributed. A workflow to define any REE-HFSE mineral system is presented: (a) Identify and hierarchically organize a mineral system’s genetically related sub-divisions and deposits, (b) map its known and possible maximum extents, (c) name it, (d) discern its known mineral endowment, and (e) assess the favourability of the system’s critical components for preserving project value. The workflow is designed to improve predictive targeting along under-evaluated plays, in order to prioritise further investigations and expenditure. It provides the foundation to compare, risk, and rank REE-HFSE provinces, plays and projects. And it is easily adaptable for other mineral commodities.

1 Introduction, aims and target audience

The global plan to decarbonise energy and transport systems is increasing the demand for rare earth elements (REE) and high field strength elements (HFSE) (e.g. Kalvig and Machacek, 2018). These metals were designated as “critical raw materials” for the European Union (EC 2010; EC 2017) due to their high economic importance and high supply risk. They are mainly associated with alkaline igneous rocks (that includes carbonatites) and their weathered products (e.g. Kalvig and Machacek 2018; Pirajno 2015; Verplanck et al 2016). REE-HFSE recycling is unlikely to meet increasing demand (Du and Graedel 2010; Binnemans et al 2013), thus appraisal and mining (Goodenough et al 2018) of known mineralisation and as-yet-undiscovered deposits will probably be required. However, most REE-HFSE exploration and research projects focus on/below the deposit scale and neglect the broader context, where significant undiscovered potential may exist. Predictive targeting capability of these metals remains limited (Verplanck et al 2016). In consequence, REE have been mined from only a few deposits so far (e.g. Kalvig and Machacek, 2018; U.S. Geological Survey 2018) and many alkaline igneous occurrences remain under evaluated. Closer collaboration between industry, research and government policy will be essential for organisations to quantify geological risks and demonstrate acceptable geological probability of success.

To help address this REE-HFSE targeting requirement we present a workflow to define any mineral system associated with alkaline igneous rocks at the province scale. This is a necessary foundation to prioritise data acquisition and discern geological uncertainties before commencing district- to ore-shoot scale evaluations. The workflow is designed for geoscientists, economists and strategists to summarise the current knowledge status of any mineral system together: quickly, cheaply and easily. It is for use at any exploration targeting or research project stage. However, it will generate optimal efficiency and value if used at province-scale to select district- or deposit-scale license/research locations. The product will also provide context for upside endowment potential around occurrences, prospects and mines.

The overall aim is to assist industry, research, financial and government policy stakeholders to more effectively visualise and target under-evaluated mineral systems at province-scale. Using it should facilitate discussion and understanding between stakeholder groups, and improve decision quality across the REE-HFSE sector.

For an overview of the mineral system concept refer to McCuaig and Hronsky (2014).

2 Mineral system definition and use

Despite the spectrum of published mineral system concepts, approaches and purposes there is a paucity of information on how to actually characterise an individual mineral system. So one alkaline igneous-associated REE-HFSE mineral system has been defined as the entire set of naturally occurring and genetically related mineralisations that originated from one commodity provenance ‘batch’ (Fig. 1) by Banks et al. (2019, adapted from Magoon and Beaumont 1995). Each REE-HFSE
mineral system extends from its active/once active provenance of sub-lithospheric mantle, through the magmatic/hydrothermal fluid charge pathways, to all the resultant REE-HFSE mineralisations throughout the province. It encompasses, and links, the magmatic, metamorphic, weathering and basinal facies associations and processes (Fig. 1). A single mineral system therefore encapsulates all the geologic components critical for mineralisation to exist present-day, regardless of economics (adapted from Magoon 1995 and Royal Dutch Shell 2013). The mineral system definition presented emphasises the chronologic relationships between genetically linked mineralisations (Fig. 2).

Using a tree geometry analogy, one REE-HFSE mineral system has a sub-lithospheric mantle provenance root network, a magmatic-hydrothermal trunk that focused REE-HFSE-transporting magmas and fluids into the upper crust (vertical charge), and district- to ore shoot-scale migration branches in/on the upper crust (horizontal charge). REE-HFSE deposits/mineralisations are akin to fruit (each at various stages of ‘richness’ and inspection) that cluster on mineral system branches (plays). Some mineral system branches may no longer exist due to the province’s climatic and erosional history.

The known mineral system ‘tree’ needs to be mapped to aid spatial modelling of a province’s potential remaining endowment and value. Applying the proposed mineral system definition workflow can enhance mapping, risking and optimal targeting of REE-HFSE mineral systems in underexplored regions, regardless of their data volume.

The proposed mineral system definition is Stage 2 of a holistic exploration business process (e.g., Banks 2018; Banks et al. 2019), whereby exploration prospects are built progressively through province to prospect scales with a ‘proceed or stop?’ business decision after each stage.

3 REE-HFSE play definition and importance

The base unit of targeting should be a chronostratigraphically-bound mineral play (Figs. 1, 2) instead of a mineral deposit: to build a REE-HFSE prospect portfolio. An alkaline igneous-associated REE-HFSE play is a group of geologically related ore deposits, mineral deposits and untested prospects within a chronostratigraphic unit (Banks et al. 2019). A mineral play is an appropriate entity because it brings chronologic and genetic context between deposits and prospects. As an ore deposit is a locus of the mineral system-scale processes that generated a play, understanding how a mineralised play operated provides predictive capability, and appropriate analogues, to generate other prospects within that play. Uncertainty and risk can be quantified with play analysis methodology, to link geoscience with business and strategy decisions (e.g. Banks 2018). Also, using the exploration play enables cross-pollination of ideas with exploration stakeholders of other commodities (e.g. McCuaig et al 2018) using mutual vocabulary.

4 The mineral system definition workflow

The REE-HFSE mineral system definition workflow is summarised below (more detail in Banks et al. 2019).

Task 1. Organise province framework knowledge
All available data-knowledge about the host province’s 4D evolution and mineralisation—including all historic exploration and production data—should be summarised and geospatially organised.

Task 2. Clarify mineral system critical components and the project’s investigation products
The critical components will be different at province, district and deposit scales, so will require differing mappable criteria. Then list the project’s products that will summarise the mineral system in 4D (e.g. Fig. 3).

Task 3. Identify the mineral system
Demonstrate it exists via at least one REE-HFSE mineralisation that is geochemically anomalous to the local lithologies. Next, correlate the genetic relationships between occurrences and to their provenance.

Task 4. Hierarchically organise the mineral system’s sub-divisions
Organising a mineral system into exploration targeting sub-divisions (Figs. 1 and 2)—from mantle expulsion to the most distal mineralisation—can improve 4D mapping and quantifying a mineral system.

Task 5. Estimate the known mineral endowment (size) of the mineral system
The size is the sum of produced and unrecovered REE-HFSE mineral resources yielded from one provenance commodity ‘batch’. Size is one way to compare mineral systems. It could also be used to estimate the system’s yield—mineralisation efficiency.

Task 6. Name the mineral system
Each mineral system needs a name to distinguish it from other mineral systems. We display a standardising naming convention that incorporates the certainty of the correlation between the commodity provenance and occurrences, and the dominant mineral play, e.g. the Southwest Germany, Tentative, Variscan-Miocene Carbonatite REE-HFSE mineral system.

Task 7. Map the known mineral system extent
A mineral system’s known geographic, stratigraphic and temporal extents are mapped, to identify possible play extensions and new play concepts that could contain additional deposits and value.

Task 8. Summarise the mineral system’s favourability
To indicate if a REE-HFSE mineral system could yield more prospective play opportunities, the favourability (for project value preservation) of each critical component should be summarised. We then recommend translating a mineral system’s critical components into mappable targeting criteria (McCuaig et al. 2010) because this translation is crucial for subsequent Play Analysis and Prospect Maturation exploration stages.
Figure 1. A schematic display of one REE-HFSE mineral system’s possible extent and examples of facies associations, plays, deposit types and prospect types. It emphasises how genetically linked deposits and prospects form plays, and that plays are genetically linked ‘branches’ from one mantle provenance ‘root’. Reproduced from Banks et al. 2019.

- A mineral system
  - Its facies associations (regional deposition/trapping environments)
    - Their play types (regional deposition/trapping processes)
      - Their plays (chronostratigraphically-bound mineralised units)
        - Their mineral occurrence types (resource, deposits and showings categorised into one or more deposit/trap types)
          - Their host lithology types.

Figure 2. Scale-based, Linnean (1758) hierarchy recommended for mineral system sub-divisions. Reproduced from Banks et al. 2019.

Figure 3. A mineral system events chart showing the province-scale, magmatic facies, critical components at Kaiserstuhl Volcanic Complex (KVC). KVC is a district in the Southwest Germany, Tentative, Variscan-Miocene Carbonatite REE-HFSE mineral system. Reproduced from Banks et al. 2019 (see there for references within Fig. 3).
5 Implications

This standardised mineral system definition ‘recipe’ for 4D mapping is recommended because a mapped mineral system provides a firm foundation to estimate remaining endowment potential and to optimise an organisation’s often limited resources. Once the known extent of a REE-HFSE mineral system has been defined, a project can switch from a descriptive to a predictive approach to: (a) predictively determine the most favourable mineral system branches to target/research, (b) probabilistically rank REE-HFSE mineral systems globally. Optimal mineral exploration ground selection can be achieved after mineral system facies, depositional processes, chronostratigraphic plays and mineralisation loci have been linked. Using a chronostratigraphically-bound mineral play as the base unit of exploration/evaluation enables comparative and probabilistic valuation of a ‘family’ of prospects. We recommend that industry, geological surveys, research and government policy stakeholders collaborate closely to define alkaline igneous-associated REE-HFSE minerals systems: to optimise targeting, highlight knowledge gaps requiring further budget and increase the quality of business decisions.

Acknowledgements

This research and ability to attend this conference were funded within the HiTech AlkCarb project, under the European Union’s (EU) Horizon 2020 research and innovation programme, grant agreement number [689909]. We thank the HiTech AlkCarb project team for frequent discussions. GJB also thanks many GEUS and former colleagues for stimulating discussions and insight on commodity systems and geological risk mapping.

References


Late-orogenic W-Sn vein-type mineralization at Minas da Panasqueira (Portugal): a structural and in-situ Rb-Sr geochronological study

Dominique Jacques, Philippe Muchez, Manuel Sintubin
KU Leuven, Department of Earth and Environmental Sciences, Belgium

Thomas Zack
University of Gothenburg, Department of Earth Sciences, Sweden.

Abstract. The W-Sn Panasqueira deposit consists of an extensive swarm of coplanar, subhorizontal veins that are laterally overlapping and connecting. Segmentation structures, a local zigzag geometry and straight propagation paths indicate that the veins are exploiting regional cross-fold joints. These joints are associated with subvertically-plunging F_3 folds, which developed during late-orogenic oroclinal buckling. Veining reactivated the joints under hydraulic overpressures and low differential stress. The consistent orthogonal relationship between the veins and non-cylindrical F_3 fold hinges indicates that veining occurred in a similar stress regime as jointing, i.e. with the minimum principal stress subparallel to the fold hinges. In-situ Rb-Sr dating (LA-ICP-MS/MS) of muscovite selvages bordering the vein walls has demonstrated that W-Sn mineralization occurred in a time range of 305-302 (± 2.3 to 4.1) Ma. Hence, the structural emplacement of the vein swarm occurred in a late-orogenic setting, simultaneous with transpressional F_3 folding and prior to the tectonic inversion at ca.297-295 Ma. Iberian vein-type W-Sn mineralization and oroclinal buckling thus appear not only to share their late-Variscan timing, but could also be considered as kinematically related processes.

1 Introduction and geological setting

The world-class W-Sn Panasqueira deposit is situated in the southwestern part of the Iberian Massif (Portugal) (Fig. 1), part of the Variscan orogenic belt present throughout Europe. More specifically, Panasqueira is located within the Central Iberian zone (CIZ), the axial zone of the Iberian Massif. The CIZ is a predominantly autochthonous domain, consisting of metasedimentary rocks deposited at the northern continental margin of Gondwana during the Neoproterozoic to early Palaeozoic (Martínez Catalán et al. 2014). Regional metamorphism in these sequences ranges from lower greenschist to amphibolite facies (Martínez Catalán et al. 2007). Late-to post-tectonic with Variscan deformation (310-285 Ma), widespread granite intrusion occurred throughout the CIZ (Gutiérrez-Alonso et al. 2011; Martínez Catalán et al. 2014). W-Sn mineralization is spatially and temporally associated with this granite suite.

The Panasqueira deposit consists of an extensive network of subhorizontal quartz veins, which are cross-cutting the strongly folded metasedimentary host rock peripheral to a greisen cupola (Fig. 1). The vein swarm is a textbook example of a greisen-affiliated W-Sn vein-type deposit, but is characterized by a conspicuous flat attitude. A variety of structural emplacement modes have been proposed (Marignac 1973; Kelly and Rye 1979; Ribeiro and Pereira 1982; Derré et al. 1986; Foxford et al. 2000), but none of these studies have focused on the intimate relationship with the Variscan deformation structure nor are there adequate time constraints available.

Figure 1. Geological map and cross-section of the Panasqueira deposit indicating the location of the underground mine and vein swarm relative to the contact metamorphic aureole and greisen cupola (data source Beralt Tin & Wolfram S.A.). The inset displays the location of the mine (yellow star) within the Iberian Massif.

To clarify the structural emplacement mode of the vein swarm and its relationship with the Variscan orogenic framework we have performed an integrated structural
or ac -joints, which developed orthogonal to the mesoscale F3 folds (Fig. 2).

Variscan deformation structure and the late-orogenic relationship between the geometry of the vein swarm, the analysis. The aim of this study is to highlight the geodynamic setting.

2 Structural analysis

2.1 Fold and foliation generations

Detailed mapping over an area of ca. 15 km² overlying the underground mine has highlighted the presence of two superimposed fold generations, which correspond to the regionally defined F1 and F3 fold stages (cf. Diez-Balda et al. 1990). Both fold generations are characterized by subvertical axial planes and fold axes, and define a Type 3 fold interference (cf. Ramsay 1967). F1 folds are isoclinal with an axial planar S1 cleavage parallel to S0, and are thus generally only discernable in the hinge zones. During late-orogenic transpression (D3), F3 folding refolded the vertical S1 fabric along a vertical axis. F3 folds show a M-, S-, and Z-type parasitic geometry depending on the position in the first-order fold structure, but S3 has a consistent axial planar, NW-SE attitude. The F3 folds have a strongly non-cylindrical nature, with F3 fold hinge plunge often varying within a single outcrop. S1 is the main penetrative fabric of the host rock, which is strongly microfolded by a spaced S3 crenulation cleavage.

2.2 Regional joint system

Within the mining area, and regionally throughout the southern Central Iberian Zone (Derré et al. 1986; Jacques et al. 2018a), a systematic joint network with a subhorizontal to moderately-inclined attitude is omnipresent. The joints are planar, regularly-spaced and often continuous over a length up to tens of metres. In addition, no apparent fractographic features (e.g. plumose structures, hackle fringes, etc.) nor any mineral infilling away from the mine is present.

Geometric analysis of the joints demonstrates that they have a consistent orthogonal orientation relative to the S0-S3 intersection lineations and F3 fold hinge lines, even when the latter show strong variations in plunge. This relationship is obvious from the outcrop- to the regional scale. Hence, the joints correspond to cross-fold or ac-joints, which developed orthogonal to the mesoscale F3 folds (Fig. 2).

2.3 Vein swarm

The W-Sn bearing vein swarm consists of coplanar veins that are overlapping in a relay-stepping geometry and connecting laterally over large distances, without any mutual cross-cutting relationship. Connection occurs along subhorizontal splays, or along high-angle veins forming rock bridges (Fig. 2 – type 1). Straight vein tips, various segmentation structures and a zigzag geometry demonstrate that the veins have exploited a pre-existing joint system, i.e. the regional cross-fold joints.

The veins are predominantly subhorizontal (dip < 20°), although locally inclined veins with a dip of ca. 40-50° occur (‘galo’ veins). These inclined veins are preferentially exploiting pre-existing joint sets with a moderate dip. Inclined veins are related to the strongly non-cylindrical nature of the F3 fold axes, i.e. they occur where the S2-S3 intersection lineation switches from a general subvertical to a local moderate plunge (Fig. 2 – type 2). Dilation in the inclined veins occurred consistently at a high angle to the vein wall, hence they are extension veins similar to the subhorizontal ones. These observations have important repercussions for the kinematic model for the Panasqueira vein swarm (see section 4).

3 Rb-Sr dating

3.1 Methodology

The recent innovation of installing a reaction cell in between two quadrupoles within an inductively-coupled plasma mass spectrometer has eliminated the predicament of isobaric overlap, allowing online separation of 87Sr from 87Rb in MS/MS mode (Zack and Hogmalm 2016; Hogmalm et al. 2017). In addition, the use of a laser ablation system with a small spot size (50 µm) allows inclusions and alterations to be avoided during analysis, while controlling the mineral paragenesis and potential internal zonations.

The in-situ Rb-Sr dating was performed at the University of Gothenburg (Sweden) using an ESI 213NWR (TwoVol2) Nd-YAG laser ablation system connected to an Agilent 8800 QQQ ICP-MS/MS with an octopole reaction cell (ORS). N2O was used as reaction gas for all samples. NIST610, 612 and BCR-2G glass and Mica-Mg nanopowder pellet standards were measured systematically between the different samples to allow for the detection of drift during the analysis day. Muscovites from mineralized vein selvages were subjected to three analytical runs each consisting of a minimum of 10 spots, which combined gave a robust and reliable age for each sample. Glitter© was used for signal revision and to generate the background-subtracted count rates. Isotope ratios were calculated with an in-house spreadsheet, using correction factors obtained from (i) low Rb-moderate Sr (NIST 610, 612, BCR-2G) and (ii) high Rb-low Sr standards (Mica-Mg). Isochron ages were calculated using the Isoplot 4.15 software using the most recent 87Rb decay constant (λ87 = 1.3972 ± 0.0045 × 10⁻¹¹ a⁻¹) of Villa et al. (2015). Mica-Mg and Högsbo-Ms nanopowder pellets (Hogmalm et al. 2017) and Högsbo, GA1550 and MMHb mica crystals were used for data quality control by comparing the isochron age with constraints from literature.
3.2 Results

Errors on the primary standards were calculated from the standard deviations of repeated analysis, giving a precision of 1.7-2.4% for $^{87}$Rb/$^{86}$Sr and 0.13-0.19% for $^{87}$Sr/$^{86}$Sr. Isochron age calculation for the secondary standards indicates quite good reliability. Standards which were subjected to at least 10 spot analyses show reliable ages that typically deviate less than 0.5% from the ages constrained in literature.

Muscovites bordering the vein walls were analyzed for five samples spatially distributed across the mine. The muscovites from the vein selvages represent the earliest stage of vein opening and are overlapping with or just preceding W and Sn mineralization (Kelly and Rye 1979). Besides muscovites (high Rb, low Sr), tourmalines (low Rb, moderate Sr) within the vein selvages were also analyzed. The presence of tourmaline is advantageous because it allows constraint of the initial $^{87}$Sr/$^{86}$Sr ratio. Tourmaline is present in the selvages associated with muscovite, topaz and arsenopyrite and is thus cogenetic with the first stage of mineralization (Codeço et al. 2017; Launay et al. 2018).

The five samples display a quite consistent age of ca. 305-302 Ma (± 2.3 to 4.1 Ma), with an average isochron age of 302.8±1.3 Ma when all 5 samples are grouped together (Fig. 3). The isochrons are characterized by relatively small errors (2σ = 0.7-1.3%) and good MSWD values (between 0.6 and 1.2). Muscovite shows a large variation in $^{87}$Rb/$^{86}$Sr ranging generally from ca. 500 to ca. 10,000, but with a maximum of 40,000 (Fig. 3). The measured tourmaline $^{87}$Sr/$^{86}$Sr ratios vary from 0.720±0.004 to 0.739±0.004 with an average value of 0.730±0.012 and a coefficient of variation equaling 0.81%.

4 Metallotectonic model

Our structural analysis has successfully demonstrated a close kinematic relationship between late-orogenic F$_3$ folding, regional cross-fold jointing and W-Sn vein-type mineralization. Veining reactivated the regional joint system in the vicinity of the Panasqueira cupola, under hydraulic overpressures and low differential stresses (Jacques et al. 2018b). The consistent perpendicular orientation of the veins relative to the non-cylindrical F$_3$ fold axes indicates that the reactivation did not occur during far-field horizontal contraction, as formerly suggested in literature (Kelly and Rye 1979; Foxford et al. 2000). Instead, our study of the inclined ‘galo’ veins indicates that vein reactivation was controlled by local stress states, i.e. the minimum principal stress consistently subparallel to the F$_3$ fold axis (Fig. 2). Veining thus occurred in a similar stress regime as the cross-fold joints, i.e. simultaneous F$_3$ folding and associated with hinge-parallel stretching (Jacques et al. 2018b). This interpretation is supported by in-situ Rb-Sr age dating, which gives an average isochron age of 302.8±1.3 Ma for
the onset of W-Sn mineralization (Fig. 3). This timing is late-orogenic, simultaneous with regional D3 deformation and prior to the tectonic inversion at ca. 297-295 Ma (cf. Pastor-Galán et al. 2015).

Temporal and kinematic constraints indicate that vertical-axis F3 folding reflects transpressional deformation within the outer arc and southern limb of the late-Variscan Cantrabrian orocline (315-297 Ma) (Jacques et al. 2018a). W-Sn vein-type mineralization and-orocline buckling are thus cogenetic and kinematically related processes.

Figure 3. Rb-Sr isochron diagram for the five different Panasqueira samples combined (n=126). The data-point error crosses are 1σ.

Acknowledgements

We thank Beralt Tin & Wolfram (Portugal) S.A. for the possibility to study the Minas da Panasqueira underground mine and for the excellent assistance during our research stays. D. Jacques is financially supported by a postdoctoral fellowship of the Research Foundation Flanders (FWO).

References


Zack T, Hogmalm KJ (2016) Laser ablation Rb/Sr dating by online chemical separation of Rb and Sr in an oxygen-filled reaction cell. Chem Geol 437:120–133. doi: 10.1016/j.chemgeo.2016.05.027
Stream sediment geochemistry for regional prospectivity analysis: Tin, cesium, tantalum and tungsten anomalies in Leinster, southeast Ireland

David Kaeter, Julian F. Menuge
Irish Centre for Research in Applied Geosciences (iCRAG) and University College Dublin

John Harrop
Blackstairs Lithium Ltd.

Abstract. Sediments of streams draining the Leinster Batholith, SE Ireland, are rich in rare elements such as Cs and Sn. After correcting regional stream sediment data from the Geological Survey Ireland Tellus project for the lithological background, geochemical anomalies could be identified. Prominent anomalies (>1.5 SD – >2.5 SD) for residuals of Sn, Ta and W appear in and downstream of catchments with known deposits of rare-element pegmatites and Sn-W veins. Anomalies for Ta and Sn on the same regional trend suggest the presence of undiscovered rare-element pegmatites. High Cs residuals for streams draining metasedimentary rocks east and southeast of the granitoids are best explained by glacial transport and regional drainage. High to anomalous Cs residuals for streams draining volcanic rocks in the SE of the area are a likely artefact of the background correction. Future work includes mineralogical investigation of heavy minerals in stream sediment samples from catchments with known rare-element pegmatites, local stream sediment surveys as well as optimization of background correction and principal component analysis to identify multi-element anomalies for the regional geochemical data.

1 Introduction

1.1 Regional geology and mineral deposits

The geology of the province of Leinster is dominated by late-Caledonian S-type composite granitic intrusions forming the Leinster Batholith (Fig. 1). The plutons are products of prolonged multi-episodic magmatism of Ordovician to Devonian age during and after Caledonide orogenic development (Fritschle et al. 2018a; 2018b). The granitoids intruded Ordovician to Silurian metasedimentary rocks of the Leinster–Lakesman terrane which lies directly southeast of the Iapetus suture. Among the oldest rocks in Leinster are Cambrian turbidites and quartzites. These are overlain by Cambrian to Middle Ordovician metapelites, which are themselves unconformably overlain by Ordovician volcanogenic rocks. Silurian deep-marine turbidites in the north and Devonian Red Sandstones in the southwest are located above the Ordovician units. The youngest rocks in the area are Carboniferous limestones, mudstones and shales.

A major SW–NE trending dip-slip ductile shear zone, the East Carlow Deformation Zone (ECDZ; McArdle and Kennedy 1985), parallels the Iapetus suture from the southwestern end of the Leinster Batholith to the east coast and possibly extends into the Irish Sea. Where it follows the eastern flank of the Leinster Granite it contains a belt of Li-Cs-Ta-enriched (LCT) rare-element pegmatites. The LCT pegmatites have been subject to research and exploration since the 1970s (e.g. Steiger and von Knorring 1974; O'Connor et al. 1991; Barros and Menuge 2016; Kaeter et al 2018). The best explored and studied LCT pegmatite occurrences are at and NE of Aclare.

Bedrock deposits of Sn and W are located near Tinahely on the same regional trend in sheets of (greisenized) granodiorite trending parallel to the ECDZ and in sediment-hosted veins (McArdle et al. 1986).

Mineral deposits in Leinster not illustrated in Fig. 1 include Zn–Pb veins in Glendalough, Cu–Fe Kuroko-type VMS deposits in Avoca, and sub-economic Quartz–Au veins on the same regional trend but further east as Sn–W deposits. Furthermore, alluvial Au is associated with the Goldmines River ~6 km east of Tinahely.

1.2 Topography and catchments

Most of Ireland’s present-day topography formed during glaciations 10–30 ka ago. Glacial transport in the Leinster area during the Weichselian was restricted to a NW–SE direction (c.f. Ó Cofaigh et al. 2012, Clark et al. 2018) and the transport distances are assumed to be limited. However, glacial erratics from the Leinster granite are found all the way to the east coast.

Streamlines were delineated from a 25-m digital elevation model (European Environment Agency 2016). Tellus stream sediment sample points (Geological Survey Ireland 2016) were snapped to the nearest stream lines and used as pour points to delineate the catchments of each sample (Fig. 2). Regionally, the rivers drain towards W and N for most of the Northern Pluton; towards E and SE, east of Tinahely; and towards SW to S, west of Tinahely.

2 Data and methodology

A geochemical survey of low-order streams covering an area of 7544 km² in Leinster was undertaken by Geological Survey Ireland in 1986–1988 (O’Connor and Reimann 1993). Recently, 1851 archived samples have been re-analyzed as part of the Tellus project and the
data was made available to the public (Geological Survey Ireland 2016).

Figure 1. Geological map of Leinster, southeast Ireland. Produced with data from Geological Survey Ireland.

Figure 2. Topography, Tellus stream sediment sample points, regional watersheds and local catchments in Leinster, SE Ireland. Major watersheds are represented by the bold white lines; dashed grey lines outline granite intrusions. Produced with data from Geological Survey Ireland and EU Copernicus data.

Geochemical data sets are so-called closed-number systems, because each compositional variable is part of a whole and therefore not independent (Carranza 2011). Furthermore, the values of each variable are typically log-normally distributed. The data must be transformed to open the system for compositional data analysis. Multiple data transformations were compared for this study; data presented here was transformed by centered log-ratio (clr) transformation, which enhances recognition of geochemical anomalies associated with mineralization (Carranza 2011).

Data was corrected for the lithological background by a linear-regression approach, where background composition is inferred from the composition of all catchments and the areal proportions of the respective underlying lithologic units (Bonham-Carter and Goodfellow 1986). Background concentrations were then subtracted from these measured concentrations and the residuals were investigated for anomalies.

3 Results and discussion

3.1 Background correction

Most of the variation for Cs in the clr-transformed data prior to background correction (Fig. 3A) derives from the underlying lithologies. The plutons are generally rich in Cs, with catchments of the Northern Pluton showing highest Cs, while the metasedimentary rocks in the east show generally low Cs. These signals are reduced after
background correction (Fig. 3B). High residuals south of Aclare might be caused by transport of granite-derived material by glaciers or rivers. The signal of the volcanogenic rocks SE of Tinahely was enhanced by the background correction, possibly due to the lithologic heterogeneity of this unit. It was treated as one lithology for background correction but comprises basic to felsic volcanic rocks and metasedimentary rocks. However, most of the variability of the Cs residuals is within ±1.5 SD and anomalies >1.5 SD appear only locally.

In Fig. 4, clr-transformed data for Ta is compared to the residuals after background correction. The residuals (Fig. 4B) show that some of the high Ta concentrations can be attributed to the background lithologies. The number of anomalous catchments is clearly lower than concentrations of Ta >1.5 SD in the original data.

### 3.2 Geochemical anomalies

Geochemical anomalies >1.5 SD for Ta (Fig. 4B), Sn (Fig. 5A) and W (Fig. 5B) around Aclare and Tinahely are associated with known mineralization in the area. Tin anomalies correspond to both LCT pegmatites and Sn–W veins. The >2.5-SD Ta anomaly in the east, distal to the granite margin (Fig. 4B), is located downstream of a quarry and likely anthropogenic. Anomalously low Ta residuals in catchments downstream of known LCT pegmatites deserve further investigation.
Background correction drastically reduces the amount of prospective catchments, with prominent anomalies (>1.5 SD) for Sn and Ta mostly associated with catchments containing known LCT pegmatites. The residuals for these elements effectively delineate the pegmatite belt and suggest the occurrence of additional but so far unknown deposits on the same regional trend. While this is preliminary work, it already highlights the potential of stream sediment geochemistry for prospection of rare-element deposits.

Artefacts, especially in maps for Cs, suggest that background correction can be improved. However, generalizing geologic units into too many lithological units, each only represented in a few catchments, will add uncertainty to the linear regression.

Future work includes mineralogical investigation of heavy minerals in stream sediment samples from catchments containing LCT pegmatites and local stream sediment surveys. Furthermore, background correction will be optimized, and principal component analysis will be applied to characterize multi-element anomalies in the regional data.

Acknowledgements

This work was supported in part by Science Foundation Ireland [Grant Number 13/RC/2092] and is co-funded under the European Regional Development Fund and by iCRAG industry partners. Maps were produced using Copernicus data and information funded by the European Union (EU-DEM layers).

References


Impact of subduction zone seismotectonics on magmatic systems and porphyry deposits

Alex Jenkins, Juliet Biggs, Alison Rust
University of Bristol, UK

Rosa Jara Torres
BHP-Exploration Peru

Abstract. This project investigates the interactions between subduction zone seismotectonics and magmatism. Specifically, how faults and transient stresses associated with the earthquake cycle influence the development of magmatic systems and associated porphyry ore deposits. Recent work has showed that magmatic systems at the volcanic and sub-volcanic level can be affected by large earthquakes, resulting in surface deformation and eruptions. We apply the mechanisms implicated in these studies to much greater depth, covering the entire transcrustal magma system. Initial modelling is of coseismic elastostatic stress changes, particularly the normal stress change on planar structures (such as magma conduits) of varying orientations. It is hypothesised that increasing normal compressive stress (clamping of magma conduits) will impede magma rise, whilst decreasing normal compressive stress (unclamping) will open magma conduits and facilitate magma rise. Future work will investigate how subduction zone tectonics (slab dip, tectonic stress state) affect the stress changes associated with the seismic cycle. The outcome will have implications for the development of magmatic systems and the physical processes responsible for the formation of ore deposits.

1 Introduction

Understanding the geological processes occurring at subduction zones is important in both mitigating the hazard associated with earthquakes and volcanoes and understanding the formation and distribution of ore deposits. The crustal stress field, which is largely controlled by global plate tectonics, is a first-order control on the occurrence of many large earthquake events. Changes to the crustal stress field may occur over timescales of millions of years, caused by changes in subduction rate or geometry, such as dip of the subducting slab (Lallemand et al. 2005). However, earthquakes themselves also modify the crustal stress field (Steketee 1958). The timescales involved may vary from a few minutes for coseismic elastic stress changes (Stein 1999) to decades for processes such as viscous flow (Freed and Lin 1998).

Magmatic systems and associated porphyry ore deposits may also be controlled by processes acting across a variety of timescales. For example, copper porphyry deposits may be found within metallogenic belts formed over millions of years (Sillitoe and Perelló 2005), whilst individual porphyries may form on the order of 100,000 years (Shinohara and Hedenquist 1997). Further, it is possible that individual porphyries form from discrete pulses of magma and magmatic fluids on even shorter timescales, as is believed to occur for larger magmatic bodies (Glazner et al. 2004).

Many models of (deep) magmatic systems and porphyry ore deposits focus on geological processes acting over longer timescales associated with plate tectonics (e.g. Sillitoe 2010; Wilkinson 2013; Bertrand et al. 2014). Whilst such processes are no doubt critical in controlling magmatic and porphyry systems, research into potentially important processes operating at much shorter timescales, such as those associated with the seismic cycle, may help further our understanding of how these systems work (e.g. Richards 2018).

2 The crustal stress field

2.1 Long-term tectonic stresses

Long-term stress field variations, caused by plate tectonic changes such as dip of the subducting slab, are known to affect magmatic systems and consequently mineralisation prospectivity. For example, porphyry copper deposits form within discrete metallogenic epochs (Sillitoe and Perelló 2005), which have been linked to the stress state in the magmatic arc (Bertrand et al. 2014). One hypothesis to explain this involves the trapping and accumulation of water-rich magma at the base of the continental crust during periods of compression (Wilkinson 2013). When the stress then relaxes, suitable pathways open and the magma can escape upwards through the crust.

Other models for porphyry formation also highlight the importance of compression in trapping magma within upper crustal reservoirs which are then able to fractionate and exsolve the fluids responsible for porphyry formation (Takada 1994). This compression has been linked to tectonic factors such as fast plate convergence rates (Bertrand et al. 2014) or flat-slab subduction (Kay et al. 1999, Cooke et al. 2005).

2.2 Seismic cycle

Here, we investigate the role stress field variations on shorter timescales, associated with the seismic cycle, play in controlling the development of magmatic systems and porphyry deposits. Earthquakes act to decrease regional differential stress by releasing elastic stresses...
accumulated largely because of plate motions. Differential stress increase is also possible beyond the fault tips due to the finite length of earthquake ruptures. If these coseismic stress changes are accommodated elastically as is reasonable for at least the upper crust, the stress changes are instantaneous and permanent and referred to as static or coulomb stress changes (Stein 1999). Such stress changes can be computationally modelled using software such as Coulomb 3.3 (Lin and Stein 2004; Toda et al. 2005).

Although Coulomb stress changes are often relatively small (<1 MPa), they have been observed to be important in controlling the location of both aftershocks and subsequent earthquakes (e.g. Stein et al. 1992; King et al. 1994; Stein et al. 1997; Toda et al. 1998). Coseismic stress changes have also been implicated in affecting magmatic systems, as discussed in the following section.

### 3 Earthquake-magmatic interactions

Porphyry deposits form the upper parts of magmatic systems and so any effect on the magmatic system caused by an earthquake will have implications for their development. The idea that earthquakes can affect magmatic systems is not new (e.g. Darwin 1840), although most studies have investigated the link between earthquakes and volcanoes as the response of the magmatic system at the surface is easiest to observe.

The exact mechanism for triggering of eruptions by earthquakes is not currently understood, and various theories have been suggested involving time delays from hours to tens of years. Trying to pick triggered events out of the volcanic record is thus difficult. However, several studies have found there to be a statistically significant link between large earthquake events and nearby volcanic eruptions (e.g. Linde & Sacks 1998, Watt et al. 2009, Sawi & Manga 2018).

Volcanic eruptions are only one component of the magmatic system and non-eruptive responses can also be observed. For example, subsidence was observed at volcanic regions following two recent large subduction zone earthquakes in Chile and Japan. This has been attributed to coseismic stress decrease across the volcanic arc following the earthquakes, though the mechanisms are still debated. After the Maule earthquake in Chile, subsidence was attributed to escape of fluids along fractures opened by the stress decrease (Pritchard et al. 2013), whereas in Japan, subsidence after the Tohoku earthquake was attributed to deformation of weak hot magmatic rock in response to stress relaxation (Takada & Fukushima 2013). Coseismic stress changes are also important at greater depths and have been associated with affecting mantle flow (e.g. Barbot 2018, Agata et al. 2019).

### 4 Preliminary modelling

This project aims to apply the mechanisms implicated in studies of earthquakes affecting the shallow parts of magmatic systems to the entire transcrustal magma system, across which coseismic stress changes have not been greatly previously considered. We study the change in normal stress on planar structures (potential magma conduits) of varying orientations (e.g. Bonali et al. 2013) following large synthetic earthquake events. Increasing compressive normal stress is expected to act to clamp structures shut, preventing magma rise, whereas decreasing compressive normal stress is expected to open or unclamp structures, encouraging ascent of magma (Fig. 1).

Preliminary modelling has been carried out using Coulomb 3.3 software, modified for automation. The results presented here are calculated using a Mw 8.7 magnitude earthquake, arising from 25 m of reverse slip on a 500 km long north-south trending dislocation with a dip of 30° east from the surface to 15 km depth. This dislocation represents the upper part of the subduction zone interface. The distance of the magma conduits in the volcanic arc from the subduction zone interface is assumed to be controlled by the dip of the subducting slab. This will control the location at which the down going material dehydrates, causing partial melting of the overlying mantle wedge. For a dip of 30° and dehydration depth of 100 km, this places the volcanic arc 175 km east of the fault surface trace.

Three end-member structure geometries are chosen based on structures typical of subduction zones; these are vertical structures trending north-south parallel to the subduction zone boundary, east-west trending structures perpendicular to the subduction zone boundary and horizontal structures. Coseismic normal stress change is resolved onto these structures at every grid point in the model. The mean normal stress change, which is the average of the three end-member models is also calculated (Fig. 2).
5 Preliminary Results

For vertical structures parallel to the subduction interface, a large lobe of unclamping is visible in the overriding plate, with decreasing magnitude downdip and along strike away from the fault (Fig. 3). This result is similar to that previously described for subduction zone earthquakes, implying large subduction zone earthquakes may unclamp trench-parallel magma conduits in the volcanic arc (Walter and Amelung 2007). Vertical structures orientated perpendicular to the subduction interface also show a normal stress change response, with a lobe of unclamping in the overriding plate. However, the unclamped lobe is smaller in magnitude and extent in this instance and there are also two small off-fault lobes of unclamping for the trench-perpendicular structures in the region around the fault tips. Both vertical structure orientations display clamping around areas of stress concentration at the fault tips (along strike from the rupture).

Within the volcanic arc 175 km east of the subduction zone interface (Fig. 4), trench-parallel structures show decreasing unclamping along strike away from the earthquake and with depth. Trench-perpendicular structures show a smaller unclamping effect, although this decreases much more slowly with depth and along strike, due to the presence of the off-fault lobes. Horizontal structures (e.g. sills) have an interesting response in that, while the amount of unclamping also decreases along strike away from the earthquake, unclamping increases with depth.

6 Discussion

Two interesting points arise from these preliminary results. Firstly, there is a strong unclamping at depth for horizontal structures. Many models of crust structure include sills at the base of the crust, and this shows that earthquakes can create space for those sills. Secondly, both the trench-parallel and trench-perpendicular vertical structures are unclamped in the magmatic arc adjacent to the earthquake. In both ore deposit models and volcanology, intersections of structures can be important loci for economic ore deposits and volcanoes respectively. That both of these structures can be unclamped by the earthquake makes intersections between such features highly favourable for fluid flow following such an earthquake as modelled here.

7 Future work and implications for porphyries

The work presented here forms part of the first year of a PhD study. Immediate future work will focus on further Coulomb modelling, to investigate how changing parameters such as earthquake size and location, the dip of the subducting slab and location of the magmatic arc, and whether or not fault slip is tapered affects the normal
stress change on the magma conduits. These Coulomb models are a simplification of the real-world situation. For example, all deformation is considered to be elastic, whereas in the deeper crust where temperatures are greater, other deformation mechanisms (visco-elastic, pore-fluid diffusion) are also likely to be important. More advanced models accounting for this, and non-homogeneity of the model space with depth, will be developed.

From the porphyry perspective, a key theme will be addressing how these short-term earthquake-induced stress changes fit into the overall development of porphyries. Questions to be investigated include: what are the characteristics of earthquakes that occur under tectonic conditions suitable for porphyry formation, what are the physical implications of coseismic stress changes on magmatic systems and porphyry deposits, and under what conditions are these stress changes important, relative to the overall tectonic stresses?

Acknowledgements

AJ is supported by a NERC GW4+ Doctoral Training Partnership studentship from the Natural Environment Research Council [NE/L002434/1] and is thankful for support and CASE funding from BHP.

References

Darwin CR (1840) On the connexion of certain volcanic phenomena in south america; and on the formation of mountain chains and volcanos, as the effect of the same power by which continents are elevated. Trans Geol Soc Lond 5:601-631
Glazner AF, Bartley JM, Coleman DS, Gray W, Taylor RZ (2004) Are plutons assembled over millions of years by amalgamation from small magma chambers? GSA today 14:4-11
Metallogenic controls of mantle plumes on platinum-group elements and precious metals

Jordan J. Lindsay, Hannah S. R. Hughes, Jens C. Ø. Andersen
Camborne School of Mines, University of Exeter, UK

Iain McDonald
School of Earth and Ocean Sciences, Cardiff University, UK

Abstract: Mantle plumes, buoyant upwellings of hot material from deep within the Earth, share a spatial and temporal link with orthomagmatic platinum-group element (PGE) mineralisation e.g. the Greenlandic Skaergaard intrusion from the proto-Icelandic plume and Noril’sk Talnakh complex from the Siberian plume. Crustal processes ultimately focus PGE into economic-grade deposits, but the role of mantle plumes in the magmatic metal budget is poorly constrained. Given that plumes can interact with two suggested PGE reservoirs, the core and the sub-continental lithospheric mantle (SCLM), we expect that metal baskets in plume-derived magmas will reflect this. This project examines the major, trace and PGE element geochemistry of ocean island basalts from Hawaii, Iceland, the Canary Islands, Ontong-Java and Paraná–Etendeka in order to uncover the metallogenic signatures of these plume-related igneous provinces and in doing so highlight the controls on plume fertility. Osmium, W and He isotopes will contextualise plume properties and source localities as we attempt to recognise the geochemical trends and patterns conducive to higher PGE abundances in magma. The generated geochemical data will be compared to data available for plume lavas around the world, in an attempt form a global model for plume-PGE metallogeny.

1 Platinum-group elements on Earth

During Earth formation and segregation ~4 Ga ago, highly siderophile elements (HSE) such as the PGE and Au, preferentially partitioned into the Earth’s metallic iron-alloy core (Wood et al., 2006). However, magmas produced from subsequent melting of the (silicate) mantle are not as depleted in these elements as geochemical modelling would imply, and it has therefore been suggested that the ‘late veneer’ of meteoric bombardment re-stocked the mantle after the core formation (e.g. Kimura et al., 1974; Maier et al., 2009). Together, these two predictions of HSE and PGE concentration in the Earth’s core vs. mantle have important implications for the metallogeny of plumes and resultant large igneous provinces.

Magmatic plumes are thought to rise from different depths in the mantle as hot diapirs of silicate material – some plumes are thought to derive from shallower melting in the asthenosphere and some are thought to derive from deep melting. Upon eruption, the lavas they produce provide us with geochemical information about melting conditions within the plume and thus an insight into the composition of the Earth’s mantle (Courtillot et al., 2003; Stracke et al., 2005). It is hypothesised that some of the deepest plumes may incorporate a component of liquid outer core material at the D” layer (Fig. 1) (Brandon and Walker, 2005). Given that HSE (including the PGE) are likely concentrated to levels an order of magnitude greater in the core than that in the mantle, we would expect these deep mantle plumes to be more enriched in HSE than other shallower plumes (Fig. 2). For example, the inclusion of as little as 0.5% of material of the predicted outer core composition would enrich the magmas in Os by 4 times (Andersen and Power, 2002).

If plumes impinge below the continental crust and cause decompression melting in an intracratonic setting, they can incorporate lithospheric material in resultant magmas. Subducting oceanic plates often delaminate and underplate the continental crust/SCLM with high melting point or compatible metals (including PGE) otherwise not incorporated into arc magmatism. Plumes interacting with the lithosphere will have access to these metals (Hughes et al., 2014), just as they have access to core material (Fig. 1).

Pressure, temperature, density, and melt/fluid flow dynamics all play a key role in the eventual composition of plume magmas but are difficult to quantify in the context of this project. These factors will be considered on a case-by-case basis in the geodynamic setting of each locality studied, but plume depth and plume-lithosphere interaction will be the main factors tested.
Figure 1 Schematic cross-section of Earth, showing hypothetical plumes interacting with the core, SCLM and D'' layer.

Figure 2 The rationale behind Hypothesis 1; plumes originating from different depths (a, b and c) will have different PGE/HSE concentrations, in addition to the core (x), the mantle (y) and Bulk Silicate Earth (BSE; z) having fundamentally different PGE/HSE contents to each other.
2 Hypotheses & Methods

Through this project, two major hypotheses will be tested through laboratory analyses, following from the literature implications regarding global PGE concentrations. The first [H1], that plumes sourced from the lowermost mantle (i.e. at the core-mantle boundary) will have higher PGE/HSE concentrations than plumes sourced from the transition zone (Fig. 2), will be tested on plume-derived lavas from different source depths. The second [H2], that plumes erupting through or near continental crust/SCLM will have different PGE ratios than plumes erupting through oceanic crust, will be tested on the migrating Tristan plume. The bulk major and trace geochemistry of each lava sample obtained via XRF and ICP-MS analyses, respectively, will contextualise their magma source properties. PGE concentrations will be obtained from NiS fire-assay analysis. Osmium and helium isotope signatures for a sub-set of samples will provide a proxy for plume depth to test the first hypothesis (Brandon and Walker, 2005). There is also scope to include Hf-W and stable S isotope in the study. The generated data set will be compared to global plume geochemical signatures to model the PGE concentrations/relative ratios with respect to isotope signatures, with a view to extend this framework to plumes outside this study.

3 Study localities

3.1 Hawaii

The Emperor-Hawaiian hotspot trail is possibly the most well-known surface expression of a mantle plume in the world. Isotopic evidence (e.g. Pb, Os and He) strongly suggests a core-mantle boundary source locality and material derived from recycled oceanic crust (with distinctive isotope signatures) at the D” layer has been recognised in magma components (Harrison et al., 2017). Hawaii will contribute to the testing of [H1].

3.2 Iceland

The proto-Icelandic plume initiated under the conjoined continental landmass of Greenland and Britain, before they rifted apart and volcanism continued in an oceanic setting (Momme et al., 2003). The Icelandic hotspot lies geographically on top of the Atlantic Mid-Ocean Ridge, which can make its geochemical signature a complex mix between shallow and deep melting sources. The focus will be on Icelandic lavas of pure plume/deep magma sources, to test [H1].

3.3 The Canary Islands

The Canary Island plume has two spatial and geochemical trends, dividing the seven islands into two groups. The varying geochemical signatures are thought to represent the varying effects of sources from the African and Atlantic sides of the mantle (Marcantonio et al., 1995). Helium and Os isotopic evidence suggests that the Canarian plume is shallow (Day and Hilton, 2011) and subject to influence from the African landmass to the east (Hieronymus and Bercovici, 1999), and will thus contribute to testing [H1] and [H2].

3.4 Ontong-Java

In comparison to Hawaii and Iceland, the Ontong-Java plume has a relatively straightforward geochemical signature, albeit with a wider and less focused hotspot expression due to formation via the plume head (Chazey and Neal, 2004). Isotopic evidence (mainly Os and He) very clearly shows it to be from a deep source (Courtillot et al., 2003) and it will contribute to testing [H1].

3.5 Paraná-Etendeka

Similarly to the Icelandic plume, the Cretaceous Tristan plume initiated between the then-joined South America and Africa to form the Paraná-Etendeka Large Igneous Province (PELIP) (Peate et al., 1992). After rifting, volcanism continued across the newly formed ocean to its current location under Tristan da Cunha. The effect that gradual removal of continental crust/SCLM has on plume magma PGE concentrations can be tested [H2]. Results should form a direct analogy with work completed on the north Atlantic plume (Hughes et al., 2015).

References


Mantle metasomatism in SCLM under the Grib kimberlite pipe, Arkhangelsk province, Russia

Nataliya M. Lebedeva, Anna A. Nosova, Alexey V. Kargin, Yulia O. Larionova,
Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry Russian Academy of Sciences (IGEM RAS), Moscow, Russia

Yana S. Tikhomirova
Vernadsky Institute of Geochemistry and Analytical Chemistry (GEOKhi), Moscow, Russia

Abstract. This study presents new Sr-Nd-O isotope compositions for minerals from metasomatised xenoliths from the Grib kimberlite pipe. The garnet, orthopyroxene, and clinopyroxene were formed during the interaction of an enriched ancient lithosphere mantle and depleted isotopic kimberlite. Clinopyroxene and phlogopite from clinopyroxene-phlogopite (Cpx-Phl) xenoliths and wall rock (WR) garnet lherzolites have additionally reflected the contribution of a more radiogenic source to the metasomatic agent, which was responsible for phlogopite subcratonic lithospheric mantle (SCLM) metasomatism.

1 Introduction

Kimberlite commonly comprises multiple units that originated from discrete magma pulses. Early kimberlite magma do not reach the surface frequently due to the fact that it reacts with ambient peridotite. (Kargin et al., 2016, Kargin et al., 2017a, Kargin et al., 2017b).

Xenoliths from kimberlite have evidence of mantle metasomatism (Shchukina et al., 2015, Kargin et al., 2017b). Dating metasomatic events is a great issue and link of metasomatic processes with kimberlite generation are discussed. At least two models of mantle metasomatism beneath Arkhangelsk province are described: 1) several stages of metasomatic enrichment (Shchukina et al., 2015); 2) metasomatic events associated with the generation of the kimberlite (Kargin et al., 2017b and reference therein). Metasomatism of the lithospheric mantle beneath Arkhangelsk province led to the formation of sheared peridotite, garnet lherzolites, phlogopite-garnet lherzolites and Cpx-Phl rocks (Kargin et al., 2016, Kargin et al., 2017a, Kargin et al., 2017b).

Rb-Sr, Sm-Nd and oxygen isotopes’ compositions were determined for xenolith minerals. This preliminary data can discuss the time of mantle metasomatism and its source.

2 Geological position

The Grib kimberlite is an industrially mined pipe which is located in the central part of the Arkhangelsk Diamondiferous Province (ADP) in a Paleoproterozoic collisional suture zone underlain by roots of Archean lithosphere (Samsonov et al., 2009). The pipe intruded into Neoproterozoic sedimentary rocks and is overlain by Carboniferous siliciclastic and carbonate rocks and Quaternary sediments. The age of the Grib kimberlite pipe can be defined as 376 ± 3 Ma on mineral phlogopite isochrones (Larionova et al., 2016).

3 Results

Isotopic compositions were analyzed at the Laboratory of Isotopic Geochemistry and Geochronology at Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry Russian Academy of Sciences (IGEM RAS) and the Laboratory of Isotopic Geochemistry and Geochronology at Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences (GEOKhi RAS). The oxygen isotopic composition of minerals was analyzed by fluorination with laser heating (Sharp, 1990) at IGEM. (87Sr/86Sr)ø and ᵋNd for orthopyroxene, clinopyroxene and wall rock (WR) analyses calculated at kimberlite age (376 Ma years ago).

3.1 Sheared peridotite

The xenolith consists of olivine, orthopyroxene, clinopyroxene, and garnet with subordinate phlogopite and Cr-spinel. The clinopyroxene partially replaces the orthopyroxene grains. The trace-element composition of garnet grain rims and clinopyroxene from sheared peridotite suggests their chemical equilibrium with a high-
Fe-Ti metasomatic agent (Kargin et al., 2017a). The sheared peridotite comes from the deepest layer of the lithosphere (~210 km) and was equilibrated at a temperature about 1200 °C (Kargin et al., 2017a). The minerals and WR have a broad range of isotopic composition (Table 1).

### Table 1. Sr-Nd-O isotopic data for minerals in xenoliths from the Grib kimberlite.

<table>
<thead>
<tr>
<th></th>
<th>87Sr/86Sr</th>
<th>143Nd/144Nd</th>
<th>δ18O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sheared peridotite</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opx</td>
<td>0.704842</td>
<td>1.5</td>
<td>5.51</td>
</tr>
<tr>
<td>Cpx</td>
<td>0.703439</td>
<td>3.7</td>
<td>5.36</td>
</tr>
<tr>
<td>WR</td>
<td>0.706664</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td><strong>Garnet lherzolites</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grt</td>
<td>0.706327–0.710572</td>
<td>-2.5</td>
<td>5.2-5.7</td>
</tr>
<tr>
<td>Cpx</td>
<td>0.702662–0.705822</td>
<td>-4.4–0.2</td>
<td>5.36</td>
</tr>
<tr>
<td>WR</td>
<td>0.703957–0.709724</td>
<td>0.7–3.1</td>
<td></td>
</tr>
<tr>
<td><strong>Cpx-Phl xenoliths</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cpx</td>
<td>0.704857–0.708132</td>
<td>-0.1–1.3</td>
<td>5.11-5.33</td>
</tr>
<tr>
<td>Phl</td>
<td>0.706552–0.708792</td>
<td>1.01.2</td>
<td></td>
</tr>
</tbody>
</table>

### 3.2 Garnet lherzolites

Isotopic analyses performed for four garnet lherzolite xenoliths. They consist of olivine, orthopyroxene, clinopyroxene, and garnet with minor ilmenite, magnetite, Cr-spinel, and phlogopite. They have typical granoblastic and medium- to coarse-grained textures. The composition of clinopyroxene has been interpreted as a result silicate metasomatism. Equilibrium conditions for those xenoliths have ranged from 3.5-3.8 GPa and temperature from 600 to 800 °C (Kargin et al., 2016). Minerals of garnet lherzolite have a wide range of Sr-Nd isotopic composition (Table 1).

### 3.3 Cpx-Phl xenoliths

Cpx-Phl xenoliths are represented by four medium to coarse-grained rocks with granoblastic. Clinopyroxene-phlogopite xenoliths were formed during the metasomatic equilibration with the kimberlite melt at depths corresponding to 3.5–5 GPa (Kargin et al., 2019). Clinopyroxenes from Cpx-Phl xenoliths exhibit a large variation in the range in 87Sr/86Sr (Lebedeva et al., 2018) and narrow range Nd and O isotopic composition (Table 1).

### 4 Discussion

The Sr-Nd isotope composition of clinopyroxene and orthopyroxene from sheared peridotite is non-equilibrium. Clinopyroxene shows depleted isotopic composition and overlaps with clinopyroxene from PIC (Phlogopite-Ilmenite-Clinopyroxene). Orthopyroxene has considerably more radiogenic 87Sr/86Sr than clinopyroxene from the same sample (fig.2). WR xenoliths have more radiogenic 87Sr/86Sr ratios than minerals separate.

The δ18O clinopyroxene value is below typical mantle values (5.57 ± 0.18, 1sd; Mattey et al., 1994).

![Figure 2. Ranges of 87Sr/86Sr for clinopyroxene and orthopyroxene in this study compared to MARID and PIC clinopyroxene (Giuliani et al., 2015; Fitzpayne et al., 2019) and pyroclast Grib kimberlite (Kononova et al., 2007).](image)

Garnets from garnet lherzolite have considerably more radiogenic 87Sr/86Sr than clinopyroxene and the host pyroclastic kimberlite (~0.704) (Kononova et al., 2007). Similar observations were noted for xenoliths from Siberia and Kaapvaal cratons (Pearson et al., 1995). Clinopyroxene from garnet lherzolite display is close 87Sr/86Sr values with sheared peridotite clinopyroxene. Nd isotope composition of clinopyroxene from garnet lherzolite shows wide variation (Table 1). One of them is located in the MARID (Mica-Amphibole-Rutile-Ilmenite-Diopside) area (Nd from -1 to -11) (fig.4). MARID rocks originally display extremely radiogenic isotope compositions, the fluids/melts parental to MARID rocks might be related to partial melting of recycled crustal components. The oxygen isotopic compositions of MARID phlogopite and zircon have crustal signatures (averaging more than ~5.9) (Giuliani et al., 2015; Banerjee et al., 2018)

The WR xenoliths are more enriched initial Sr isotopic composition than the pyroclastic host kimberlite (~0.704). It could reflect the contribution of a more radiogenic source than the metasomatic agent. The WR xenoliths Sr isotope systematics suggest that these xenoliths have suffered a small amount of kimberlite phlogopite (with high 87Rb/86Sr ratios) contamination during sample transport (Schmidberger et al., 2003, Kargin et al., 2019). Strontium isotopic compositions of clinopyroxenes from the Cpx-Phl xenoliths are heterogeneous. Isotopic composition of studied clinopyroxene is overlapped with secondary MARID clinopyroxene (fig. 2).

Oxygen isotopic composition clinopyroxene from Cpx-Phl xenoliths overlap with clinopyroxene from sheared peridotite. The δ18O values for all studied clinopyroxene are below then typical mantle values (Mattey et al., 1994) (fig. 3).
more 87Sr/86Sr radiogenic source. This metasomatic
between an enriched component (ancient lithospheric
(Fig. 4). They were formed as the result of mixing
clinopyroxene present a continuous compositional range
mantle) and a depleted component (kimberlite).

2017)

The authors thank Elena Dubinina for her invaluable help
with oxygen isotopic analyses. This work was supported
by the Russian Science Foundation under Grant No. 19-
17-00024.

We can distinguish two genesis processes according
to Sr-Nd-and O isotope composition minerals in
lherzolites, sheared peridotite and Cpx-Phl rocks:

The Sr-Nd isotopic data for garnet, orthopyroxene and
clinopyroxene megacrysts from the Grib kimberlite, Arkhangelsk
province, Russia: Relation to clinopyroxene–phlogopite

peridotite xenolith from the V. Grib kimberlite pipe, Arkhangelsk
Diamond Province, Russia: Texture, composition, and origin.

Kargin A. V. Sazonova L.V., Nosova A. A., Lebedeva N. M.,
Tretyachenko, V. V., & Abersteiner, A. (2017b) Cr-rich
clinopyroxene megacrysts from the Grib kimberlite, Arkhangelsk
province, Russia: Isotopic Geochronologic Rb–Sr and Ar and Mineralogical Data on Phlogopite. Petrology
24:562–593.

Lebedeva N., Nosova A., Kargin A, Sazonova L., Tikhomirova Y.
(2018) Geochemical and Sr–Nd isotopic characteristics of
clinopyroxene from Clinopyroxene-Phlogopite xenoliths from the V. Grib kimberlite (Arkhangelsk diamond province, Russia).
Melbourne.

evidence for thick achaean lithospheric mantle beneath the
siberian craton modified by multistage metasomatism.
Geochemica et Cosmochimica Acta 59:959–977. doi:
10.1016/0016-7037(95)00014-3.

Samsonov, A. V., Nosova, A. A., Tretyachenko, V. V., Larchenko, V.
Precambrian crust as a factor responsible for localization of
diamondiferous kimberlites in the northern East European

periodicity of kimberlite volcanic activity in the Lac de Gras
kimberlite field, Canada and some recommendations for
kimberlite geochronology. Lithos 218–219:155–166. doi:


Petrography, geochemistry and geochronology of rocks related to rare elements (RE) outcropping in southeastern Colombia

Héctor Ricardo Campos Rodríguez1,2, José Alejandro Franco Victoria2,3, Alejandro Piraquive4, Jimmy Alejandro Muñoz5, Thomas Cramer2,3, Amed Bonilla Pérez2,3, Zeze Amaya Perea2,3,
1Université de Rennes 1
2Grupo de Estudios en Geología Económica y Mineralogía Aplicada (GEGEMA)
3Universidad Nacional de Colombia.
4Servicio Geológico Colombiano

Abstract. Rock samples from nepheline syenites, as well as samples of active sediment and colluvion were collected in February of 2017 in SE Colombia. This, in order to gain knowledge about mineral deposits related to rare elements (RE) in this unexplored area. Petrographic analyses, showed that the syenites are composed mainly of potassium feldspar, nepheline, plagioclase, and biotite and calcite; with total absence of quartz. In both, active sediments and colluviums heavy minerals such as zircons (up to more than 1cm in diameter), ilmenite and magnetite were found. Whole rock geochemistry (XRF) indicate subsaturated and peralcaline rocks. The geochemical analyzes in zircon (XRF, SEM-EDX) showed enrichments in Hafnium (Hf), traces of rare earth elements (REE) such as Yb, Dy, Ho, Er, La, Pr, Sm, Nd, Pm, Eu and other RE such as U, Th and Nb. Cathodoluminescence analyzes show typical zonation of magmatic zircons. LA-ICP-MS U-Pb results on zircons showed concordant Neoproterozoic-Cambrian ages that can be correlated with previously obtained ages for this unit. Currently, the presence of RE in the study area can only be associated with zircons. For future researches it is suggested a greater exploration of the area for searching other minerals associated with RE.

1 Introduction

The Amazonian Craton is one of the largest and least known Archean-Proterozoic areas of South America, and one of the main tectonic units in the continent. The craton is divided into two Precambrian shields: the Guatapore shield and the Guayana shield, which are separated by the Paleozoic sedimentary basin of the Amazon. Many models have been proposed to describe the craton, among them by Santos et al. (2000), who divides it in seven geochronological provinces and one shear belt: 1) Carajás-Imataca (3.2-2.53 Ga). 2) Transamazônica (2.25-2.0 Ga). 3) Tapajós-Parima (2.10-1.87 Ga). 4) Amazonia Central (1.88-1.70 Ga). 5) Rio Negro (1.86-1.52 Ga). 6) Rodonia Juruena (1.76-1.47 Ga). 7) Sunsas (1.33-0.99), (which includes the K’Mudku shear belt with ages of 1.33-1.10Ga)

The nepheline syenite of San José del Guaviare (NSSJG), corresponding to the main unit studied in this work, outcrops in the area of San José del Guaviare (Guaviare Department) as part of the Rio Negro Province (Santos et al. 2000).

The very few studies about the NSSJG made by Ingeominas (current Colombian Geological Survey, SGC) and university researchers describe it as an igneous body composed of microcline, nepheline, albite, cancrinite (aureols), with smaller amounts of biotite, magnetite, zircon, sphene, monazite, apatite and pyrochlore? (Galvis et al. 1979; Celada et al. 2006; Arango et al. 2012; García and Cramer 2015; Campos Rodríguez and Cramer 2017)

Pinson et al. (1962) obtained a K-Ar age in biotite of 445-495 Ma, whereas Arango et al. (2011), with U-Pb in 29 zircons obtained an age of 577.8 ± 6.3 Ma, interpreted as rock crystallization age; Ar-Ar ages of 494 ± 5 Ma were interpreted as closing age of the cooling process. The rocks are of peralkaline character and geochemically fall in the field of intraplate granites.

Celada et al. (2006) report these rocks as possible sources for rare earths elements (REE) in the surroundings of San José del Guaviare in a potential area of 200 km².

Cramer et al. (2011) define the Guaviare Department as an interesting area for finding primary and secondary mineralizations of REE.

Arango et al. (2011) performed geochemical analyzes, which indicate that nepheline syenite rocks are enriched in RE like Rb, Zr, Ba, Th, U, Nb and K; and impoverished in RE like Dy, Ho, Er, Tm, Yb, and Lu.

This work describes in detail the geochemistry of the body in the surrounding area of El Jordán, in the Guaviare Department. This, in order to analyze which minerals are carriers of RE and to improve the knowledge of mineral deposits related to RE for future explorations in this area.

2 Study Area

The study area is located 30km southwest of San José del Guaviare, near to the municipality of El Retorno, in the surrounding area of El Jordán, in the Guaviare Departament, SE Colombia (Fig. 1).
3 Petrography and sediment analysis

Petrographic analysis show two different types of lithologies: non-silica-saturated igneous rocks, mainly foid syenite and foid monzosyenite composed of potassium feldspar, nepheline, plagioclase, and biotite and calcite; with total absence of quartz.

Minerals found in both, active sediments and colluviums near to the outcrops of the NSSJG, correspond to heavy minerals such as zircons (up to more than 1cm in diameter), ilmenite and magnetite. The NSSJG was intruded by acid dykes with more than 1cm thick minerals, which are mainly magnetite, ilmenite and zircons. All of the minerals found in sediments are inferred to come from the NSSJG. Other possible source for the zircons could be the igneous basement (see Fig. 1). Nevertheless, these rocks present a different mineralogy compared to minerals in active sediment and show an aphanitic texture which does not match with the size of zircons that are inferred to come from pegmatitic phases of the NSSJG.

4 Geochemistry

4.1 Whole rock Geochemistry

All rock samples analyzed by means of XRF fall in the shoshonitic series field (Peccerillo and Taylor 1976) (Fig. 2); and in the foid-syenite field (Middlemost 1985) (Fig. 3), which is consistent with the results obtained with petrographical analyses.

### Table 1. XRF analysis of zircons

<table>
<thead>
<tr>
<th>Element</th>
<th>XRF-4301 Jordán-wt%</th>
<th>M-Zircon</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂</td>
<td>61.809</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>31.937</td>
<td></td>
</tr>
<tr>
<td>HfO₂</td>
<td>1.550</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.336</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.267</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.634</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>0.335</td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.314</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.109</td>
<td></td>
</tr>
<tr>
<td>ThO₂</td>
<td>0.106</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.095</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>0.090</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.088</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>0.076</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.049</td>
<td></td>
</tr>
<tr>
<td>K₂O₈</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.023</td>
<td></td>
</tr>
</tbody>
</table>
XRF analyses of zircons in the sediments show that these minerals present 1.55%wt HfO₂, which correspond to normal Hf-values in nepheline syenites between 0.55-1.78%wt (Pavlenko et al. 1957).

5 SEM-EDX-Zircons

Scanning Electron Microscopy (SEM) and SEM-EDX (Fig. 4) revealed the heterogeneous character of some of the zircons with inclusions with high contents of Nb and Y.

6 Cathodoluminiscence Imagery

Cathodoluminiscence imagery showed growth and oscillatory zoning, typical of magmatic crystals (Corfu et al. 2003); sometimes convolute zoning and deep fracturing, also frequently crystals displayed cores (Fig. 5).

7 U-Pb LA-ICP-MS Geochronology

U-Pb dating was performed in 25 zircon crystals coming from active sediment at the facilities of the Colombian Geological Survey by LA-ICP-MS method. Our results showed concordant Neoproterozoic-Cambrian ages that can be correlated with previously obtained ages of c.a. 577.8 ± 6.3 – 9 Ma (Arango et al. 2011) in a site 17 km towards the NW of our location. In this case our results correspond to a first magmatic pulse and the results of Arango et al. (2011) to a second one. Confirming thus the extent of this intraplate magmatic unit and its regional character (Franco et al. 2018) (Fig. 6).
Acknowledgements

The rural and indigenous communities that provided access to the studied locations, U-Pb geochronology was performed at the facilities of the Colombian Geological Survey.

References


Campos Rodríguez HR (2017) Caracterización Geoquímica y Mineralógica de la Sienita Nefelínica de San José del Guaviare y Minerales Associated con Elementos Raros (ER). Universidad Nacional de Colombia


New discoveries – new views: Advances in the Science of Mineral Exploration
Nb-rutile: a reference mineral for timing of Sn, Nb-Ta, U-Th and REE mineralization at NW part of the Amazonian Craton

Jose A. Franco, Thomas Cramer, Amed Bonilla,
Universidad Nacional de Colombia and Grupo de Estudios en Geología Económica y Mineralogía Aplicada (GEGEMA).

Alejandro Piraquive, Héctor Campos
Grupo de Estudios en Geología Económica y Mineralogía Aplicada (GEGEMA).

Abstract. U/Pb ages measured by means of LA-ICP-MS in Nb-rutiles cogenetic with cassiterite, columbite and REE minerals proved to be a powerful tool for dating rock-forming and mineralization events. In four different locations grains of Nb-rutile were extracted from duricrust LOC (2) Cachicamo, from colluvial deposit Cerro Espina LOC (4), from colluvial and pegmatitic dykes San Jose LOC (5) and from colluvial deposit Barranquilla LOC (6) (Fig. 1). Metallographic and SEM-EDX analyses have revealed that most of the rutiles-Nb contain Fe-columbite inclusions and in some cases tantalite and cassiterite up to 0.2 mm length. The geochemical data for major oxides and trace elements was obtained using FRX-EPMA and ICP-MS, respectively. The results revealed a different variation regarding the TiO₂, Nb₂O₅, Ta₂O₅, Fe₂O₃ and SnO₂ contents of the matrix. The measurements in single Nb-Ta rutile crystals for each locality yielded enough U, Pb and Th for LA-ICP-MS analyses that were performed at the University of Rennes 1 and in ETH Zurich. There, 40 Nb-Ta rutile crystals were dated obtaining concordant U/Pb ages coherent with rocks and mineralization.

1 Introduction

Rutile is a common mineral in almost all lithologies. These minerals have considerable concentrations of Nb and Ta mainly by coupled titanium diadoxy. Substitution of Ti⁴⁺ by Nb⁵⁺ or Ta⁵⁺ requires charge balancing by a cation with less charge such as for example Al³⁺ or Fe³⁺ (e.g. 2Ti⁴⁺ ↔ Nb⁵⁺ + Fe³⁺). The titanium in the structure has a coordination number of 6. Half of the octahedral vacancies are occupied by the titanium cations [TiO₆] which form tetragonal octahedron columns connected by the edges [TiO₄/2 O₂/1] parallel to the crystallographic axis c. Additionally, the columns are connected through joint corners forming a three-dimensional network of [TiO₆³⁻], which leads to the short formula TiO₂.

Most of the rutiles in the world are extracted in placers coming from metamorphic rocks especially in Sierra Leone and Cameroong (Elsner 2010). Much less common are Nb-rutiles or ilmenorutile (Ti, Nb, Fe++) O₂ with more than 13 wt% Nb₂O₅ which have been reported by (Cerny et al. 1981) in pegmatities of Manitoba, Canada and classified in (Möller et al. 1986). Rutiles with Nb and Ta present diverse paragenesis in mineralized miazkites, in deposits associated with metasomatic deposits and veins.

The Parguaza batholith, emplaced 1500-1550 My ago, represents nowadays a primary source of Sn, Nb, Ta and REE mineralization (Aarden and Davidson 1977), although it is largely covered by partially laterized Cenozoic sediments in plains and valleys. However, In the localities of El Burro, La Fortuna and Aguamena colluvial - alluvial deposits contain (sub-?) economic concentrations of minerals like cassiterite, Nb-Ta rutile, columbite-tantalite and REE minerals.

The application of rutile in earth sciences was reviewed by Meinhold (2010). The material for standardization, petrochronology and geochronology has been described and reviewed (Bracciali et al. 2013; Zack et al. 2017).

It has already been shown that some crystals of Nb-rutiles, columbite-tantalite and cassiterite have enough U and Pb contents to allow radiometric U/Pb dating using the LA-ICP-MS technique. The radiometric dates of the Nb-rutiles follow the methodology described in Franco (2015) and for comparison we reviewed the columbite-tantalite and cassiterite methodologies used by several authors (e.g., Che et al. 2015; Li et al. 2016; Melcher et al. 2015; Chew et al. 2014; Rösel et al. 2014; Bracciali et al. 2013; Sitnikova et al. 2007).

2 Methodology

The samples were selected manually in the field and 30 crystals of Nb rutile from each locality were identified using portable FRX Bruker tracer. The determination of major and minor elements was made on pearls, prepared by melting at 1200 ºC. For the geochemical characterization, powders of the fragments (made in agate mortar) were analyzed using the PANAnalyticalAXios equipment of the National University of Colombia. For EPMA we used a polished epoxy mounting covered with graphite.

The analysis for major oxide were made using JEOL electron microprobe (EMP), JXA-8900 model, at LMA-CM-UFMG - Universidade Federal de Minas Gerais (UFMG), Brazil. The recognition of Nb-rutiles was confirmed by energy-dispersive X-ray spectroscopy (EDS).
SEM photographs of the Nb-rutile crystals were taken for choosing the most homogeneous zones, with no inclusions or in very low proportion. To perform ICP-MS analyses we use the equipment Agilent 7700 ICP-MS spectrometer brand Terre, Temps, Traçage with an excimer laser system 193 nm ESI (NWR193UC) in the Laboratory of geochronology of the University of Rennes 1 in France; and the Thermo Scientific Element XR, a single collector, high resolution, magnetic sector ICP-MS with an excimer ArF laser (193 nm) laser at the Institute of Geochemistry and Petrology of ETH-Zurich. Standards R10 and R19 (rutiles) were used. The conditions of ablation change depend on the behavior of the material.

3 Results of characterization and LA-ICP-MS dating

3.1 LOC (2) Cachicamo – Orinoco River

The Nb-rutiles of Cachicamo are found together with quartz magnetite, ilmenite and zircons embedded in a layer (duricrust) composed mainly of Fe-Al (hydro-oxides) covering a latitic profile over the Parguaza rapakivi granitoids. The EPMA analyses exhibit up to 67 wt% TiO$_2$, 11% Nb$_2$O$_5$, 11% Ta$_2$O$_5$, 6% Fe$_2$O$_3$ and 3% SnO$_2$. For the minor elements ICP-MS analyses show up to 800 ppm of Si, V, Zr, Nd and Mn; up to 405 ppm of Hf, less than 50 ppm of P and Ca, and less than 10 ppm of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tb, Dy, Ho, Pb, Tm, y, Lu, Cr, P, Co and Y. The SEM-EDS images show inclusions of Fe-columbite and Mn-tantalite. The concentrations of U and Pb were not detected by EPMA, but ICP-MS U-Pb results showed viability for dating purposes.

Due to the size of the crystals, the laser ablation of the grains was performed in spots of 65 microns, using a frequency of 5 Hz and an intensity of 8.44 J/cm$^2$. The LA-ICP-MS data acquired yielded concordant ages of 1512±12 Ma (Fig. 2). This data coincides with the ages of 1550-1500 Ma reported for the Parguaza rapakivi granite in Venezuela with Sn, Nb-Ta and REE mineralization.

3.2 LOC (4) Cerro Espina- Inírida River

The Nb-rutiles of Cerro Espina are found in colluvial deposits together with crystals of xenotime, monazite, samarskite, betafite and REE-zircons. The EPMA analyses exhibit up to 62% TiO$_2$, 13% Nb$_2$O$_5$, 6% Ta$_2$O$_5$, 10% Fe$_2$O$_3$ and 0.1% SnO$_2$. For the minor elements, ICP-MS analyses show up to 600 ppm of Si, Al and Zr; up to 405 of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tb, Dy, Ho, Pb, Tm, Lu, Hf and less to 50 ppm of Mn and Mo and below to 10 ppm of Cr, P, Co and Y. The SEM-EDS images show a paragenesis with monazite and several inclusions of Fe-columbite and tantalite. The initial EPMA and ICP-MS U/Pb results show a viability for dating purpose.

Due to the size of the crystals, laser ablation of the grains was performed in spots of 30 microns, with a frequency of 4 Hz and an intensity of 7 J/cm$^2$. The LA-ICP-MS data acquired yielded concordant ages of 1342±27 Ma (Fig. 3). This data match with the U/Pb ages of 1343±11 and 1381±8 acquired from monazite and xenotime, respectively.
3.3 LOC (5) San Jose - Guainía River

The Nb-rutiles of San Jose are found in pegmatitic dykes together with Fe-columbite near to the Guainía river and in colluvial deposits with crystals of Fe-columbite, monazite, xenotime, tourmaline and magnetite in some places. The pegmatite and colluvial deposits are related to migmatisites of the Mitú Complex with some young rapakivi granite intrusions like the Tabaquen Granite and other with small outcrops. The EPMA analyses exhibit up to 64 wt% TiO₂, 19 % Nb₂O₅, 4 %Ta₂O₅, 10% Fe₂O₃ and 0.5 % SnO₂ confirming a genetic relation with Ta and Nb ore mineralization. For the minor elements ICP-MS analyses show up to 700 ppm of Si, W and Al; up to 405 ppm of Mn, Zr, Cr, Y and Pb, less than 50 ppm of Cr, P, and Hf, and below 10 ppm of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Rb, Tb, Dy, Ho, Rb, Tm, Lu, Hf, less than 50 ppm Mn and Mo, and below 3 ppm of Zr, Cr, P, Co, Y. The SEM-EDS images shows inclusions of Fe-columbite and Mn-tantalite. Low W and Mn contents indicate pegmatitic or pneumatolytic affinity of the rutiles. The EPMA and ICP-MS U/Pb results show viability for dating purposes.

Due to the size of the crystals, the laser ablation of the grains was performed in spots of 30 microns, with a frequency of 5 Hz and an intensity of 7 J/cm². The LA-ICP-MS data acquired yielded concordant ages of 1377.8±1.1 Ma (Fig. 4). This data coincides with the ages of 1410 Ma for Fe-columbite from alluvial deposits in Colombia (Melcher et al. 2017).

3.4 LOC (6) Barranquilla – Cuyari River

The Nb-rutiles of Barranquilla are found in colluvial deposits together with blocks of pegmatites of quartz, muscovite, beryl and Fe-columbite, crystals of monazite, xenotime, tourmaline and REE-Zircons and with spessartine garnets from pegmatitic dikes. The garnet pegmatite and the colluvial deposits are related to the granites of the Mitú Complex with rapakivi texture. The EPMA analyses exhibit up to 58 wt% TiO₂, 19 % Nb₂O₅, 10% Ta₂O₅, 12% Fe₂O₃ and 0.1 % SnO₂. For the minor elements ICP-MS show up to 600 ppm of Si, Al, and V, up to 405 ppm of Mn, Zr, Cr, Y and Pb, less than 50 ppm of Cr, P, and Hf, and below 10 ppm of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Rb, Tm, Lu, Hf, less than 50 ppm Mn and Mo, and below 3 ppm of Zr, Cr, P, Co, Y. The SEM-EDS shows inclusions of Fe-columbite and Mn-tantalite. The initial EPMA and ICP-MS U/Pb results show viability for dating purposes.

Due to the size of the crystals, the laser ablation of the grains was performed in spots of 20 microns, using a frequency of 4 Hz and an intensity of 7 J/cm². The LA-ICP-MS data acquired yielded concordant ages of 1411±5 Ma (Fig. 5). This data matches with the ages of 1410 Ma for Fe-columbite from alluvial deposits in Colombia (Melcher et al. 2017).
4 Conclusion

The data acquired is very solid, and the ages interpreted as crystallization can be correlated with the ages of rocks and mineralization reported for this part of the Amazonian craton. Low W and Mn contents indicate pegmatitic or pneumatolytic affinity of the Nb-rutiles confirming a genetic relation with Sn, Nb and Ta ore mineralization. The Nb-rutiles showed a great variability of the matrix, but crystals having less than 15 wt% of Nb$_2$O$_5$ and no inclusions provide the best results for LA-ICP-MS.

Acknowledgements

We express our gratitude to the communities of Cachicamo, Chorro Bocon-Cerro Espina, San Jose y Barranquilla. Special thanks to the laboratories of the National University of Colombia, to professors Marc Poujol and Albrecht Von Quadt for the acquisition and processing of data. To COLCIENCIAS and the governances of Vichada and Guainía departments for the financial support.

References


Elsner H (2010) Heavy Minerals of Economic Importance. BGR, Hannover


Sulphide–sulpharsenide Re-Os geochronology and the wide-angle lens on Earth’s history – emerging views for new discoveries in ore deposit research

Nicolas J. Saintilan1,2,3, Robert A. Creaser2, David Selby3,4.
1Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Switzerland
2Department of Earth and Atmospheric Sciences, Alberta, Canada
3Department of Earth Sciences, University of Durham, United Kingdom
4State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Resources, China University of Geosciences, Wuhan, China

Abstract. A look through the wide-angle lens has been the way by which pioneers in Earth sciences (e.g., Canfield 1998) have spawned concepts and views in benchmark studies that drove a generation of research on frontiers topics. In ore deposit research, this methodology has only recently been systematised to achieve an improved understanding of the relationships between unprecedented conditions in the evolution of Earth, and the origin of the world’s largest mineral provinces (e.g., Heinrich 2015). Here, we suggest that direct dating of ore minerals using rhenium-osmium (Re-Os) geochemistry holds a key role in order to synthesize multi-disciplinary ore data sets and assess their significations within the wider scope of the evolution and interaction of Earth’s biosphere, atmosphere, hydrosphere, lithosphere, and asthenosphere. Using a tried and tested, yet constantly evolving, methodology for the production of mono-phase ore mineral separates, we have used Re-Os isotope geochemistry data to, e.g., propose a refined view for the origin of the Central African Copperbelt, possibly as one more outstanding consequence of the dramatic Cryogenian Snowball Earth, which caused the erosion of kilometres of material from the continents, and may explain the Great Unconformity, the rise of metazoans in the Neoproterozoic, and the first-order pattern of Phanerozoic sedimentation.

1 The Re-Os geochronometer – the tool to directly date sulphide, sulpharsenides & arsenides

Sulphide, sulpharsenide and arsenide minerals (collectively termed “ore minerals” hereafter) contain siderophile and/or chalcophile (e.g., Fe, Ni, Co, Cu) elements. Two siderophile elements, rhenium (Re) and osmium (Os), may be concentrated in crustal ore minerals at the part per million level (e.g., ppm in molybdenite; Selby and Creaser 2001; Stein et al. 2001; Selby et al. 2007) or more commonly at the part per billion to part per trillion levels (e.g., ppb in bornite or carrolite; Saintilan et al. 2018; ppt in cobaltite; Saintilan et al. 2017a). Thus, those minerals are amenable to absolute geochronology using the long-lived 187Re-187Os isotope system with a half-life of 41.6 Ga (λ187Re = 1.666 ± 0.005 \times 10^{-11} a^{-1}; Smoliar et al. 1996; Selby et al. 2007). State-of-the-art Re-Os isotope geochemistry is based on our capacity to obtain Re and Os aliquot fractions from ore minerals at low Re and Os blanks (Shirey and Walker 1995; Selby et al. 2009), in addition to being able to obtain intense ion beams of Os and Re by negative thermal ionization mass spectrometry (N-TIMS; Creaser et al. 1991; Völkening et al. 1991). Therefore, in the last 15 to 20 years, there has been significant development of the Re-Os chronometer applied to ore minerals, with particular focus on the robust molybdenite Re-Os geochronometer (e.g., Stein et al. 2001; Selby and Creaser 2001; Selby et al. 2007). In light of these findings, the Re-Os geochronometer in pyrite and arsenopyrite has received a steady interest contributing to constant developments and applications to the ore deposit environment (e.g., Davies et al. 2010; Morelli et al. 2007, 2010; Ootes et al. 2011) but also in sedimentary rocks (Bekker et al. 2004; Morelli et al. 2004) or in high-grade metamorphic rocks (Saintilan et al. 2017b). In recent years, we have focused on and successfully constrained the absolute Re-Os ages of several Cu- and/or Co-sulphide and sulpharsenide species in major sedimentary rock-hosted ore deposits (e.g., carrolite, cobaltite, bornite; Saintilan et al. 2017b, 2018).

2 The critical role of analytical methodology in modern Re-Os geochronology

Some existing ore minerals Re-Os geochronology studies have led to problems with interpretation of these data and the significance of the ages produced (e.g., Muchez et al. 2015; Selley et al. 2018).
This situation stems from multiple issues including, but not limited to: (1) Re-Os isotope geochemistry of ore minerals is recognized as analytically challenging. For example, in cases where sulphides have very low Re and Os abundances, control of both the abundance and isotopic composition of the laboratory Re and Os blanks can materially affect the age outcome; (2) Re-Os isotope geochemistry procedures have been applied to sulphide mineral fractions comprising mixtures of several sulphide species, and in some cases, by combining analytical data from different deposits and ore locations; (3) age data derived from single analysis ‘model ages’ and those from isochron ages have been used equivalently. Here, we explain our approach to modern Re-Os sulphide geochronology in terms of analytical and mineralogical protocols, and show the effect such protocols have when applied to sulphide mineral geochronology in the Central African Copperbelt.

Most ore minerals contain common Os. The term “common Os” encompasses any isotope of Os (192Os, 190Os, 188Os, 186Os, 184Os in crustal ore minerals) that was incorporated at the time of ore mineral precipitation prior to closure of the Re-Os system and decay of 187Re to radiogenic 187Os. Such an Os budget justifies the use of a "185Re+188Os spike" solution for analysis. With such a spike, Re-Os model ages cannot be calculated, and, we therefore use the Re-Os isochron approach which is based on our capacity to determine the 187Os/188Os isotopic compositions and the 186Re/188Os values for each aliquot (Case 1, Figure 1). In this approach, the positive correlation of 187Re/188Os values with variably radiogenic 187Os/188Os compositions yield a Re-Os date for which the 2σ precision is a function of the spread in the 187Re/188Os values, the variability in the initial 187Os/188Os compositions, and the propagated uncertainty in the standard mass spectrometry measurements, spike calibrations and blanks.

When an aliquot of a given ore mineral (e.g., molybdenite, in some instances arsenopyrite or pyrite) does not contain any common Os, the budget of Os that we currently measure by using a “mixed spike of Re & normal Os” (Selby and Creaser 2001; Stein et al. 2001; Selby et al. 2007) or a “mixed double spike of 185Re+188Os+190Os” (Markey et al. 2007) only comes from the radioactive decay of 187Re. In this case, a model Re-Os age may be calculated (Case 2, Figure 1). In some instances (Case 3, Figure 1), the 186Re/188Os values for ore minerals (except molybdenite) are extremely high (>>5,000). These values translate into the fact that the analysed ore mineral contains little common Os, including 188Os (e.g., 1.3–1.6% common Os in carrolite, Saintilan et al. 2018). Yet, at low Re and Os blank conditions and with state-of-the-art Re & Os analyses by N-TIMS, such low contents of common Os can be precisely and accurately quantified. Although, the isochron approach may yield a precise and geologically robust Re-Os age and provide the 187Os/188Os initial ratio (Os_i) with reasonable uncertainty (e.g., Saintilan et al. 2018), an isochron regression in the 187Re vs. 187Os space, after a minimal correction for common Os, is advised for such mineral species (Stein et al. 2000).

3 Re-Os geochronology of individual ore minerals: ‘what it takes and what it brings’

Specialists of the uranium-lead (U-Pb) isotope geochronometer produce individual mineral separates of, e.g., zircon and baddeleyite, and proceed with U-Pb geochronology of those minerals individually, supported by petrography and scanning electron microscopy (SEM) imaging in cathodoluminescence mode (e.g., Schoene et al. 2010; Schaltegger and Davies 2017). Similarly, Re-Os isotope geochemistry must be carried out on mineral separates of individual ore minerals, as the behaviour of the Re-Os system is known to differ markedly between sulphide minerals (Morelli et al. 2004, 2010). Such mineral separates are produced by following a demanding and time-consuming protocol that relies on preliminary detailed ore mineral petrography (Figure 2). Prior to performing Re-Os isotope geochemistry on those mineral separates, a quality control is performed by using SEM microscopy in back-scattered electron mode (SEM-BSE) with point EDX chemical analyses or extensive electron microprobe mineral chemistry (e.g., Saintilan et al. 2017a, 2017b, 2018). The protocol presented in Figure 2 is the recommended way to produce reliable (i.e., precise and reproducible) Re-Os isotope data of a given ore mineral. Those data can then be utilised for ore
deposit research by converting Re-Os dates into geologically- and petrographically-supported Re-Os ages. Yet, we recognize that imprecise Re-Os age determinations with high scatter are known to exist with this bulk analysis method. Therefore, Hnatyshin et al. (2018) have stressed the importance of linking Re-Os age data to the mineralogical location and distribution of Re by using LA-ICPMS mapping methods that can now quantify and spatially map Re distribution in sulphides at the low ppb level.

4 The Central African Copperbelt case study

Absolute geochronology of sulphide minerals using the above-described methodologies yield accurate and precise Re-Os ages of individual sulphide minerals at specific stratigraphic locations within a given deposit (e.g., carrolite and bornite at Kamoto, Saintilan et al. 2018). Those Re-Os ages may then be used to constrain the three following aspects that are central to ore deposit research: (1) the absolute timing of sulphide precipitation is critical knowledge that links the various components (e.g., metal-bearing fluids, reducing agents, geodynamic engine) that converge to form a mineral deposit; (2) constraints on the discrete timing of precipitation of individual sulphide minerals within a given deposit contribute to assess the timescales of mineralizing processes; (3) evaluating the timing of major (often called “world-class”) metallogenic provinces relative to unprecedented and peculiar evolution and interaction of the Earth biosphere, atmosphere, hydrosphere, lithosphere and asthenosphere.

At Kamoto in the Congolese part of the Central African Copperbelt, our Re-Os isochron ages include: epigenetic carrolite in an evaporite breccia (609 ± 5 Ma), and, bornite (473 ± 4 Ma) that replaces carrolite in this breccia and is disseminated in the stratiform carrolite ores. In addition, we produced two less precise Re-Os isochron ages for carrolite in an evaporite breccia (609 ± 5 Ma). Yet, those less precise ages are concordant with the timing of Cu mineralisation on the Zambian side of the Copperbelt, as previously identified by Sillitoe et al. (2017). Those new Re-Os ages for carrolite and bornite are in stark contrast with previous Re-Os evaluations (e.g., Barra et al. 2004; Muchez et al. 2015), for which caution is warranted based on features including a large spread of non-concordant model ages from a single deposit, the analysis of mixtures of sulphide phases, and aspects of the analytical data and their treatment, as previously pointed out by Sillitoe et al. (2017).

The ca. 717 to ca. 635 Ma Cryogenian Snowball Earth period was constrained by a series of benchmark studies (Hoffman et al. 1998; Hoffmann et al. 2004; Condon et al. 2005; Rooney et al., 2014; Rooney et al. 2015; Calver et al. 2013; Prave et al. 2016). This period dramatically caused the removal of kilometres of material from the continents (DeLucia et al. 2017; Keller et al. 2018), led to the deep erosion of copper-enriched crust (Parrell & Boyce 2019) and influenced the first-order pattern of Phanerozoic sedimentation (Keller et al. 2018). The Central African Copperbelt, which is the largest sedimentary rock-hosted Cu-Co province in the world, is hosted by a sedimentary sequence deposited prior, during and after the Snowball Earth period. By using the Re-Os age constraints for Cu-Co sulphide mineralisation (Sillitoe et al. 2017; Saintilan et al. 2018) and the “wide-angle lens on Earth history”, a refined view for the origin of the Copperbelt is emerging by reconciling (1) the Cryogenian geochronology, (2) the inspiring views for a connection between Snowball Earth and the Copperbelt (Robb et al. 2002; Hitzman et al. 2010), and (3) all available multi-disciplinary ore deposit research data (e.g., Selley et al. 2018).

Acknowledgements

Nicolas J Saintilan acknowledges the financial support of the Swiss National Science Foundation via the Early and Advanced Postdoc Mobility Grants (P2GEP2_162075 & P300P2_171496) and the Ambizione Fellowship (PZ00P2_180133). The authors are indebted to the Royal Museum for Central Africa, Belgium for the supply of the precious samples from the Kamoto deposit. D. Selby acknowledges the TOTAL Endowment Fund.

References

Saintilan NJ et al. (2017a) Re-Os systematics and geochemistry of

Saintilan NJ et al. (2017b) Sulphide Re-Os geochronology links orogenesis, salt and Cu-Co ores in the Central African Copperbelt. Scientific Reports 8:14946.


Elvira: a new shale-hosted VMS deposit in the Iberian Pyrite Belt

Guillem Gisbert, Emma Losantos, Fernando Tornos
Instituto de Geociencias (CSIC, UCM)

Juan Manuel Pons, Juan Carlos Videira
Minas de Aguas Teñidas S.A. (MATSA)

Abstract. The late Paleozoic Iberian Pyrite Belt (IPB), southwestern Iberian Peninsula, hosts one of the largest concentrations of volcanic massive sulphide deposits on the Earth’s surface. The ore-bearing sequence includes felsic-rock-hosted VMS deposits formed by host rock replacement in the northern area of the IPB, and shale-hosted deposits formed by direct sulphide precipitation on the seafloor in the southern area. The high-grade Elvira Cu-Zn-Pb deposit is the most recent discovery, and is located eastward of one of the largest orebodies in the southern IPB, the Sotiel-Migollas cluster. This deposit consists of a single massive sulphide lens located ca. 250-500 m below the surface and is hosted in an overturned and thrusted sequence dominated by dark shales dated to uppermost Devonian. The stratigraphic footwall includes a well-developed stockwork zone and pervasive chlorite-rich alteration. The massive sulphides show abundant sedimentary structures typical of deposition on the seafloor but also a large zone of sub-seafloor replacement of muds which marks the transition from the feeder zone to the exhalative massive sulphides.

1 Introduction

The Iberian Pyrite Belt (IPB) is an E-W 250 km long by 20-70 km wide VMS district in the southwestern Iberian Peninsula. It represents one of the most important ore provinces in Europe and the largest concentration of sulphides in the Earth’s crust (Tornos 2006). It holds over 1600 Mt of massive sulphides originally in place, and about 250 Mt of stockwork ore, distributed in around 90 VMS deposits (Tornos 2006).

Detailed geophysical exploration by MATSA of the areas nearby the Sotiel-Migollas VMS deposits, which have been mined since Roman times, has led to the discovery of a new massive sulphide body called Elvira (37°36'17"N, 6°49'51"W; Fig. 1). Exploration drilling of an electromagnetic (VTEM) anomaly located near the eastern end of the Migollas orebody intersected massive sulphides. This new deposit has been delineated by over 80 drill holes and will start production in late 2019.

2 Geological background

The formation of the IPB is related to the Late Paleozoic (Devonian to Carboniferous) Variscan orogeny. Oblique collision between the South Portuguese Zone, to which the IPB domain belongs, and the Autochthonous Iberian Terrane produced an evolving depositional setting with formation of continental pull-apart basins and intraplate magmatism to which the mineralization is related (Barriga 1990; Leistel et al. 1998; Tornos 2006). The geological record of the IPB consists of a 1000-5000 m thick stratigraphic sequence. Three main units have been described. The lower Phyllite-Quartzite (PQ) Group (Middle-Late Devonian) consists of interbedded quartz sandstones and shales deposited in a stable and shallow epicontinental platform (Moreno et al. 1996). Subsequent trans-tensional regime related to left-lateral northwards oblique continental collision generated pull-apart basins with lowered, tilted and uplifted blocks that subdivided the depositional environment into several sub-basins separated by shallow marine to subaerial areas (Tornos et al. 2005). Depositional-induced mantle partial melting generated mafic magmas that underplated and intruded the continental crust, promoting its partial melting and the generation of hot dry felsic magmas (Mitjavila et al. 1997). These magmas reached the surface producing a volcanic sequence in which alkaline-tholeiitic basalts and calc-alkaline andesites to rhyolites coexist with mudstone and some chemical sediments (Volcanic Sedimentary Complex; VSC). The massive sulphides formed in response to the accelerated dewatering of the PQ Group and degassing of felsic magmas (Tornos 2006). Finally, compressional tectonism related to the main collisional stage of the Variscan orogeny formed a foreland basin in which syn-orogenic flysch sediments (Baixo Alentejo Flysch Group) were deposited (Oliveira 1990).

The collision-related compressive deformation produced tectonic inversion and deformation forming a S-SW-verging thin-skinned foreland fold and thrust belt (Oliveira 1990; Quesada 1998). Regional metamorphism associated to Variscan orogeny is low grade, from prehnite-pumpellyite to low greenschist facies (Sánchez España 2000). Deformation and metamorphic grade tend to increase from south to north although a general metamorphic gradient is not clear, and are locally enhanced close to high strain zones (Sánchez España et al. 2000).

Two styles of VMS deposit formation have been described in the IPB: shale-hosted and felsic volcanic rocks-hosted deposits (Tornos 2006). Shale hosted deposits are mostly interpreted to have been formed in sub-oxic to anoxic third order basins where upwelling deep sulphur-depleted fluids mixed with modified seawater rich in biogenically reduced sulphur, leading to the precipitation of the massive sulphides on the seafloor. Felsic volcanic rocks-hosted deposits are interpreted to...
have formed by stratabound replacement of porous or reactive massive and volcaniclastic (vitriclast- or pumice-rich) volcanic rocks. It is suggested that mineralization was triggered by mixing of the deep sulphur-poor fluids with modified seawater bearing variably reduced sulphur acquired from leaching of the host volcanic rocks or by thermochemical reduction of the marine sulphate.

Most of the massive sulphide deposits are underlain by, or imbricated with, large stockwork or stringer zones despite subsequent Variscan thrusting that produced major tectonic inversion (Quesada 1998).

3 The Elvira VMS deposit

The Elvira deposit is located in the eastward continuation of the Sotiel-Migollas massive sulphide cluster (Santos et al. 1996; Velasco-Acebes et al. 2018), located in the south-eastern IPB. It is a polymetallic (Cu-Zn-Pb) pyrite-rich massive sulphide body with evidence of having been dominantly deposited in a sub-oxic to anoxic basin and rooted on a large stockwork zone.

3.1 Local stratigraphic sequence

The stratigraphic sequence in the Sotiel-Migollas-Elvira area is highly tectonized, with individual units limited by major thrusts (Fig. 1). It consists of: (1) a structural footwall dominated by felsic dome complexes intruding and interbedded with dark shales; (2) an overlying shale unit which hosts the massive sulphides; and (3) the structural hanging wall including the PQ Group, which hosts a well-developed stockwork in the Migollas deposit (Santos et al. 1996; Velasco-Acebes et al. 2018). The contact between the VS Complex and the PQ Group is interpreted to be a major thrust located in the inverse limb of a major south-verging fold (Velasco-Acebes et al. 2018). This contact is delineated by abundant bands of mylonite developing zones of tectonic mélange with lenses of mixed lithologies from both groups and that show widespread chlorite and carbonate alteration (Velasco-Acebes et al. 2018). This surface was interpreted to have favoured the widespread remobilization of the sulphides in the Sotiel-Migollas-Elvira area, showing abundant thin sulphide-rich veins parallel to the foliation and zones of high grade copper with massive chalcopyrite concentrations along shear bands (Velasco-Acebes et al. 2018).

If overturned to its original position, the stratigraphic sequence would include:

1) A footwall dominated by the PQ Group, consisting of a monotonous sequence of shale and quartz-rich sandstone with only some minor lenses of limestone, which is crosscut by abundant microdiorite sills and dykes (Velasco-Acebes et al. 2018).

2) A 400 m-thick dark shale sequence which is host to the massive sulphides. This sequence is locally carbon-rich and presents a cm-thick sedimentary layering. It includes sparse levels of volcaniclastic sandstone of dacitic composition, some layers of quartz-rich sandstone, and abundant disseminated to stratiform pyrite, with local bodies of likely sedimentary breccias with chloritized fragments supported by unaltered shale
In addition, in the direct structural footwall to the Sotiel-Migollas massive sulphides the shale hosts a discontinuous layer of black limestone with organic matter and disseminated pyrite. At the Elvira deposit, the massive sulphides are hosted in a shale-dominated sequence that includes black shales both in the footwall and hanging-wall to the ore body, with only minor fragmental volcanic rocks (Fig. 1). This suggests that its position is more distal to the domes than Sotiel-Migollas. The age of the ore-hosting sequence is uppermost Devonian (Gonzalez et al. 2006).

3) A felsic volcanic sequence which is several hundred meters thick and is dominated by felsic volcanic rocks with abundant lateral changes; these are mostly dacites forming dome complexes (Velasco-Acebes et al. 2018). It also presents abundant intercalations of mafic rocks; these are likely submarine lava flows, related volcanoclastic rocks, and subvolcanic sills that become gradually more abundant towards the structural footwall. In the structural footwall of Elvira, a coherent (lava/dike) volcanic to subvolcanic mafic rock has been intersected (Fig. 1).

3.2 Location and shape of the deposit

The Sotiel-Migollas-Elvira is one of the largest clusters of massive sulphide deposits in the IPB, with a tonnage well above 100 Mt. The Sotiel-Migollas part consist of three large stratabound massive sulphide bodies (Sotiel, Sotiel Este and Migollas) and several smaller lenses, which are aligned along a E-W 2 km-long narrow area (Velasco-Acebes et al. 2018). Elvira deposit represents the eastward continuation of the Sotiel-Migollas cluster.

The Sotiel orebody is up to 60 m thick and consists of three stacked lenses separated by up to 20 m thick barren shale; Sotiel Este is up to 40-50 m thick and is distributed in six stacked lenses; Migollas is up to 120 m thick and includes two large stacked dome-shaped lenses separated by shale (Santos et al. 1996). These massive sulphides occur at depths between near surface to ca. 700 m.

Elvira consists of a single sulphide lens located 250 to 500 m below the surface (Fig. 1). As in the Migollas deposit, the stockwork related to Elvira deposit is located in its hanging-wall.

3.3 Ore mineralogy

Most of the shale-hosted VMS deposits in the IPB do not display either clear metal zonation or zones of major base metal enrichment (Tornos 2006). In Sotiel-Migollas, Cu and Zn–Pb rich zones are common, but they do not show a well-defined distribution (Santos et al. 1996), and neither does Elvira. The style of mineralization in the Sotiel-Migollas cluster has been observed to vary between the individual orebodies (Velasco-Acebes et al. 2018). The mineralization at Sotiel and Sotiel Este is banded and dominated by alternating layers of massive sulphides and hydrothermally altered shale. On the other hand, the mineralization at Migollas, the deposit closest to Elvira, is mostly massive and with no interbedded shale, and is dominated by a siderite-rich massive sulphide. The style of mineralization in Elvira is yet to be studied in detail, but exhalative massive sulphides and dark shale interbedding is locally observed (Fig. 2).

The mineral assemblage of the massive sulphides in the Sotiel-Migollas-Elvira area is dominated by massive pyrite with variable amounts of chalcopyrite, sphalerite and galena, lesser amounts of arsenopyrite, pyrrhotite, magnetite and tetrahedrite-tennantite, as well as trace amounts of sulfosalts (boulangerite, bournonite, jaskolkiite and meneghinite), cassiterite, native bismuth and electrum (Velasco-Acebes et al. 2018 and references therein).

3.4 Alteration characteristics

Characteristics of the hydrothermal alteration related to the shale-hosted massive sulphide deposits in the southern IPB differ from those of deposits located in felsic volcanic rocks in the northern IPB. The alteration is conspicuous in the footwall, less pervasive and irregular adjacent to the mineralization and almost non-existent above it, and mostly produces a unique zone of massive chlorite ± quartz.

Alteration characteristics in the Sotiel-Migollas area have been described by Velasco-Acebes et al. (2018). The less hydrothermally altered shale mainly consists of a foliated groundmass of fine-grained illite ± muscovite, sparse pyrite, disperse grains of anhedral quartz, carbonates, ilmenite (altered to rutile) and zircon. In areas affected by hydrothermal alteration chloritic alteration is
closely associated to zones of brecciation or veinlets of carbonates and sulfides ± quartz. Primary shale layering was lost during chloritization, and the illite was replaced by massive chlorite. The resulting mineral assemblage contains clinochlore ± chamosite, variable amounts of carbonates, abundant anhedral pyrite (10-30%), and small amounts of disseminated sphalerite, chalcopyrite, galena, monazite and a significant amount of hydrothermal zircon. In the Migollas area, the shale between the individual lenses and lateral to the mineralization shows irregular chloritization and a subtle carbonate-rich alteration.

Like Elvira, Migollas deposit has an associated stockwork, which in this case is hosted by the PQ Group rocks in the structural hanging wall. The stockwork includes a zone of pervasive chloritization with a network of abundant 1-20 cm thick veins of medium- to coarse-grained sulphides, dominantly disseminated pyrite, and abundant stratabound layers of massive pyrite. The altered shale in the stockwork area shows zones of widespread carbonatization with abundant sparsely disseminated carbonate. The Migollas stockwork also has a carbonate-rich zone with veins of coarse-grained siderite and scarce sulphides that postdate the pyrite-rich veins. Despite major deformation, the intensity of alteration seems to increase downwards towards the contact with the massive sulphides (Velasco-Acebes et al. 2018).

Remarkably, the volcanic rocks in the footwall of the massive sulfides in the Sotiel-Migollas-Elvira area lack hydrothermal alteration and only the peperites host some alteration with replacement of the volcanic fragments by quartz, sercite and pyrite; in contrast, the few layers interbedded with the sulphide-hosting shales show a conspicuous replacement by illite and pyrite (Velasco-Acebes et al. 2018).

Acknowledgements

The authors thank MATSA for providing information and access to drill cores from Sotiel-Migollas and Elvira deposits. This research has been conducted within the NEXT (New Exploration Technologies) project and has received funding by the European Union’s Horizon 2020 research and innovation programme under Grant Agreement No. 776804.

References

Why magnesite, talc, and MVT ore deposits are associated with burial dolostones: Serpentinization provides the magnesium

Enrique Merino
Dept of Earth and Atmospheric Sciences, Indiana University, SA

Àngels Canals
Dept of Mineralogy, Petrology and Applied Geology, Universitat de Barcelona, Spain

Abstract. Magnesite, talc, and MVT ore deposits are hosted in burial dolomites in several districts because they all form from the same deep hot Mg-rich brines that first drive replacement of limestone by dolomite. Then talc and magnesite replace the dolomite. These replacements are Mg-driven and happen by precipitation-pressure-dissolution, which is why mineral volume is preserved, which warrants adjusting replacement mass balances on volume. The dolomite-for-calcite replacement is self-accelerating via the Ca$^{2+}$ released and affects huge volumes of limestone. Continued infiltration of the dolostone by the Mg-rich brine causes its replacement by magnesite and talc. The talc, magnesite, and MVT ores, and dedolomitization too, are part and parcel of the dolomitization process.

We propose that the huge amount of Mg needed to dolomitize limestones and form associated magnesite and talc ores, comes most likely from another huge process, the serpentinization of peridotites, which – only if we adjust the serpentine-for-olivine mass balance on volume – is seen to release much Mg$^{2+}$(aq) and SiO$_2$(aq). The release of these two ingredients makes the replacement self-accelerating, which in turn, through a rheological-kinetic feedback, accounts for the typical mesh and/or zebra displacive veining of serpentinites, and for the fact that even huge peridotite massifs are serpentinized completely.

1 Introduction

Burial dolomites around the world are host to Mississippi-Valley-type ore deposits (Zn-Pb sulphides or carbonates, barite, celestite, fluorite), and also to magnesite (MgCO$_3$) and talc (Mg$_3$Si$_4$O$_{10}$(OH)$_2$) ores. One such association of burial dolomites hosting MVT, magnesite, and talc ores occurs across the northern Iberian Peninsula (e.g., Velasco et al. 1987; Tornos and Spiro 2000). Another example is the set of MVT, talc, and magnesite ore deposits hosted in dolomites of southeastern British Columbia (e.g., Powell et al. 2006; Paradis and Simandl 2018).

Why are those ores typically hosted in burial dolomites? To drive dolomitization as well as magnesite and talc mineralization, magnesium is needed. The minerals involved form by replacement: dolomite replaces entire limestones. Magnesite replaces dolomite (Velasco et al. 1987; Lugli et al. 2000). Talc replaces dolomite and may also replace quartz in quartzites (Tornos and Spiro 2000).

However, saying that Mg is needed to make magnesite and talc does not make it clear which are the mineral reactions involved, or what are their driving forces, or how to account for the fact that all the ores and the dolomite that hosts them occur as replacements, or where the necessary magnesium comes from. Our approach below is to adjust replacement mass balances on volume (as required by the conservation of volume shown in Figures 1-3), and to take account of the new replacement physics (Merino and Dewers 1998; Merino and Canals 2011), by which replacement forms not by dissolution-precipitation as widely assumed, but by its opposite, precipitation/pressure-solution.

We very briefly discuss below the dynamic model of dolomitization and MVT mineralization by deep hot Mg-rich brines also rich in Sr, Ba, Zn and Pb (Merino and Canals 2011). The model shows how the brines drive the dolomite-for-calcite replacement essential to dolomitization, along with associated MVT ores, and how the same brines – if they continue infiltrating the dolostone – can drive the replacement of (some of) the dolomite formed by magnesite and talc.

The second question raised is: What is the source of the colossal amount of aqueous Mg$^{2+}$ needed to make burial dolomites and their associated magnesium ores, magnesite and talc? Again, it is by studying the serpentine-for-olivine replacement according to the new physics of replacement that we realize that the serpentinization of peridotites releases much magnesium and can provide the Mg needed by dolomitization.

2 Replacement and self-accelerating dolomitization

The phenomenon of replacement is essential in all types of metasomatism. (Please refer in detail to Merino and Canals (2011) and Merino et al. (2006).) Replacement is characterized by its spatial property of pseudomorphism - that the new mineral preserves both the volume and some ‘ghosts’ of the host. That double preservation implies two kinetic properties already grasped by Bastin et al. (1931, p.603): that the two ‘half-reactions’ of any replacement must be simultaneous and equal-rate. The pseudomorphism and the kinetic properties it implies can be produced only by precipitation/pressure dissolution,
not by dissolution-precipitation as generally assumed.

Merino and Canals’s (2011) comprehensive model of dolomitization dynamics rests on that view of replacement. Dolomite grows within a rigid limestone from a Mg-rich brine, exerting a local induced stress on the adjacent calcite and on itself. The stress pressure-dissolves the calcite and automatically equalizes the rates of calcite dissolution and dolomite growth (Nahon and Merino 1997), thus preserving mineral volume. As an increment of dolomite grows,

$$\text{Mg}^{2+} + \text{Ca}^{2+} + 2\text{CO}_3^{2-} = \text{CaMg(CO}_3\text{)}_2$$

it pressure dissolves an equal volume of calcite. The mass balance, adjusted on volume (Merino and Dewers 1998), is:

$$1.7\text{CaCO}_3(\text{Cal}) + \text{Mg}^{2+} + 0.3\text{CO}_3^{2-} = \text{CaMg(CO}_3\text{)}_2 + 0.7\text{Ca}^{2+}$$

The $\text{Ca}^{2+}$ released drives the growth of a new increment of dolomite by eq1, which will pressure dissolve more calcite, releasing more $\text{Ca}^{2+}$, and so on. This replacement is thus self-accelerating via $\text{Ca}^{2+}$.

Numerous predicted consequences of this self-acceleration are all confirmed by independent observations (Merino and Canals 2011). One prediction is that, when the dolomite-for-calcite replacement becomes fast enough, it lowers the local rock viscosity (because crystalline carbonate aggregates are strain-rate softening), and it should convert itself into a late minor phase of displacive growth, and indeed displacive is precisely what the characteristic zebra and breccia-like dolomitic veins are (Merino et al. 2006). Also, the self-acceleration makes it easier to understand why burial dolostones are so large and why they replace the original limestone completely. Another prediction of the model is that, because of the positive feedback between $\text{Ca}^{2+}$ concentration and replacement rate, when the fast dolomite growth shuts itself down by using up all local $\text{Mg}^{2+}(\text{aq})$, the huge $\text{Ca}^{2+}$ concentration in the local brine immediately drives precipitation of calcite as so-called late-stage calcite and as calcite-for-dolomite replacement, or dedolomitization.

3 Mass balances for the dolomite replacements

If the Mg-rich brine continues to infiltrate the dolostone, it can then drive the replacement of the dolomite by talc (Fig. 1) and/or by magnesite (Fig.2) according to the following mass balances:

3.1 Talc-for-dolomite, Figure 1:

$$2.3\text{CaMg(CO}_3\text{)}_2 + 0.7\text{Mg}^{2+} + 4\text{SiO}_2 + 4\text{H}_2\text{O} = \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 2.3\text{Ca}^{2+} + 4.6\text{CO}_3^{2-} + 6\text{H}^+$$

where 2.3 (=145/64 or quotient of formula volumes) equalizes mineral volume. This replacement is not self-accelerating, since it does not release Mg or $\text{SiO}_2$ that would reinforce further talc growth. Note that published replacement reactions for the talc-for-dolomite replacement are adjusted to conserve Mg among the minerals. For example, Tornos and Spiro (2000) gave:

$$3\text{CaMg(CO}_3\text{)}_2 + 4\text{SiO}_2 + 4\text{H}_2\text{O} = \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3\text{Ca}^{2+} + 6\text{CO}_3^{2-} + 6\text{H}^+$$

which has the unintended consequences of hiding that $\text{Mg}^{2+}$ drives the phenomenon and of violating the petrographically observed volume conservation.

3.2 Magnesite-for-dolomite, Figure 2:
CaMg(CO₃)₂(Dol) + 1.3Mg²⁺ + 0.3CO₃²⁻ ≈
≈ 2.3MgCO₃(Mgs) + Ca²⁺ (eq5)

where the 2.3 factor (= 64.5/28.1) equalizes mineral volume, as required by petrography (Fig. 2). This mass balance tells us that when magnesite grows (from Mg²⁺ and CO₃²⁻) and pressure dissolves an equal volume of dolomite, only Ca²⁺ is released, which does not reinforce the growth of more magnesite. Thus magnesite-dolomite is not self-accelerating.

**Figure 2.** (A) Large porphyroblasts of magnesite (only visible in frame B) have completely replaced many sparry dolomite crystals, perfectly preserving their outlines and volumes, under PP. (B) Same area as in frame (A), rotated 50° clockwise around tip of red arrow, under XP. The magnesite porphyroblasts are distinguishable only by their uniform birefringence. Sample from the magnesite mine at Eugui, Spain.

### 3.3 Talc-for-quartz:

6.4SiO₂(Oaq) + 3Mg²⁺ + 4H₂O ≈
≈ Mg₃Si₂O₅(OH)₄(Srp) + 2.4SiO₂(Oaq) + 6H⁺ (eq6)

where the 6.4 factor (=145/22.7) equalizes volumes. This mass balance releases SiO₂(Oaq) which does make this replacement self-accelerating, and which could help talc to replace dolomite by providing silica (eq3) especially if the site of talc-for-dolomite was downflow from the site of the talc-for-quartz replacement.

All texturally correct mass balances, eqs 2, 3, 5 and 6, explicitly have Mg²⁺ on the left side, confirming that these replacements are driven by Mg-rich brines.

### 4 Serpentinization: Mg source for dolomitization and its magnesium ores

Burial dolomites and the associated magnesite and/or talc deposits require huge amounts of hot Mg-rich brines that rise from deep sedimentary basins. Where does the Mg come to those basins from?

We propose that the Mg²⁺ needed comes from the serpentinization of peridotites and dunites, which consists primarily of the replacement of Mg-rich olivine by serpentine. Again, because the replacement preserves volume (Fig. 3B), we adjust its mass balance on mineral volume:

2.5Mg₂SiO₄(Ol) + 4H⁺ =
Mg₃Si₂O₅(OH)₄(Srp) + 2Mg²⁺ + 0.5SiO₂(aq)  (eq7)

where a round factor of 2.5 (=106.6/43.7) on olivine equalizes volumes. Thus, every increment of serpentine growth pressure dissolves olivine and releases Mg and silica, which reinforce growth of the next increment of serpentine by:

3Mg²⁺ + 2SiO₂(aq) + 5H₂O =
Mg₃Si₂O₅(OH)₄(Srp) + 6H⁺ (eq8)

replacing more olivine, releasing yet more Mg and silica, and so on. Thus, the serpentine-for-olivine replacement is self-accelerating. Once each olivine crystal starts to be replaced by serpentine, it propels its own replacement faster and faster, simultaneously with all the others, until completion – unless water runs out first. That’s probably why “incompletely serpentinized peridotite and the nearby co-occurrence of little-altered and highly altered peridotite are both commonly observed” (Evans 2013, p.103). That serpentinization, if it starts, always tends to go to completion is significant for geophysical model calculations in gravity and magnetics surveys (e.g., Pedrera et al. 2017). The combination of self-accelerating feedback with the known strain-rate-softening rheology of olivine-rich rocks (Faul et al. 2011), leads – exactly as for dolomite-for-calcite replacement (Merino and Canals 2011) – to driving the conversion of replacive serpentine growth into displacive veins of serpentine, zebra-like (Fig. 3A).

The dynamics just described – the release of Mg²⁺ plus silica, the self-accelerating replacement, and the kinetic-rheological feedback producing veins – has remained hidden from geochemists and petrologists because serpentinization reactions proposed in the literature, such as

3Mg₂SiO₄(Ol) + 4H₂O + SiO₂(Oaq) =
= 2Mg₃Si₂O₅(OH)₄(Srp), (eq9)

and others (Deer et al. 2009, p.213), are routinely adjusted conserving Mg between the minerals involved, which unintendedly violates petrographic evidence of volume conservation and makes it impossible to realize that Mg is actually lost to the pore fluid.

The fact that the serpentine-for-olivine replacement is self-accelerating means that serpentinization of an ultramafic body takes place roughly simultaneously...
everywhere, not at a travelling hydration front.

Figure 3. A) Zebra serpentine veins in ophiolite, Val d’Aosta, from Merino et al. (2006). B) The serpentine lizardite completely replaces an olivine crystal with hourglass and mesh textures. PP light. Northern Serpentinite Belt, Dominican Republic. Courtesy of Benoit Saumur. The zebra veins in frame A are displacive and result from the fact that the serpentine-for-olivine replacement is self-accelerating. The rheological-kinetic feedback involved is the same that produces zebra and breccia-like displacive veins in dolostones (Merino et al. 2006; Merino and Canals 2001).

5 Conclusions

Magnesite and talc ore deposits are hosted by burial dolostones because they are actually – along with MVT ores and dedolomitization – part and parcel of the burial dolomitization process, and are driven by the same deep Mg-rich brines that drive the dolomitization itself. This is seen when mass balances are adjusted on volume (eq 2-5), not on Mg.

The huge amount of Mg\(^{2+}\) needed to make burial dolomites and their associated magnesium ores is most likely provided by serpentinization of peridotites and dunites, among the largest alteration processes in the crust (Evans et al. 2013), which releases up to 40 percent of the Mg in olivine upon its replacement by serpentine.

Volume-adjusted mass balances combined with replacement-by-precipitation/pressure-solution leads to the discovery that some replacements are self-accelerating. Two of these, both huge, are dolomite-for-calcite in dolomitization and serpentine-for-olivine in serpentinization of peridotites. The former requires Mg, the latter releases it.

Acknowledgements

We thank Prof. Benoit Saumur of the University of Quebec at Montreal for permission to reproduce the photo in Fig. 3B. The second author acknowledges support from the Applied Mineralogy, Geochemistry and Geomicrobiology 2017SGR-1733 Research Group.

References


Fluid histories and controlling factors on mineralisation in the Cornwallis Zn-Pb district, Arctic Canada

Mathieu, J., Turner, E.C., Kontak, D.J.
Laurentian University

Fayek, M.
University of Manitoba

Abstract. The Cornwallis Pb-Zn district in Canada's Arctic has over 80 base-metal showings, in addition to the past-producing world-class Polaris Zn-Pb deposit (Paleozoic). The district can be geographically divided into regions based on their location relative to the Polaris deposit. The majority of showings are hosted in the same Paleozoic carbonate rock as Polaris (Thumb Mountain Formation), but other strata also contain mineralisation. This study uses an integrated multiple in-situ analytical approach to establish fluid histories recorded throughout the district. Consistent paragenetic, textural, $\delta^{18}$O Carbonate (~25‰), and fluid inclusion characteristics (T, and salinity 80-100°C and 25-30 wt.% NaCl equiv., respectively) suggest that a single regional rock-buffered fluid was involved throughout the district. Different $\delta^{34}$S values among showings, even in the same region, suggests independent, isolated sources of sulphur for each showing. Shale-normalised REEY patterns of dolomite gangue and trace-element concentrations in sphalerite are shared within regions, but differ among regions, suggesting local stratigraphic influences. Collectively, these results indicate that mineralisation was facilitated by a single regional fluid that interacted with local strata and sulphur sources, and that the size of the Polaris deposit was a function of local structural controls, in addition to local geological and fluid variation.

1 Introduction

The Cornwallis district in Canada's Arctic (Fig. 1) has over 80 MVT mineralised showings in its 450 km by 200 km area, including the high-grade Polaris Zn-Pb deposit, which closed in 2002 (20.1 Mt at 17% Zn+Pb; Dewing et al. 2007). Despite the large economic potential in the area, most attention has been paid to Polaris, with little attention has been paid to understanding the fluid histories of the showings and how they relate to the Polaris deposit (e.g., Mitchell et al 2004). Even with the amount of work focused on Polaris, there is no consensus to the mode of mineralisation (e.g. Dewing et al. 2007; Reid et al. 2013). This study uses an integrated multi-analytical approach to determine the fluid source(s) and relative mineral paragenetic histories of the different sites for the mineralisation throughout the district. This information will then be used to determine and assess possible controlling factors among mineralised showings and the Polaris deposit.

2 Geologic setting

The Cornwallis district is composed of a thick succession of Paleozoic mixed carbonate, clastic, and evaporite strata (Franklinian succession) that overlies Precambrian basement (Fig. 1; Dewing et al. 2007). The majority of showings in the district (42.5%) are hosted in the Ordovician Thumb Mountain Formation (Dewing et al. 2007), a fossiliferous, organic-rich limestone that is locally dolomitised. Other showings are hosted in other carbonate formations. Tectonically, this area has been exposed to numerous Phanerozoic events, including, Silurian Caledonian orogeny (Miall 1986), Devonian Ellesmerian orogeny, Carboniferous rifting (Sverdrup Basin; Davies and Nassichuk 1991), and Cenozoic Eurekan orogeny (Piepjohn et al. 2016). The Ellesmerian orogeny is credited as the most probable cause of fluid mobilisation related to mineralisation (Dewing et al. 2007; Mathieu et al. 2018). However, faults, which initially developed during the earlier Caledonian orogeny controlled, the spatial distribution of
mineralisation at Polaris during the Ellesmerian orogeny (Turner and Dewing 2004).

3 Materials and Methods

Representative dolostone samples (n=20) were selected from the different geographic regions in the district, for comparison. Regions are generalised based on their position (north, south, east, west, and central) relative to Polaris (Fig. 1). Samples include sphalerite (+/- galena), dolomite gangue, and post-mineralisation calcite. This study focuses on the sphalerite and dolomite phases.

The samples were subjected to standard petrographic analysis including SEM-EDS imaging and analysis, assessment of fluid inclusion assemblages (FIA) with follow up microthermometry on FIAs, secondary ion mass spectrometry (SIMS) for $\delta^{34}$S$_\text{sphalerite}$ and $\delta^{18}$O$_\text{carbonate}$, and laser ablation inductively coupled mass spectrometry (LA ICP-MS) for sphalerite and carbonate.

4 Results

The paragenesis in the district is presented in Figure 2 and can be divided into an early-, main, and late-stage. Main-stage mineralisation, the focus of this study, consists of dolomite gangue, sphalerite, and galena. These three phases are found overprinting and being overprinted by each other. Sphalerite can be divided into early (Sph1 and Sph2) and main (Sph3) generations. Sphalerites 1 and 2 have colliform texture and only present in some showings, whereas Sph3 is coarsely crystalline and is ubiquitous. Dolomite and Sph3 will be the focus of the study in order to compare fluid characteristics across the district.

![Figure 2. Simplified paragenesis of Polaris and the Cornwallis district (from Reid et al 2013).](image)

Fluid inclusion microthermometric data for FIAs in sphalerite and gangue dolomite yielded homogenisation temperatures ($T_h$) that average 101 °C with an unknown salinity because of metastability for the northern region; 88 °C and 28.8 wt. % NaCl equiv. for the eastern region, 82 °C and 28.9 wt. % NaCl equiv. for the western region, and 92 °C and 28.7 wt. % NaCl equiv. for the southern region (Fig. 3).

Gangue dolomite $\delta^{18}$O$_\text{VSMOW}$ values ranged from 22.8 to 26.9‰ for northern showings, 27.7 to 30.7‰ for eastern showings, 21.5 to 24.8‰ for central showings, and 19.7 to 26.4‰ for southern showings (Fig. 4). Water-mineral fractionation equations (Horita 2014) using average $T_h$ values indicate $\delta^{18}$O$_{H_2O}$ values of 3.5 to 7.6‰, 6.8 to 9.8‰, -1.0 to 5.7‰, and -0.7 to 6.0‰, for northern, eastern, central, and southern showings, respectively.

Sphalerite $\delta^{34}$S data of the same generation vary for each region, and even among showings within the same region (Fig. 5). Values in the district range from -4.0 to 33.5‰ (VCDT). When present, Sph1 and Sph2 have slightly lighter (~5‰) $\delta^{34}$S values than Sph3.

Average sphalerite trace element compositions and Polaris-normalised are present in Figure 6. In general, most elements from the different regions are within an order of magnitude of Polaris, with Fe, Ag, Ga, Cu, and Pb having the greatest difference (can be more than an order of magnitude).

Shale-normalised REEY patterns of gangue dolomite (Fig. 7) fall into two groups: positive slopes (La/Yb<1), and negative slopes (La/Yb>1). Southern, western and Polaris dolomite patterns have negative slopes, whereas, northern, eastern, and non-Polaris central samples have positive slopes. Patterns for northern samples are flat. Positive Eu and Y anomalies in Polaris gangue minerals are also (varying intensities) in western and southern dolomite.

![Figure 3. Fluid inclusion data, plotted as FIAs, from sphalerite and gangue dolomite show uniform (A) homogenisation temperatures and (B) salinities throughout the district. Black line represents range in values for Polaris (from Savard et al., 2000).](image)
Figure 4. Calculated $\delta^{18}$O$_{H2O}$ values using $\delta^{18}$ODolomite values and complementary homogenisation temperatures.

Figure 5. $\delta^{34}$S$_{CDT}$ values of sphalerite from each region.

5 Discussion

The presence of gangue dolomite with shared fluid inclusion characteristics (80-100 °C and 28 wt. % NaCl equiv.) and $\delta^{18}$O$_{H2O}$ values (-1 to 10 ‰) for each showing indicate the possibility of a single regional fluid being present throughout the district. This fluid likely originated as seawater and was mobilised by the Ellesmerian orogeny, when it equilibrated at depth, acquired elevated temperatures and dissolved evaporites to modify the isotopic composition.

The region-specific trace and rare earth element characteristics of the gangue dolomite indicate a fluid composition strongly influenced by local stratigraphy. The negative-sloped dolomites from the south, west, and Polaris regions (Fig. 7A) indicate a fluid-dominant, open system, whereas the positive-sloped dolomite from the east, west and central regions (Fig. 7B) indicates inheritance from host dolostone in a relatively closed, rock-buffered system (Azmy et al. 2011).

The distinct $\delta^{34}$S values of sphalerite for each showing indicate a shared sulphur source was not dominant throughout the district. Local pools of reduced S may have controlled the location of smaller showings, therefore limiting the extent of mineralisation. A general increase in $\delta^{34}$S values from early to later sphalerite may indicate the depletion of the initial S source and/or the progressively increasing influence of a heavier S source, possibly related to the regional fluid. Rayleigh fractionation is unlikely because of the relatively open fluid-dominant system.

Geochemical data (fluid inclusion temperatures and isotopes) from Polaris has characteristics of both BSR and TSR source of S, thereby resulting in contradicting mineralisation models (Dewing et al. 2007; Reid et al. 2013). This can be resolved by a condition whereby a pre-existing bacterially reduced sulphur pool interacted with a regional sulphate-bearing fluid; when the bacterially reduced S was consumed, TSR became the dominant reduced S source.

The positive Eu in gangue dolomites may indicate TSR processes (Jiang et al. 2015) associated with Polaris. The limitation of these Eu anomalies to the Polaris and southwest regions may indicate a predominance of TSR processes. A possible controlling factor for where TSR was able to take place may have been the availability of reductants (e.g. organics). However, because these anomalies are not restricted to Polaris, it is unlikely that this process controlled the successful development of the deposit.
It is probable that although all regions experienced a generally similar fluid history, local variations in stratigraphy and fluids probably were not dominant controlling factors in formation of the Polaris deposit. The main controlling factor, therefore, must be the ease and volume of fluid circulation – fluid flux was simply higher at Polaris than elsewhere. The concept of reactivated Boothia-aged (Caledonian) faults during the Ellesmerian orogeny being the main mineralisation control in the district (Turner and Dewing 2004) is the most reasonable explanation for the size and grade of the Polaris deposit. The relatively lower mobility of fluid at the other showings resulted in less mineralisation, which may also have been limited by the local volume of initial sulphur, even though the regional fluid that was responsible for mineralisation was everywhere the same as Polaris.

Figure 7. Average shale- normalised REEY plots for gangue dolomite throughout the district (two showings in each region) that can be grouped into two patterns (A and B), with the exception of northern showings (shown in both). PAAS values from Pourmand et al. (2012).

6 Conclusions

Despite similar host rocks, paragenesis, fluid characteristics, and timing throughout the Cornwallis district, the Polaris deposit stands out in size. The most probable control on mineralisation in the district is the presence of isolated sulphur pools that were present, in various abundances, at the time of regional migration of the mineralising fluid. Local variation in stratigraphy was probably the reason for the varied trace element concentrations in sphalerite. The main controlling factor for the size of the Polaris deposit must have been the position of mineralisation relative to reactivated faults during the main fluid mobilisation event (i.e. the Ellesmerian orogeny), which supports the topographic fluid-flow model for carbonate-hosted Zn-Pb deposit formation (MVT; Garven 1995).

Acknowledgements

Funding was provided by NSERC Discovery grant to ECT and Goodman School of Mines to JM. The fluid inclusion microthermometry laboratory is funded through NSERC to DK. Thanks to R. Sharp at University of Manitoba for SIMS analysis and J. Petrus at Laurentian University for LA ICP-MS analyses.

References


Geochemical characterization of felsic metavolcanic rocks hosting the Archean Taivaljärvi Ag-Zn-Pb-Au deposit in the Tipasjärvi greenstone belt, Finland.

Axel Cima  
University of Oulu, Sotkamo Silver Oy

Eero Hanski  
University of Oulu

Erkki Kuronen  
Sotkamo Silver Oy

Tapio Halkoaho  
Geological Survey of Finland (GTK)

Abstract. The Taivaljärvi Ag-Zn-Pb-Au deposit is located in the Archean Tipasjärvi greenstone belt (TGB) in eastern Finland. The deposit is hosted by strongly altered felsic meta-volcanic rocks and has silver as its main commodity. Geochemical characterization of the host sequence (Koivumäki Formation) was carried out using lithogeochemical data, normative mineralogy plots, mass-balance calculations, alteration indexes and petrographic observations. For this purpose, samples from different profiles across the TGB were analyzed for whole-rock geochemistry. The main alteration processes are sericitization, chloritization and silicification. Felsic rocks from the mine area are of FII affinity, gently sloping REE patterns, La/YbN ratios of 5.5-7.99, moderate Zr/Y ratios, intermediate HFSE concentrations and negative Eu anomalies (0.35-0.55). They show considerable mass gains in K2O, SiO2, MgO, and metals (e.g. Ag, Pb, Zn, Au), moderate FeO mass gains and depletion in Na2O and CaO. Once fertile areas were delineated, they were contrasted against areas of yet unproven fertility. Areas of lesser and greater potential for mineralization styles similar to those of Taivaljärvi deposit were subsequently identified.

1 Introduction
The Taivaljärvi Ag-Zn-Pb-Au deposit is located in the Archean Tipasjärvi greenstone belt, which is part of N-S-trending Tipasjärvi-Kuhmo-Suomussalmi (TKS) greenstone complex in eastern Finland. The deposit is hosted by strongly altered felsic metavolcanic rocks and has silver as its main commodity. It is characterized by a low content of sulfide minerals (<5%), disseminated and vein-type ore textures, and well-defined alteration zones (Papunen et al. 1989). Two models have been proposed for the formation of the Taivaljärvi deposit. Kopperoinen and Tuokko (1988) describe the deposit as a volcanic hosted exhalative (VMS) type, whereas Papunen et al. (1989) and Lindborg et al. (2015) favor a low-sulfidation epithermal type of ore formation. Both models emphasize the role of hydrothermal fluids in the metal enrichment. The Nimbus Ag-Zn-(Au) VHSM deposit in the Yilgarn Craton of Western Australia shares many features with the Taivaljärvi deposit, such as a quartz-carbonate-sericite dominated alteration assemblage, pyrite, sphalerite and galena as well as some Ag-Sb-Pb-Bi sulfosalts in the sulfide mineralization and a similar geotectonic setting. This deposit has been interpreted as a hybrid VHMS-epithermal deposit resulting from low temperature and shallow water conditions (Hollis et al. 2017, Caruso et al. 2018).

![Figure 1. Detailed geological map of the Tipasjärvi greenstone belt after Pietikäinen et al. (2008), as modified by Lindborg et al. (2015) with the location of the main areas of this study added. 1: Koraminvaara. 2: Mine. 3: South Jäkäläsuuo. 4: Koivumäki. 5: Katajasuo. 6: Kivisuo-Talassuo. 7: Lapasuo. 8: Palovaara. Volcanic lithogeochemistry is a powerful tool in the exploration for volcanic-hosted massive sulfide (VHMS) deposits (Piercey 2009). The combination of...](Image)
lithogeochemical data together with mass balance calculations, normative mineral plots, alteration indexes, and geological and geophysical data allow exploration targets to be easily contextualized within a VHMS system.

The purpose of this study is to make a geochemical characterization of the host rock unit of the Taivaljärvi Ag-Zn-Pb-Au deposit across several areas of the Tipasjärvi Greenstone Belt (TGB) in order to identify potential areas for new discoveries in the belt.

The study began with an extensive sampling campaign performed during the summer of 2018 as part of Sotkamo Silver’s brownfield exploration program. Sixty-five samples were selected for whole-rock geochemical analysis and 19 for thin sections. Observations were made by studying thin sections under polarized optical microscope and calculating normative alteration mineralogy based on whole-rock geochemical analyses. A least altered sample was chosen as a precursor for mass-balance calculations. Trace element geochemical analysis and fertility plots for VHMS deposits in rhyolites were applied. Samples from different parts of the mine were used as a frame of reference for fertile areas. Their compositions were compared with those of samples from other profiles in an attempt to delineate areas of potential new silver ore discoveries.

2 Geological background

The Taivaljärvi Ag-Zn-Pb-Au deposit is located in the central part of the Tipasjärvi Greenstone Belt (Fig. 1). The ore deposit is hosted by felsic metavolcanic rocks in the upper part of the Koivumäki Formation. The orebody crops out at the surface has a size of 40x400 m and a lens-shaped structure. It dips 65° to southeast, plunges 60° to south-southwest and extends at least to a depth of 600 m (Papunen et al. 1989). Geophysical “Sampo” surveys indicate that the mineralized zone may even go down to a depth of about 2 km (Lindborg et al. 2015). The Taivaljärvi deposit has been interpreted as part of an isoclinally folded antiform structure, lying in the eastern flank of the antiform. With a cutoff grade of 30 g/t Ag, the current resource estimate amounts to 6.6 Mt of measured and indicated resource with additional 4.3 Mt of inferred resource.

3 Alteration

The rocks studied range from intermediate to felsic metavolcanites and quartz-kyanite rocks of which the latter are interpreted in previous studies as a metamorphosed bleached lithocap (Papunen et al. 1989). Most of the samples show a high degree of alteration following sericitization trends (Fig. 2) and few show evidences for chloritization. Moreover, when heading eastwards, samples start showing strong silicification as well as paragenetic Al-bearing minerals such as staurolite, kyanite, garnet and no mafic phases.

Normative alteration mineralogy was calculated based on the program developed by Kackstaetter (2014) and then used to construct ternary diagrams allowing to assess alteration processes, such as sericitization, chloritization and silicification (Fig. 3).

Figure 2. Na/Al vs K/Al molar ratio diagram (modified after Davies and Whitehead 2006). Circled area represents the least altered zone.

Figure 3. a: Qtz-Src-Ab ternary plot that shows sericitization and silicification processes. b: Ab-Src-Chl ternary plot that shows sericitization and chloritization processes. c: Qtz-Src-Chl integrated plot that shows silicification, sericitization and chloritization processes. Circled areas represent those of relatively less alteration.

4 Trace element geochemistry and fertility evaluation

4.1 REE patterns

Figure 4 shows selected chondrite-normalized rare earth element patterns for samples from the mine area, representing the mineralized zone and the hanging-wall and footwall rocks. They show steep LREE, flat HREE and a pronounced Eu anomaly, being similar to the patterns reported from Archean mineralized felsic rocks such as the Wabigoon and Abitibi belts (Lesher et al. 1986). Samples from the Koivumäki and Kivisuo-Talassuo profiles share a similar REE signature but
those from Lapasuo are characterized by flat to slightly LREE-depleted REE patterns and low REE and HFSE abundances.

Samples from the Koraminvaara and Katajasuo profiles have a lower level of YbCN than the previous profiles (Fig. 5) and they do not show strong a negative Eu anomaly.

Figure 4. REE profiles of samples from the mine area. AC-63: Hanging-wall, AC-64: Mineralized zone, AC-65: Footwall. Normalized values after Taylor and McLennan 1985 in Rollinson 1993.

Samples from Palovaara profile have not only a low level of YbCN, but also a steep REE pattern, with high La/YbCN and depletion in HREE.

According to MacLean and Hoy (1991) some alteration processes might affect the distribution and concentration of LREE. For instance, chloritization may cause the rocks lose REE and sericitization gain REE. This is because REE are leached from high-temperature Fe-rich chlorite alteration zones and deposited in lower temperature quartz-sericite zones.

4.2 Fertility plots

Fertility was assessed according to the methodology described in Lesher et al. (1986) and Hart et al. (2004). Most of the samples fall into the FII category (Fig. 5). Footwall, deposit and hangingwall rhyodacite samples all fall in this category, and show moderate Zr/Y values of 3.35-9.73, [La/Yb]CN of 5.53-7.99, Eu/Eu* of 0.35-0.55 and intermediate HFSE contents.

Other areas such as Koivumäki and South Jäkäläsuo, show similar trace element characteristics to those of the mine area. The Kivisuo-Talassuo samples show also FII trends whereas the Lapasuo samples, fall into the FIV category, consisting of rhyodacites, rhyolites and high-silica rhyolites characterized by flat to slightly LREE-depleted REE patterns and low REE and HFSE abundances.

On the other hand, the Koraminvaara and Katajasuo samples fall near the edge of the FII field but they have a lower level of YbCN than the previous profiles. The Palovaara samples have not only a small Yb content, but also a steeper REE pattern, with higher La/YbCN ratio.

Figure 5. Fertility of felsic volcanic rocks hosting VHMS after Hart et al. (2004).

In summary, the Kivisuo-Talassuo and Lapasuo as well as Koraminvaara areas show similar trace-element characteristics to those from the silver mine, representing areas of higher potential of new discovery.

5 Mass Balance Calculations

In mass-change calculations, sample AC-6 from the Koraminvaara profile was considered as the precursor after petrographic, normative alteration mineralogy and major/trace elements geochemical evaluations. Mass changes were calculated using the single precursor method outlined by MacLean and Kranidiotis (1987) and Barrett MacLean (1994). Aluminum was chosen as the least mobile element for the enrichment factor.

Figure 6. $\Delta$K2O [wt.%] vs $\Delta$SiO2 [wt.%] showing silicification, sericitization + silicification, sericitization (src) + chloritization and total sericitization alteration processes (modified after Buschette and Piercey (2016)).

Positive $\Delta$K2O values are clearly highest in the mine area, correlating well with positive $\Delta$Zn, $\Delta$Ag and $\Delta$MgO values and moderately well with $\Delta$SiO2 and $\Delta$Fe2O3. This area also shows one of the greatest depletions in $\Delta$Na2O (Fig. 6). The Lapasuo and Kivisuo-Talassuo
areas display a similar behavior, which could indicate potential anomalies related to the same type of mineralization.

Some samples from the Lapasuo profile (AC-43, AC-44, AC-45) show a trend towards the same behaviour as that of the Silver Mine. Furthermore, it is observed as well that samples AC-31, AC-26 and AC-27 from Kivisuo-Talassuo profile are on the field of interest.

6 Conclusions

The main alteration processes on the host unit are sericitization, chloritization and silicification with different degrees of intensity. The rocks from the mine area are characterized by FII affinities, gently sloping REE patterns with La/YbN ratios of 5.5-7.99, moderate Zr/Y ratios, intermediate HFSE concentrations and negative Eu anomalies (0.35-0.55). They show gains in K₂O, SiO₂, MgO, and metals (e.g., Ag, Pb, Zn, Au), moderate gains in FeO and depletion in Na₂O and CaO. After integrating the trace-element geochemical data, alteration indexes and normative alteration mineralogy plots, and mass-balance calculations, the Lapasuo and Kivisuo-Talassuo areas, followed by Koraminvaara were identified as those of the highest discovery potential of silver ore.

Acknowledgements

This research is part of Axel Cima’s ongoing MSc. thesis project, funded and co-supervised by University of Oulu, Sotkamo Silver Oy and the Geological Survey of Finland (GTK).

References


How will technology facilitate Agile Discovery?

James S Cleverley
Global Product Manager – Geosciences, Imdex Limited, Iford, East Sussex, UK

Abstract. The process of Ore Discovery, and the delivery of a reportable resource, is often driven by waterfall processes. Each step in the process is sequential, with long delays waiting for data and information to decide on the best action. In many cases the decision about what to do next is made long after the drilling or sampling program has finished, or, without reliable information to support the decision. Cleverley et al. (2017) discussed the impact on the minerals discovery process of decreasing the time spent within the drilling cycle, from changing the technology of drilling to managing data workflows, to changes in behaviour and systems. The technology now exists that can be used to change the drilling to decision paradigm, but are we ready as an industry to adapt to this change? What is the impact of technology adoption on our ability to act on a quicker decision – business systems, people and regulatory process. Implementing technology is just the start of the change we need to address in order to achieve the potential value that new technology will unlock.

1 Waterfall or Agile?

In the business world, especially prevalent in technology start-ups in the last 15 years, there has been a shift from traditional waterfall project management to Agile processes. The Agile manifesto was a set of four values developed in 2001 (https://agilemanifesto.org/) that provided a framework for software development moving from rigid, onerous, pre-determined plans to value feedback, and dynamic learning as part of the development process. This approach is more recently finding its way into other product development disciplines. The key driver behind the agile approach to projects is not to operate in chaos, but to follow a roadmap with the ability to test, learn and revise as you go.

Figure 1 compares the timeline of a project delivered by waterfall process versus an agile framework. In the latter the project is continually evolved, and each iteration delivers a refinement of understanding, reducing risk and informing the next iteration. In the waterfall process the planning becomes critical and there is little room to change the direction or intent half way through without restarting the whole process. This same process can be applied to the way we discover resources, or plan to mine them. Replace the software release with a resource update. The long and comprehensive waterfall approach will deliver a high-quality resource at the end but the time to deliver is long and is not influenced by testing the model along the way. The resource update is comprehensive but high risk in that it is still dependant on the very first data. In the alternative approach an exploration project will deliver incremental resource updates along the way. These will be fast, lower resolution, less complete but will inform what is done next to reduce risk, improve resources or even walk away early. At each step the program will be optimised to maximise information entropy. The ultimate reported resource is higher quality with more confidence because we have taken risk away throughout the process – this de-risking requires informed geoscience thinking where it’s needed along the way, but it also requires lots of feedback built on rapidly delivered geoscience data and analysis.

2 How can Agile Exploration be delivered?

Operating a project in an Agile framework values the understanding over the process, allowing rapid iterations in order to refine your model. In software development this is about quickly testing your understanding of what the customer wants with releases. Refining the learnings about the customer allows the project to circle back and try something new – the feature release.

In the process of minerals discovery or resource definition it is harder to conceptualise being able to rapidly iterate our understanding. The length of time taken to plan, execute, interpret and make a decision is typically on the scale of weeks or months, certainly in many cases longer than a single campaign. However, the last few years as seen the introduction of new connected sensing technology that can provide near real-time data during drilling and sampling. This allows for a different approach to exploration programs, one that is built on the ability to make a decision in near real-time.

For example, Noble et al. (2018) demonstrated the use of in-field sample preparation and analysis with portable XRF to dynamically manage a Helicopter soil sampling program in South Australia. Samples could be collected and delivered to camp, prepared and analysed, and the sampling plan modified for day 2 or 3 on the results from...
day 1. This allows for real-time follow up of anomalies and less wasted analyses of “dead” zones. The samples are still analysed at a commercial laboratory for high quality, low detection limit data, but the decision about which samples to take, and the impact on the sampling program (change, move on, infill) can be made at the time of mobilisation. There are similar examples of technology being used in the process of drilling, either downhole or top of analysis, that can be used to drive the decision process around a program.

It is not just the process of delivering near real-time data from sensors that allows for decisions to be made. Data needs to be managed, securely transmitted and presented to the geoscientist in a way that allows information to support the decision. This might be at the drill rig or field camp, but equally could be back at head office or as a collaboration across multiple functions anywhere in the globe. This ability to provide connected data through cloud infrastructure is something that we take for granted in consumer products (step trackers, google maps traffic), but is new for the minerals industry. IMDEXHUB-IQ™ is an example of web

### 3 What are the challenges to adoption?

The minerals industry is facing a world where IoT connected sensing devices will allow the delivery of geoscience data from the drill rig or sampling program to the decision maker. This data will need to be analysed in a timely manner using analytics to support the interpretation, but critically requiring good, quantitative, numerical geoscience. In an Agile Exploration framework, the workflows of people are impacted, with more emphasis on using the data to decide in a time frame that adds value. As highlighted in Cleverley et al. (2017) there are barriers to adoption of technology not driven by whether the technology itself works, but by understanding how to implement all of the workflows and processes around the new Agile paradigm to realise the maximum value. These include business systems, data systems and security, workflow of people, remote collaboration, regulatory frameworks, and the speed of program cycles (Fig. 1).

We are entering a period of rapid change in the way that geoscience is embedded into the decision processes of mineral discovery and mining. There are as many barriers to adoption in processes and people, as implementation of smart technology. Future research needs to be more adept at delivering the results in the context of practical application, change management and systems. Regulatory frameworks inside and external to the business need to address the speed of decision making, the dynamic nature of exploration drilling and the potential to minimise environmental impact.

Agile exploration will be a paradigm that delivers greater value, reduced risk and better shareholder return. Technology is needed to deliver this framework, but people and systems will need to adapt to new and different processes. Core to all of this is better quality, quantitative, technology savvy and numerical geoscience. Are we as a community (academia, industry, METS and government) ready for this change?

### Acknowledgements

This abstract has benefited from many conversations, discussions and training used in my job as a Product Manager.

### References


A Comparison of random forests and cluster analysis to identify ore deposits type using LA-ICPMS analysis of pyrite

Daniel D. Gregory  
Department of Earth Sciences, Earth Sciences Centre, Toronto, Canada

Chao Liu, Shaunna M. Morrison, Robert M. Hazen  
Carnegie Institution for Science, Washington DC, USA

Mathew J. Cracknell, Ross R. Large, Peter McGoldrick, Stephen Kuhn, Michael J. Baker, Nathan Fox, Ivan Belousov, Jeffery A. Steadman  
ARC Research Hub for Transforming the Mining Value Chain, CODES, University of Tasmania, Australia.

Adrian J. Fabris  
Geological Survey of South Australia, Department of the Premier and Cabinet, Adelaide, Australia

Valery V. Maslennikov  
Institute of Mineralogy, Urals Branch, Russian Academy of Sciences, Russia.

Timothy W. Lyons, Maria C. Figueroa  
Department of Earth Sciences, University of California, Riverside, California, USA.

Abstract. As exploration for new resources increasingly relies upon deeper and deeper drilling to investigate through overburden, exploration projects will encounter significantly higher drilling costs to sample target areas and to open new areas to exploration. Therefore, as much information as possible must be extracted from every drill hole. One tool that can be used is the in situ trace element analysis of individual mineral phases using LA-ICPMS. In this study, we investigate the use of pyrite trace element chemistry to fingerprint different ore deposit types so that appropriate geologic models can be employed at an early stage of exploration in new greenfields areas. While this data is effective at identifying ore deposit type, variability within the raw data leads to inherent complications for manual analysis. One way to deconvolute this data is to employ machine learning algorithms to aid in the classification. Here we develop a classifier using supervised machine learning (Random Forests) to identify ore deposit type using pyrite chemistry. This has been recently accepted for publication in Economic Geology (Gregory et al., in press). Here we further examine the results of unsupervised cluster analysis of the dataset.

1 Introduction

Exploring though thick unmineralized cover is costly, and leads to difficulties in determining the correct geologic model to apply from a single intersection of mineralization. Application of new analytical tools are needed to help determine the type of mineralization at early exploration stages to identify potentially fertile ground. This will be useful for projects such as the co-funded drill holes currently being drilled in a regional context in Australia. The development of such a tool is the goal of this study.

The trace element content of pyrite is dictated by both the trace element content of the fluid from which the pyrite formed and the way in which pyrite was precipitated. Different ore deposit styles have different fluid compositions and precipitation mechanisms; thus it should be possible to use pyrite chemistry to identify ore deposit type. However, the trace element content can be complicated (Fig. 1) when viewing binary chemical plots and trying to classify deposit type manually. In this study we implement supervised machine learning (Random Forests) to identify ore deposit type using pyrite chemistry. This has been recently accepted for publication in Economic Geology (Gregory et al., in press). Here we further examine the results of unsupervised cluster analysis of the dataset.

2 The data repository

2.1 Laser ablation ICPMS

This project relies on LA-ICPMS analysis of the trace element content of pyrite. All analyses were carried out at the University of Tasmania, except some of the SEDEX analyses collected by Gadd et al. (2014) at Queen’s University. Generally, each LA-ICPMS analysis used a 10-100 µm beam size and consisted of a 30s background measurement prior to a 40-60s period where the laser was turned on and material was ablated in a He atmosphere. The standard STDGL2b2 (Danyushevsky et al. 2011) was analyzed at the start
New Techniques for Ore Discovery

Figure 1: Trace element plots for training dataset for A) Zn vs Cu, B) Ag vs Pb, and C) Co vs Ni. Note that while the different deposits tend to fall within general areas there is high overlap between the different deposits.

These data were compiled from a variety of sources, including published papers, PhD theses, industry reports, and new data completed during this study see Gregory et al. (in press) for detailed reference list.

3 The Classifiers

3.1 Random Forests

To develop the classifier three main steps were utilized. First data were compiled and preprocessed; second the classifier was trained; and third the classifiers predictions were evaluated. The primary method employed here to develop the classifier of ore deposits based on the trace element abundance of pyrite utilizes supervised classification, namely Random Forests. Random Forests works by utilizing a large number of random decision trees (500 were used here) at each node of the decision tree the data set is split based on its trace element content after which it goes to another branch where it is further split until it reaches a level where a determination of the type of deposit the pyrite came from is made, based on a training data set of known deposit type. This work flow is carried out in different permutations by each of the trees. After which each tree votes for the deposit it thinks a given unknown is from and the deposit with the most votes is the one that is ultimately chosen.

Figure 2: Diagram of the random forest. Each node of the decision tree the data set was split up to 5 times based on trace element content. We used a total of 500 decision trees.

Figure 2: Diagram of the random forest. Each node of the decision tree the data set was split up to 5 times based on trace element content. We used a total of 500 decision trees.

Pyrite trace element data from 43 different deposits and barren sedimentary formations (2 IOCG, 15 orogenic gold, 2 porphyry Cu-Au, 5 SEDEX, 7 VHMS and 12 sedimentary formations were used to train the classifier. Where possible equal numbers of analyses from each deposit were used to avoid biasing the classifier towards a single deposit.

The classifier was tested in two different ways. First, additional data from the same deposits that were used to train the classifier (but not the same analyses) were used to do initial testing and refinement of the classifier. After successful initial testing a second set of data, from deposits that were not used in the training of the classifier, were used as a blind test. There was not enough data in this subset to conduct a blind test of each deposit type but we did have 681 analyses from 27 deposits and barren sedimentary formation (4 orogenic gold, 3
SEDEX, 17 sedimentary pyrite, and 3 VHMS). These analyses were put through the Random Forest classifier and the results were checked to see how well the classifier worked for a complete unknown. After classification the results were refined by removing all the classifications where the designated class received fewer than 40% of the votes from the Random Forest.

3.2 Cluster analysis

In this study we also tested clustering analysis of the pyrites based on their trace element concentrations. Various clustering techniques were tested, including K-Means, Gaussian Mixture Models, Affinity Propagation, Agglomerative Clustering, DBSCAN and so on. These are all unsupervised machine-learning models, i.e., the performance and rationality of the models can only be evaluated by domain knowledge, which, in this case, is our current understanding of pyrite paragenesis. Based on this approach, we discovered that the Gaussian Mixture model best described the clustering of pyrites in the database.

The Gaussian mixture model is a probabilistic model that assumes all the data points are generated from a mixture of a designated number (K clusters) of Gaussian distributions. The model is built and updated in a stepwise estimation-maximization process. Initially, values randomly selected within the data range are assigned for parameters of the K Gaussian distributions in the model. Based on these parameters, the probabilities of each data point following all K Gaussian distributions are calculated, and the highest probability determines which cluster (distribution) the data points belong to. Parameters of the distribution describing each cluster are then updated based on all the data points in that cluster, and then probability of all data points are calculated again based on the updated distribution parameters, and so on, until the result converges.

4 Results of the Classifiers

4.1 Results of the Test data

The results of the initial testing of the classifier were promising with all fields being classified correctly 86 to 99% of the time. Of particular interest is that the sedimentary pyrite, the stand in for "background" barren pyrite, was correctly identified 99% of the time, suggesting the classifier is effective at identifying unmineralized settings. For Tables 1 to 3, the following abbreviations are used: IG – IOCG, OG – orogenic gold, P – porphyry, SX – SEDEX, S – barren sedimentary pyrite, VS – VHMS.

<table>
<thead>
<tr>
<th>Predicted</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>IG</td>
<td>OG</td>
</tr>
<tr>
<td>IG</td>
<td>35</td>
</tr>
<tr>
<td>OG</td>
<td>7</td>
</tr>
<tr>
<td>P</td>
<td>5</td>
</tr>
<tr>
<td>SX</td>
<td>3</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
</tr>
<tr>
<td>VS</td>
<td>1</td>
</tr>
</tbody>
</table>

4.2 Results of the Blind Test data

Similarly, to the test data, the results of the blind test classifications were also promising. The classifier correctly identified which deposit a pyrite analysis came from 85 to 97% of the time. Because several analyses are taken for each deposit, this represents a significant ability of the classifier to identify unknown mineralization styles. Furthermore, again the barren sedimentary pyrite was most effectively identified (97%) by the classifier suggesting it will be useful to separate background pyrite crystals from those related to mineralization.

<table>
<thead>
<tr>
<th>Predicted</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>IG</td>
<td>OG</td>
</tr>
<tr>
<td>IG</td>
<td>2</td>
</tr>
<tr>
<td>OG</td>
<td>94</td>
</tr>
<tr>
<td>P</td>
<td>62</td>
</tr>
<tr>
<td>SX</td>
<td>1</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
</tr>
</tbody>
</table>

4.3 Effect of untrained data on the classifier

One problem with using a supervised classifier, such as Random Forests, is that it will always give an answer, thus if a sample is from an origin that is not one of the groups in the training set, a spurious result will be generated (i.e. the classifier will pick the closest category in the training dataset). To check whether pyrite types not represented in the training dataset can be identified as such by the classifier, we put a dataset from the St Ives gold district that has 7 different types of pyrite, 2 of sedimentary origin and 1 associated with the gold mineralization but 4 more not related to mineralization (Gregory et al. 2016). We established the criteria that for a conclusive designation at least two thirds of the analyses must be also be conclusive (i.e. received >40% of votes from the Random Forest). The sedimentary pyrite and orogenic Au were conclusively, correctly identified and 3 of the 4 non-mineralized pyrite
parageneses were inconclusive; which they should be as their correct designation was not represented in the training data set (Table 3). However, one pyrite type was incorrectly conclusively designated as orogenic Au. This shows that more data, from different pyrite types, needs to be accumulated to refine the classifier.

Table 3. Random Forest classification of pyrite from St Ives Gold district (Gregory et al. 2016)

<table>
<thead>
<tr>
<th>Pyrite type</th>
<th>% inconclusive</th>
<th>Most common classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedimentary</td>
<td>16</td>
<td>97.5 Sedimentary</td>
</tr>
<tr>
<td>Py3</td>
<td>14</td>
<td>62.5 Orogenic Au</td>
</tr>
<tr>
<td>Py4</td>
<td>38</td>
<td>80.0 Orogenic Au</td>
</tr>
<tr>
<td>Py5</td>
<td>76</td>
<td>100.0 Porphyry</td>
</tr>
<tr>
<td>Orogenic Au</td>
<td>9</td>
<td>84.9 Orogenic Au</td>
</tr>
<tr>
<td>Py7</td>
<td>20</td>
<td>62.5 Porphyry</td>
</tr>
</tbody>
</table>

4.4 Results of the Cluster Analysis

Using a Gaussian Mixture Model 7 different classes were identified using the cluster analysis. In general, the cluster analysis separated most of the pyrite types, similar to the Random Forest. Yet there was more overlap evident between the different fields, especially between a subgroup of porphyry and orogenic Au (Fig. 3). The reason for this is not readily apparent and will be the focus of further investigation.

5 Discussion

The high degree of correct classification and the ability to determine that pyrite types not in the training set are inconclusive in most cases suggests the use of Random Forest classification is a useful tool when combined with other methods, to identify mineralization styles in unknown samples. However, it also highlights the need to acquire more data from other deposits types (i.e. epithermal gold, Carlin etc.) and to obtain data from unmineralized pyrite to strengthen the classifier before it can be robustly applied in an exploration context.

The results were supported by the cluster analysis. However, the cluster analysis had more difficulty in separating the higher temperature varieties of pyrite. The results were still encouraging as they supported the random forest results and are likely better at identifying pyrite types that are not part of the training set. Thus, going forward we will investigate using the two techniques in conjunction with one another.

Acknowledgements

This project arose out of funding from the Geological Surveys of Western Australia and South Australia for initial data collection and testing of the classifier. Additionally, data was also obtained from the AMIRA P1060 project. The NSF FESD Program and the NASA Astrobiology Institute under Cooperative Agreement No. NNA15BB03A issued through the Science Mission Directorate provided funding for the development of the classifier and mining of pyrite data from literature sources.

References


3D ore prediction by MLAs based on computational modeling in maturely explored area: a case study in Anqing orefield, China

Liu Liangming, Qin Yaozhu
Computational Geosciences Research Center, Central South University

Abstract. In a maturely explored area, it is difficult to select targets with high potential to be drilled further, because there are so many factors disturbing the exploration and ore prediction. The Anqing orefield is such an area. Although the early geophysical works led to the initial discovery of ore deposits in this orefield, the recent intensive geophysical exploration failed to find new orebodies. For evaluating the exploration strategy based on geophysical data and facilitating discovery of hidden orebodies, we apply the random forests (RF), one robust method of the machine learning algorithms (MLAs), to process the data from both the geophysical surveying and computational modeling on geometry and geodynamics of the ore-controlling intrusion. The study not only explains why no orebodies have been discovered by drilling the geophysical anomalies, but also predicts locations with high potential in 3D. The existing orebodies absolutely occur in the locations with high prospectivity. The high prospectivity locations that have not been drilled must be the targets to be drilled further. Such prospective targets are mainly in the western segment of the intrusion’s contact zone.

1 Introduction

Prediction of hidden orebodies is generally not so easy and does not necessarily lead to successful discoveries, especially in the maturely explored setting. The critical impediments to the successful ore prediction are from the exploration data and the prospectivity modeling techniques, because the data are absolutely influenced by a lot of factors and their association with the orebodies is very complicated, and usually nonlinear (Qin and Liu 2018). With the rapid growth of computing power, the MLAs have been developed as a group of robust methods for conducting sound prospectivity model by analyzing the complex relationship between multitude evidential features and mineralization (Rodriguez-Galiano et al. 2015; Xiong et al. 2018). It has been demonstrated that MLAs are more accurate than statistical techniques commonly used in ore prediction, especially when the multi-sourced data with different statistical distributions are used. MLAs have the potential to identify and model the complex non-linear relationships between the mineral occurrences and the evidential features (Bwown et al. 2000).

The Anqing orefield, with the largest Fe-Cu skarn deposit in the Yangtze River metallogenic belt (YRMB), is a maturely explored area. The ore deposits in this field were initially discovered by drilling in the magnetic anomalies in 1959 (Liu et al. 2011, 2012). However, its recent exploration strategy for finding hidden orebodies at depth was not successful. Twelve deep drillholes were finished at the targets delineated by the Controlled Source Audio-frequency Magnetotelluric (CSAMT) data, but no orebody was discovered. For finding a way out of such awkward situation and facilitating ore discovery, we simulate the geometric shape and cooling dynamic process of the ore-controlling intrusion, and use the RF to predict the hidden orebodies.

2 Geological setting and current situation of exploration

2.1 Geological setting

The Anqing orefield is located in the middle of YRMB. The orebodies in this field are mainly Cu and Cu-Fe skarns, minor Fe skarns, occurring in the contact zone between the Yueshan intrusion and marble and dolomite marble of the low to mid Tertiary age (Fig.1). Hundreds of orebodies have more than 48.8 Mt @ 1.3% Cu ores and 100 Mt @ 48% Fe ores.

Figure 1. Geological map of Anqing orefield (modifying from Liu et al. 2012).
The Yueshan intrusion is the key ore-controlling factor in this orefield (Figs.1 and 2). It is irregular shaped and composed mostly of diorite with minor quartz diorite, with U–Pb zircon isotopic age of 138.7 Ma (or Mid Early Cretaceous). The geological and geochemical features of the intrusion and ore deposits indicate that mineralization took place during the cooling process of the intrusion (Liu et al. 2011, 2012). The orebodies are distributed very unevenly along the contact zone (Fig.2a). The ore distribution is obviously related to geometric and topographic features of the intrusion (comparing Fig.2a with Fig.2b). The E-W trending contact zones with rough irregular surface are favorable for localization of orebodies.

Figure 2. (a) Yueshan intrusion and orebodies along its contact zone; (b) variation of Gaussian curvature of the Yueshan intrusion's contact surface

2.2 Current situation of exploration

The Anqing orefield has been maturely explored and mined. Since the first drillhole in 1959, more than 1200 drillholes with a total length of more than 370000 m and more than 110000 m underground tunnels have been finished there. These works have provided abundant information of the underground geology and led to discovery of lots of orebodies as well. For increasing ore reserves through deep exploration, a recent program of CSAMT survey of 26.6 km² was carried out on a grid spacing of 200 m × 40 m within the orefield. Targeting at the low resistivities detected by CSAMT, the 12 drill holes with accumulative depth of 16725.39 m have been finished. Unfortunately, no orebody has been discovered by these works, demonstrating that the CSAMT is not effective enough to discover hidden orebodies at depth. Nowadays it is necessary to explain why the CSAMT data are not capable of giving credible prediction and to find a capable method for facilitating predictive discovery of orebodies at depth.

3 Computational modeling

To understand the spatial structures of mineralization system, we construct the 3D surface-based models of Yueshan intrusion, orebodies and carbonate wall rocks by using geological data from all exploration works. In the 3D models, we use Delaunay algorithm to construct a triangulated irregular network (TIN) to model the inter-surfaces of geological bodies, and optimize the modeling surfaces by using the DSI (discrete smooth interpolation) algorithm. The models show that the locations of orebodies are closely related to the geometric and topographic features of the intrusion (Fig.2).

As the mineralization was simultaneous with the retrograde alteration, the orebodies must have been formed during cooling process of the Yueshan intrusion. Using the finite difference algorithm in the platform of FLAC3D, we model the syn-stretching cooling process of the Yueshan intrusion (Liu et al. 2012). The modeling results show that the dilatant deformation is favorable for localization of orebodies (Fig.3).

Figure 3. Showing spatial association of orebodies (yellow) with intrusion (pink) and dilation zones with volume strain >0.8% (red)

4 Random forest algorithm

The MLAs are increasingly applied to achieve interpretation, classification and prediction in geological exploration, as they can simultaneously use multiple variables to reduce interpretation bias and outperform the traditional graphical or statistical methods (Friedman et al. 2001; O’Brien et al. 2015; Kirkwood et al. 2016; Caté et al. 2018). The most widely used MLAs include decision trees (DT) (Breiman et al. 1984), artificial neural networks (ANN) (Brown et al. 2000), support vector machine (SVM) (Abedi et al. 2012) and random forest (RF) (Breiman 2001).

The RF, an ensemble DT algorithm, combines the performance of numerous DT algorithms to classify or predict the value of a variable (Breiman 2001; Carranza and Laborte 2015). Each decision tree is built from a sample of the training set (bootstrapping) and a random portion of the discriminative variables are used at each
split. For avoiding the correlation of the different trees, RF increases the diversity of the trees by making them grow from different training data subsets created through a procedure called "bagging". Bagging generates training data for each tree by sampling with replacement a number of samples equal to the number of samples in the source dataset, i.e., with no deletion of the data selected from the input sample for generating the next subset. Hence, some data may be used more than once in the training, while others might never be used. Thus, greater stability is achieved, as it makes it more robust when facing slight variations in input data and, at the same time, it increases prediction accuracy (Breiman 2001). RF implements the Gini Index to determine a “best split” threshold of input values for given classes. The Gini Index returns a measure of class heterogeneity within child nodes as compared to the parent node (Breiman et al. 1984; Waske et al. 2009; Cracknell and Reading 2014).

5 Geological and geophysical data for RS

The data inputted for RS calculation are of 4 different features, or 4 variables: (1) volume strain produced by computational dynamic modeling; (2) curvature of the intrusion’s contact surface; (3) electric resistivity detected by CSAMT surveying; (4) wall rocks (carbonate or not).

The CSAMT surveying had only been carried out only in the eastern part of the orefield. The orebodies are not closely associated with low resistivities detected by CSAMT (Fig. 4).

![Figure 4. Low resistivity (<500 Ω.m) and orebodies](image)

6 3D prospectivity model by RF

In the eastern part of the orefield, the data of all 4 variables including resistivity are available. The domain is divided into 719459 cubes, among which 1986 cubes are occupied by ores, 11543 cubes have been drilled but no orebodies discovered, and 715687 cubes have not been drilled. 70% of mineralized cubes and 70% of un-mineralized cubes are selected randomly as training sets. The RF calculation produce the 3D prospectivity model as Fig. 5. The high prospective zones with high probability of having ores are distinctly different from the low resistivity spaces (Figs. 4 and 5). The orebodies already discovered are all located in the high probable zones (Fig. 5).

Because the CSAMT surveying has not covered the whole orefield, the electric resistivity data are not available to process RF calculation in the whole orefield. The whole orefield is divided into 2061067 cubes, among which 3186 cubes are occupied by ores, 14071 cubes have been drilled but no orebodies discovered, and 715687 cubes have not been drilled. 70% of mineralized cubes and 70% of un-mineralized cubes are selected randomly as training sets. The RF prediction model is set up by considering 3 variables, volume strain, geometric features of intrusion’s contact surface and wall rocks. The 3D prospectivity model of RF (Fig. 6) shows that the exiting orebodies are all localized in the high potential zones. The high potential zones that have not been drilled must be prospective targets that are worthy to be drilled further for discovering hidden orebodies. Such prospective targets are mainly in the western segment of the intrusion’s contact zone where the contact surface is concaved inward (Fig. 6).

![Figure 5. Prediction probability in the domain with CSAMT surveying](image)
Although the RF model with resistivity data has a better success rate than RF models without resistivity data, all models have successful behavior (Fig. 7). For percentage threshold values of prospective cubes over 3%, the success rate of RF is over 90%. No matter whether or not using the variable of resistivity, the RF models give the almost same prediction (Figs. 5 and 6). The RF prediction results demonstrate that the MLAs are useful for constructing sound exploration strategy in the maturely explored setting.

Acknowledgements

Research funding was provided by the NSFC through grants awarded to Liu (grants No. 41372338 and No. 41772351). We acknowledge the Tongling Nonferrous Metal Group Ltd. Company for the financial and logistic support during the field work.

References


Abstract. 3D geological models based on data from geological field observations, magnetic airborne surveys and combined XRF-XRT scanning of drill core are presented for the Lovisa-Håkansboda and the Stråssa-Blanka mineral systems (1.9 - 1.8 Ga). At first, the 3D architecture of several deposits was derived primarily from surface data and mine-level maps. Secondly, geochemical and structural constrains from drill core scanning (XRF-XRT) were used to refine the models locally to a detailed, in-mine scale. The constructed models were then placed in a regional context providing valuable insight on the area’s local and regional deformation pattern. All modelled deposits are plunging 50-60° towards the south-southeast reflecting D2 deformation (vertical shearing) during NW-SE-directed shortening and are locally overprinted by D3 (lateral shearing) during N-S-directed shortening.

1 Introduction

Various sulphide mineralizations of different types (Zn-Pb-Ag and Cu-Co) occur within short distances in the Lovisa-Håkansboda area (4 km²). Despite the long mining history in the area and its high potential for several critical metals including silver, gold, cobalt, antimony and bismuth, knowledge about the mineral system and ore genetic models is limited (e.g. Carlon and Bleeker 1988, Jansson et al. 2018). Difficulties arise from a high complexity in terms of chemistry, mineralogy, textures and metal content all varying within short distances. Additionally, a strong tectonic overprint mostly blurred primary features causing remobilization and secondary textures (Sahlström et al. 2019 this volume).

To resolve the area’s structural complexity, in order to better understand the mineral system, an integrated approach is necessary and includes combining of various datasets. As such, access to in-mine infrastructure and drill cores needs to be combined with data from geological and geophysical surveys on a near-mine scale. In addition, valuable, high resolution geochemical and structural datasets can now easily be obtained from combined XRF-XRT drill core scanning (X-mine project, EU/Horizon 2020).

In this study, we investigate the structural setting of the Lovisa-Håkansboda base metal and Stråssas-Blanka iron—oxide mineral systems by integrating new data from geological field observations, magnetic surveys, and XRF-XRT drillcore scanning. 3D deposit models are then constructed for each deposit. The modelled subsurface are analysed and evaluated in the light of structural control and regional deformation.

2 Geological setting

The Bergslagen mining province is part of the Bergslagen lithotectonic unit of the Fennoscandian Shield (Stephens and Andersson 2015) (Fig. 1). The unit largely consists of syn-orogenic plutonic rocks intruded in a succession dominated by felsic metavolcanics rocks, which were
deposited in a continental back-arc basin during the Svecokarelian orogeny (1.9 – 1.8 Ga) (Stephens and Andersson 2015). The metavolcanic succession is interbedded by volcanoclastic mass flow deposits, limestone, BIFs and sulphide mineralization. Deformation was polyphase and metamorphism was low-pressure up to amphibolite facies during metamorphic peak conditions. Large-scale folding and shearing resulted in the formation of inliers of the supracrustal rocks, which became bounded by plutonic rocks and shear zones. A relatively large inlier in western Bergslagen is the 45 km long, NE-trending Guldsmedshyttan syncline, hosting many iron-oxide and base metal sulphide deposits along strike. The deposits for this study (Lovisa-Håkansboda, Stråssa-Blanka) are situated in the northern tip of the syncline (e.g. Lundström1983, Jansson et al. 2018).

2.1 The Lovisa Zn-Pb-(Ag) deposit

The Lovisa sulphide deposit on the western fold limb is actively mined with a reserve of 675 000 tons ore with zinc (9,5%), lead (3,9%) and some silver (Lovisagruvan AB annual report 2018). The reserve is proven by 90 drill holes 1100 m along strike and down to 425 m and is open at depth and to the south.

The Lovisa deposit is stratiform and consists of two steeply dipping horizons (Jansson et al. 2018). A laminated, sphalerite-dominated “Sphalerite Ore” (>15% Zn) and a horizon of galena-dominated “Main ore” (>40% Zn+Pb). The ore layers are separated by a 1 to 3 meters wide zone of barren rock (< 1% Zn+Pb). The total thickness of the ore layers varies between less than 1 m to up to 3 meters. The host rock as well as the interbedded layers between the ore layers are rhyolitic ash siltstones and chloritic schists. The formation of stratiform ore layers is interpreted as syn-genetically in a vent-distal, seafloor exhalative setting (Jansson et al. 2018). Subsequently the ore layers and the surrounding rocks became metamorphosed to upper amphibolite facies and ductile and brittle deformed resulting in post-genetic ore textures (e.g. metablastic growth, shearing and folding, mineral intergrowth) and remobilization (Sahlström et al. 2019 this volume).

2.2 The Håkansboda (Cu-Co-As-Bi-Au) deposit

The Håkansboda deposit is hosted by massive limestones with interbeds of calc-silicate rocks and rhyolitic ash siltstone and is interpreted to occur on the eastern fold limb and stratigraphically below the stratiform Lovisa deposit (Lundström, 1983; Carlon & Bleeker 1988). Mineralization is known for 850 m along strike and to a depth of 600 m but is open at depth and to the south. The indicated reserve is 629.000 tons of 1,4% Cu, 0,4 g/t Au and 14,3 g/t Ag (in-situ grades) (Kopparberg Mineral AB, 2012). The dominant ore minerals are chalcopyrite, cobaltite, glaucodot, arsenopyrite, pyrrhotite, pyrite, sphalerite and galena, and accessory bismuth minerals (e.g. Magnusson 1973). The ore occurs as massive lenses, schlieren or banded mineralisation, disseminated sulphides and as breccias. The ore textures indicate post-genetic deformation and remobilization (Carlon and Bleeker 1988). Carlon and Bleeker (1988) suggested that the Håkansboda deposit formed in a feeder zone for stratiform mineralization in the area (e.g. Lovisa deposit).

2.3 The Stråssa and Blanka (Fe-oxide) deposits

The Stråssa iron-oxide deposit consists mainly of quartz-magnetite and hematite ores with variable amounts of magnetite, hematite and skarn minerals (hornblende, diopside, epidote). The iron content varies between 25% and 45%. Sulphides (pyrite, chalcopyrite, and pyrrhotite) occur only locally within the iron ores at Stråssa, however, at Blanka, which is situated at the same stratigraphic horizon 1.7 km south of Stråssa, pyrite and chalcopyrite are more common and are observed mostly in the actinolite skarns (Koark, 1960). In addition, the iron ores from Blanka are less stratified than at Stråssa and intense deformation of the ore bodies resulted in discordant stocks, specularite-schists and large-scale millons plunging 50° to the SE (Bleeker and Carlon 1988).

3 Structural framework and 3D modelling

The Guldsmedshyttan syncline is the dominant regional structure, which is mostly NE-SW trending, steeply inclined, isocinal and doubly plunging and locally overturned. In the Lovias-Håkansboda mining area the syncline is refolded along its northern tip (hook-shape) and is dismembered by predominantly NE to N trending shear zones and faults (Fig. 2). The syncline’s western fold limb comprises besides the relatively low magnetic metavolcanics rocks and carbonates, highly magnetic quartz banded iron formations and iron skarn horizons. These iron ore bearing layers stand out on the magnetic anomaly map and are often well traceable over long distances. Due to the high resolution of a recent airborne
magnetic survey (100 meters flight line spacing at 60 meters ground clearance) a complex folding pattern has been identified (Fig. 2). Additional field observations (e.g. structural measurements and strain indicators in outcrops and thin-sections) reveal that a large number of macroscopic folds are doubly plunging (locally even sheet folds) and fold a pre-existing penetrative foliation (S1). The F2 folds are sheared and boudinaged vertically as well as elongated in an NE-SW direction parallel to the main trend of the Guldsmedshyttan syncline. The limbs are locally refolded (F3) by open to isoclinal S- or Z-folds along steeply to moderately south to southeast plunging fold axes. In terms of tectonic events, the overprint between F2 and F3 folding may be explained by a stage of reverse-shearing and vertical extrusion during D2 (NW-SE directed shortening) followed up by a wrenching phase (D3) of predominantly sub-horizontal shearing in both a sinistral and dextral sense during regional N-S directed shortening.

3.2 Using XRF-XRT drill core scanning to refine 3D deposit models

Additional constraints to the Lovisa (Zn-Pb-Ag) 3D deposit model were obtained from drill core scanning data combining XRF-XRT (Orexplore, in press). This innovative scanning technology was developed by the company Orexplore and detects both the rocks geochemical signature as well as its internal textures, structures and density through X-Ray Fluorescence (XRF) measurements and high-resolution 3D tomography from X-Ray Transmission (XRT). By modelling the material using minerals as building blocks and performing stoichiometry calculations, an assessment of the plausible mineral compositions can be made, as well as providing inferred values for non-measured elements. The development of a workflow integrating this advanced technology into exploration, including 3D geomodelling, is one of the two focus areas of the X-mine project, EU / Horizon 2020.

The real-time workflow (Fig. 4) starts in-mine where scanning can be performed at a speed in line with drilling and the preferred resolution. The obtained chemical, structural and textural data can then be analyzed, interpreted and exported into formats suitable for 3D geological modelling (Leapfrog, Move, Gocad etc.). After well correlation a detailed 3D model can be constructed serving as input for new targeting.

In the Lovisa mine, XRF-XRT scanning of drill core allowed for a more precise distinction between barren rock and the laminated zinc ore occurring within layers of typically less than a meter thick (Fig. 4).
4 Conclusions

The structural setting of the Lovisa-Håkansboda and the Stråssa-Blanka mineral system has been investigated utilizing geological field observations, magnetic airborne surveys and combined XRF-XRT scanning of drill core. The 3D structure of the ore deposits was extracted from mine-level maps and was then refined using high-resolution geochemical- and structural constraints derived from drill core scanning. In a regional context, the modelling results reveal a strong imprint of D2 (vertical shearing) and D3 (lateral shearing) on the 3D architecture of all the deposits in the studied area.

Acknowledgement

The X-mine project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730270. https://xmine.eu

References


Isotope geochemistry of groundwaters in mineral exploration – the tip of the iceberg

James Kidder, Matthew I. Leybourne, Alexandre Voinot, Daniel Layton-Matthews
Department of Geological Sciences, Queen’s University, Kingston, ON, Canada

Abstract. The dispersion of elements in groundwaters can produce large geochemical footprints and has been demonstrated to be a useful proxy for mineral exploration of deep and covered deposits, where traditional techniques are either ineffective or too expensive. However, in some cases, the transfer of chemical element from a deposit to groundwaters isn’t efficient enough to generate a significant anomaly. Due to the contrast between the conditions of formation of metal ore deposits and the dissolved load of background groundwaters, the use of isotopic tracers is a promising approach to trace the source of the proxy elements as well as the mechanisms of release. Although so-called traditional light stable isotopes (H, C, O, and S) were used in that context for decades, the application of non-traditional stable as well as radiogenic isotopes is relatively new. Metals such as Mo and Cu, typical in base metal deposits, exhibit contrasting behavior in groundwaters and we can use isotopic data of these elements as vectors to mineralization. Here case studies are presented demonstrating why the use of isotopic tools in geochemistry should be commonplace for explorers.

1 Introduction

The rate of discovery of new large copper deposits has slowed down, yet significant opportunity exists in many world-class belts, where post-mineral cover obscures bedrock and can potentially hide world-class deposits beyond the reach of traditional geochemical tools. Hydrogeochemistry has been proven an effective exploration technique at both the regional and local scale. Groundwater is an essential tool in the undercover toolbox because irrespective of cover thickness it provides reliable sample medium and can form laterally extensive anomalous halos far beyond the bounds of the primary mineralization. Information on the undercover environment is scarce. Therefore, the aim of applying stable isotopic systems to hydrogeochemistry is twofold: (1) decrease the cost of undercover exploration by increasing the footprint of deposits, resulting in the collection of fewer samples; and, (2) reduce the perceived risk of targeting using hydrogeochemistry.

The fractionation of metals and mobilization as dissolved solutes in groundwaters provides a potential form of direct detection in the secondary environment, as well as providing crucial contextual information indicating water sources, evidence of mixing, and water-sulfide interaction. In the decades since Harold Urey (White 2015) pioneered the use of light stable isotopes analytical and scientific advances have seen the list of elements available for analysis increase to include light elements such as Li and B, as well as heavy elements Ca, Cl, Cu, Fe, Hg, Mg, Mo, Se, Si, U, and Zn (White 2015). Ultimately any element with 2 or more isotopes or a radiogenic or cosmogenic isotope can be used for isotopic tracing (Kyser 2017).

2 Hydrogeochemistry in mineral exploration

The use of ground and surface water hydrogeochemistry as a viable form of direct detection in mineral exploration has long been promoted by researchers including Boyle et al. (1971); Cameron (1978); Miller et al. (1982); Goodfellow (1983); and Runnells (1984). Early work focused on sedimentary uranium deposits in Canada during the 1970s and early 1980s (Cowart and Osmond 1977; Deutscher et al. 1980; Dyck and Hood 1979; and Appleyard 1984), although refocusing in recent years has seen the majority of studies focus on base metal deposits (J. Ruijin et al. 1994; Leybourne et al. 2003; Phipps et al. 2004; Patrice de Caritat 2005; Leybourne et al. 2006).

Renewed interest in the technique followed the development and application of inductively coupled plasma mass spectrometry (ICP-MS), permitting the analysis of solutions to sub-ppt level detection limits (e.g., Stetzenbach et al. 1994; Hall et al. 1995). This was a fundamental breakthrough, as previously the low solubility and abundance of pathfinder elements in groundwaters restricted the widespread use of the technique (Runnells 1984). With analysis of water now routine at commercial labs, with relatively rapid sample turnaround, it is now viable to analysis for a broad suite of elements facilitating vastly improved geochemical modeling.

3 Isotopic geochemistry

3.1 Application of traditional stable isotopes

Of the light stable isotopes (O, H, C, S), perhaps the most applicable to hydrogeochemical mineral exploration is \( \delta^{34} \text{S}_{\text{VCDT}} \) and \( \delta^{18} \text{O}_{\text{VSMOW}} \) of dissolved sulfate. As sulfide minerals oxidize and release solutes into groundwaters, \( \text{SO}_4^{2-} \) can travel significant distances, and if the original isotopic composition and sulfur source of mineralization is known, provide a
reliable tracer. This signature will vary greatly across the range of deposit types, from a mantle-derived sulfur source ($\delta^{34}$S$_{VCDT}$ -0‰) to significantly heavier ratios in sedimentary hosted systems where the recycling of sulfur associated with evaporitic sequences is common (Cu zone -2 to +6‰, Capistrant et al. 2015).

In areas such as the Atacama Desert (Chile), multiple endmembers can be identified, such as seawater SO$_4$ (+21‰ Böttcher et al. 2007), SO$_4$ associated with evaporites (+5.6 to +21.3‰, Rech et al. 2003; Boscetti et al. 2007; and Risacher et al. 2011), and SO$_4$ associated with geothermal or fumarolic source ranges (-12.8 to +4.9, Rissmann et al. 2015; and Risacher et al. 2011). However, there are two potential complications to using sulfur isotopes. Firstly, potential fractionation related to oxidation or reduction by microbial communities which can produce wide fractionation ranges. Secondly, in lower temperature hydrothermal systems, disproportionation of sulfur can produce isotopically very heavy (>+2‰) $\delta^{34}$S$_{VCDT}$ associated with mineralization (Seal 2006).

3.2 Application of non-traditional stable isotopes

The application of isotopes of transition metals such as Cu, Mo, and Zn is a relatively new yet highly powerful tool in hydrogeochemistry. In the last two decades advances in MC-ICPMS analytical techniques has allowed for very precise measurements of transition metal isotopes with typical precision around ±/− 0.1 to 0.2‰. The significant contrast in the mobility of Cu and Mo across groundwater chemistries offers an opportunity to identify groundwater anomalies and trends with a wide sample spacing and vector back to mineralization. Generally, these elements are expected to undergo mass-dependent fractionation in low temperature systems through equilibrium or kinetic effects, which produces variation that can in return trace back to the source and composition of the various endmembers.

Cu isotopic ratios of sulfide endmembers have been published for a range of Cu deposits types, including porphyry (Palacios et al. 2010; Mathur et al. 2009; and Mathur et al. 2005) and sediment-hosted systems (Asael et al. 2009). Supergene processes are common following mobilization and dissolution of elements in porphyry and epithermal deposits and the production of 'blankets' of supergene minerals in the upper portions of the deposit. Supergene mineralization has been extensively studied (Rosario, Ujina, Chuquicamata, Escondida and El Salvador deposits, Mathur et al. 2009), which observe observing a wide fraction range for $\delta^{65}$Cu, ranging -16 to +12‰ (chalcoite, copper oxides, and iron oxides), compared to -1 to +1‰ for primary sulfides (chalcopyrite and bornite). In comparison primary sulfides at Spence range from +0.29 to +0.34‰, whereas supergene chalcocite shows heavier values ranging +3.91 to +3.95‰. Oxide minerals from Spence range from +1.28 to +1.37‰ for chrysocolla and -5.72 to -6.77‰ for atacamite (Palacios et al. 2010). Such differentiation allows for the delimitation of weathering profiles and provides a useful vectoring tool in leaching portions of the profile where Cu concentrations are low.

$\delta^{65}$Cu measurements from groundwater samples have been reported from Iberian Pyrite Belt (Spain) and mining district in Idaho, Montana and Colorado (Borrok et al. 2008), the Pebble porphyry deposit (Mathur et al. 2013), and groundwaters impacted by acid mine drainage from Colorado, USA (Kimball et al. 2009). In general, these studies demonstrate fractionation around hydrothermal mineral deposits potentially related to the oxidation of deposit sulfides, yielding $\delta^{65}$Cu compositions close to 0‰. However, there is potentially that the oxidation of sulfides with low or negative isotopic values may not generate a large enough fractionation to allow for the differentiation of sources in surface waters (Mathur et al. 2014). Perhaps the most relevant case study, from an exploration perspective, is the Pebble porphyry deposit (Alaska) where heavier $\delta^{65}$Cu compositions proximal to mineralization and lighter values distally suggest preferential fractionation of the lighter isotopes in groundwaters yielding heavier isotopic ratios proximal to mineralization and lighter values downstream (Mathur et al. 2013).

Mo isotopes, on the other hand, have seen very little use in an hydrogeochemical exploration context. Generally occurring as a trace element in many hydrothermal ore deposits, the weathering of the mineralization can yield to significantly high Mo concentrations into groundwaters. Further, neutral and oxyanion species of Mo are generally unreactive, resulting in relatively long residence times in seawater and significant mobility in groundwaters. However, little to no Mo fractionation has been shown to occur during solid dissolution in euxinic environments (Wang et al. 2015). A comprehensive review of Mo speciation, concentration in aqueous solution and isotopic compositions are provided by Smedley and Kinniburgh (2017). There is potential Mo fractionation during adsorption on the surface of clay minerals during transport in water in oxic environments (Kendall 2017), but given that most Mo is dissolved in solution, adsorption to particles if of minor importance.

Thiomolybdate adsorption, typically on ferromanganese, at the bottom of the ocean can produce one of the largest isotopic fractionation range observed in Mo, with preferential adsorption of the lighter isotopes absorbed yielding an isotopically enriched signature (McManus et al. 2002; Hoefs 2009). In oxidized surface waters similar fractionation has been observed with the adsorption of molybdate (MoO$_4^{2-}$) on to Fe oxides and oxyhydroxides (Kendall 2017). Mine waters from the Antamina deposit (Peru) display variation in $\delta^{68}$Mo, from -0.55 to 0.61‰ for solid phase Mo minerals, to -0.06 to 2.07‰ downflow (Skierszkan et al. 2016), with the isotopic enrichment attributed to secondary adsorptive processes. Similar patterns have been observed in rivers and estuary waters (Archer and Vance 2008; Pearce et al. 2009;
We suggest collecting isotopic samples as standard stable isotopic systems can de-risk covered exploration. Although expensive, non-traditional groundwater should be a vital tool for explorers in covered terrains. We suggest trace element and isotope geochemistry of provide context and confidence in targeting. Therefore, we propose the dissolution and complexing of sulfate to produce isotopically heavy Mo fractionations. Smedley and Kinniburgh (2017) provide a range of fraction for δ98MoSRM-3134 with mine ore ranging -0.6 to 1.2‰ and mine drainage typically isotopically enriched ranging -0.2 to 2.2‰. Microbial effects on Mo fractionation have also been observed (Wasylenki et al. 2008; Zerkle et al. 2011) in soils, producing up to 1‰ variation in δ98Mo, as well as fractionation during adsorption onto organic matter (Siebert et al. 2015).

**Figure 1.** Conceptual model for trace and isotope geochemical footprint in groundwaters proximal and down-flow of mineral deposits.

**4 Conceptual model**

Physiochemical controls (pH, Eh, EC) govern hydrogeochemical solute speciation and transport, however we expect under acidic conditions a proximal anomaly of high concentration cations (Cd, Cu, Ni, and Zn). Under normal groundwater conditions in undisturbed deposits, Fe speciates as FeOH₃ and precipitated (Figure 1). Distally the hydrogeochemical footprint is dominated by oxyanion forming elements (As, Mo, Se, Sb, SO₄) and cations of low ionic potential (Sr, Cs). Isotopically we expect contrasting signatures. Proximal fractionation of Cu sulfides produces a heavier signature, as the bonds of lighter isotopes preferentially break and are carried further in solutions. Mo has no observable fractionation during sulfide dissolution, whereas transported Mo signatures should become increasingly heavier as preferential absorption of the lighter isotope takes place.

**5 Implications**

Layering hydrogeochemical and isotopic data allows for the definitive fingerprinting of mineralization in groundwater. Although expensive, non-traditional stable isotopic systems can de-risk covered exploration. We suggest collecting isotopic samples as standard and analyzing sub-sets of samples around anomalies to provide context and confidence in targeting. Therefore, we suggest trace element and isotope geochemistry of groundwaters should be a vital tool for explorers in covered terrains.

**Acknowledgments**

Thanks to April Vuletich, Evelyne Leduc and Donald Chipley of Queen’s Facility for Isotope Research (QFIR). Special thanks for First Quantum Minerals for supporting the project, providing samples and data.

**References**


Sonic drilling coupled with on-line-on-mine-analyses: field tests at the Villeveyrac bauxite deposit (Southern France)

Beate Orberger
GEOPS, Université Paris Saclay, Université Paris Sud, Bât 504, 91405 Orsay Cedex, France
CATURA Geoprojects, 2 rue Marie Davy, 75014 Paris, France

Monique Le Guen, Thanh Bui, Aïsha Kanzari, Céline Rodriguez, Antoine Prudhomme
ERAMET, 1 Avenue Albert Einstein, 78190 Trappes

Harm Nolte, Thijs Teerlink, Peter Koert,
Royal Eijkelkamp, Giesbeek, Netherlands

Henry Pillière, Thoma Lefevre, Anas El Mendili
Thermofisher Scientific, INEL, Artenay, France

Sylvain Delchini
BRGM, France

Saulius Grazulis, Algirdas Grybauskas, Andrius Merkys, Antanas Vaitkus
ITB, Vilnius University, Lithuania

Evgeny Borovin, Luca Lutterotti
Universitaet Trento, Trento, Italy

Emilie Marchand
Ecole de Mine Arles – Université Montpellier, France

Abstract. The field tests of the SOLSA expert system at the bauxite mine (SODICAPEI-VICAT, South France, 15th to 30th September 2018) aimed to evaluate the workflow and individual instrumental parameters, mechanics of the drill rig, the core scanner (RGB, profilometer, VNIR-SWIR (final with XRF)), the benchtop system XRD-XRF, data architecture, data transfer, software and interaction with the (open-) databases. The focus was on iron oxy-hydroxide and clay mineral rich lithologies, that is also present in Ni-laterite profiles. In total 65 m were drilled at two boreholes with a 90-100% core recovery on 52 m (80%). Core scanning recorded 40m/10h. The results on the undestroyed core surface are representative of the core. The XRD-XRF benchtop system is fast (5-7 min/sample) for validating and quantifying analyses on the regions of interest, defined by the core scanner. It will be installed at the drill site for immediate environmental analyses. Data connection was successful from drill to core-scanner. The hyperspectral database is performant for the lithologies present at this bauxite deposits. The sample database is operational based on international standards. Data superposition and fusion, and GUls are under development. (https://youtu.be/mUIs1b5xFZE).

1 Introduction

The SOLSA expert system is developed in the frame of the EU H2020 project 689868 (2/2016-1/2020 9,8 M€, www.solsa-mining.eu). X-ray detector developments are performed in the PAIRED-X (EIT-KIC) project (http://nanoair.dii.unin.it:8080/paired-x/). The expert system is composed of: (1) a sonic drill rig and a wire-line-system (2) a core scanner (RGB camera, profilometer, X-Ray fluorescence-spectrometer (XRF), Visible-Near Infrared (VNIR) and Short-Wave Infrared (SWIR) hyperspectral cameras) and (3) a benchtop system (X-Ray Diffraction (XRD)-XRF-Raman spectroscopy). SOLSA develops and extends existing open databases. Data from drill-rig and mineralogical and chemical data from the two sensor systems will be coupled to enhance the information at the exploration stage. The expert system will drill and analyze 80 m sonic drilled core per day, define regions of interests for the mining companies in real time through dedicated software and interaction with special designed databases. The prototype is designed for nickel laterites (SLN Mines, in New Caledonia). The final goal is to speed up exploration and optimize processing.

As bauxites have similar characteristics as Ni-laterites (grain size, material contrasts, clay mineralogy, iron- (aluminum) oxy hydroxides), the tests were performed at a bauxite mine in France, allowing short travel times and rapid material implementation. SOLSA was tested under field conditions in the on-line-on-mine-real-time workflow with variable drill bits, monitoring while drilling, the split liner prototype, different types of core-catchers. The different instruments of the core scanner and the XRD-XRF system were evaluated. The data architecture, data transfer from drill to core scanner, the software and interaction with the databases was established. The focus was on the (swelling-) clay mineral-rich marls, which resemble lithologies within in nickel laterites.
2 Geological characteristics

The bauxite deposit at Villeveyrac belongs to a synclinorium dipping SW. Bauxite is present to up to 800 m depth. It is a Karst-type bauxite, reaching thicknesses of 2 and 8 m (Fig. 1). The Karst is composed of dolomitized limestone. Bauxite is overlain by multicolored marls with variable iron oxy hydroxide contents and carbonate concretions with sandstone intercalations and limestone reaching up 700 m thickness in the center of the basin.

Figure 1. Schematic lithological profile at the bauxite deposit (Villeveyrac, France) (modified from Giroud et al. 2009).

3 Field test preparation

Drilling was done in collaboration with SODICAPEI-VICAT. Physical and mechanical rock parameters known from previous drilling were used for drill tool choice and definition. For calibration of the individual instruments of the core scanner and the XRD-XRF benchtop instrument, major lithologies were sampled and analyzed by laboratory XRF and XRD, portable XRF and pIR prior to field tests. A hyperspectral mineralogical database was established for the major minerals (quartz, rutile, illite, kaolinite, calcite, dolomite, montmorillonite, hematite, goethite, diaspore, boehmite; Prudhomme 2017, 2018). The SOLSA core scanner was tested on previously drilled core samples at the Thermofisher R&D laboratory (Artenay, France) to recognize the textures and minerals during the SOLSA field tests.

4 SOLSA Drill

Drilling was performed on two bore holes at the eastern boarder of the lac d’Olivet (Fig. 2). Two boreholes at about 200 m distance were drilled at 30 m and 35 m depths. At the first locality, only variegated marls were sampled. At the second location, 1-3 m thick sandstone is intercalated in the marls. The marls contain variable contents of iron oxy hydroxides and carbonate micro concretions (Fig. 3). Drill fluids (water, polymer, air) were tested in variable proportions. Spherical and ballistic drill bits of different geometries were tested. Sonic wireline and conventional sonic drilling was used. The SOLSA split liner prototype was tested, but revealed not being adapted to the clay-rich materials.

Figure 2. A. SOLSA Drill at the bauxite mine (SODICAPEI), B. variegated marls.

At the two borehole locations, 80% of the core gave 90-110 % core recovery. The clay-rich marls gave recovery rates of 101-110 %, related to the swelling clay mineral presence and interstitial water. This might be related to decompression and/or drill fluid addition. The drill core surface is covered by mud cakes (2-5 mm thick).

5 SOLSA Core Scanner

For the tests, The SOLSA core scanner was in a rented minivan to evaluate “in-field performance” at ~ 30 m distance from the SOLSA Drill (Fig. 4). The SOLSA software consists of data acquisition, data registration and data processing parts. In order to produce mineralogical maps, we implemented sparse unmixing techniques with the incorporation of spatial information using superpixel algorithms. The major mineralogy defined by laboratory studies and portable IR (Prudhomme, 2018), and by measurements performed by SOLSA core scanner at the Thermofisher R&D lab, could be confirmed under field conditions by the SOLSA core scanner (Fig. 5, 6). However, unlike the punctual analyses of the pIR, the core scanner and SOLSA software allows producing a mineralogical map of the undestroyed drill core surface.

Figure 3. A. split liner showing bursting of rubber band, a result of swelling pressure due to clay minerals in marls, B. Calcite concretion-hosting marls.
A composite drill core was recorded and a mineralogical map was produced based on the SOLSA software using SWIR hyperspectral data (Fig. 5). During the tests, 1 m of core was scanned in 15 minutes (40 m/10 h shift). Data interpretation was not yet in real time, as the data fusion software is still under development.

6 SOLSA Benchtop combined XRD-XRF-Raman spectroscopy

The benchtop system is designed for analyzing the samples previously defined as regions of interests. For this SOLSA test, the EQUINOX XRD-XRF (Thermofisher) was used in a minivan. For this instrument, a special X-ray detector is developed in the frame of the PAIRED-X projects (KIC-EIT). The Raman spectrometer was not yet added to the XRD-XRF at the time of the field tests. The software XRF-XRD data interpretation has been developed on the basis of the MAUD open software for testing XRD-XRF combined analysis and calibration of clay structure. Software for Raman data acquisition and automatic analysis is being developed and integrated into the combined XRD-XRF software to make an ultimate software for combined XRD-XRF and Raman spectroscopy for SOLSA benchtop system. While the core scanner analyses drill core surfaces with a limited accuracy due to the selected instrumental configuration to achieve fast scanning, the combined XRD-XRF analyses will be performed on sample powders. After crushing and sieving, the < 200 µm fraction is milled in a micronizer (Fig. 6). During the field tests, the sample preparation protocol was established to reach a homogenous sample powder of ~10 µm at ~ 3-5 min milling time. The micronizer, operating beside the core scanner during the field tests, generated vibrations which impacted the results of the core scanner. In total 18 samples from drill cores, drill mud and stock piles were analyzed (5-7min/sample) giving satisfactory results for the mineralogy. Comparative analyses of the material from the inner core part and outer mud cake gave identical results for the mineralogy. The core scanner analyses are thus reliable. Figure 7 shows 3 examples of bauxites (red-white and an Fe oxyhydroxide-rich pisolite), analyzed by the XRD-XRF system.

7 SOLSA databases

To provide on-line accessibility to the confidential generated data and to all open data, 4 SOLSA databases have been built: (1) The Raman Open Database (ROD) to store Raman spectra of pure mineral phases. (2) The Spectral Open Database (SOD), to store separate spectra (extracted from hyperspectral image) of pure mineral phases. (3) The Hyperspectral Open Database (HOD) to store hyperspectral images, which are 2D
images (each pixel is a spectrum). (4) The Open Sample Database (OSD) relies on international standards (ISO14688-1/14689:2017). This architecture is operational for entering petrographical and mineralogical descriptions, for its use by mining companies. All SOLSA samples have a unique persistent identifier. The SOLSA sample database is implemented as a RESTful layer on top of a standard SQL database (currently, a MySQL back-end is used); the RESTful layer, implemented as a set of Perl CGI scripts, provides access to the data over the HTTPS protocol.

**Figure 7.** A. Diffractograms of red (light blue) and white (dark blue) bauxite and pisolite (red). B. XRF spectra of the same sample.

## 8 Discussion and Conclusions

During these real mine conditions, many parameters were tested on the expert system. Two weeks were too short to obtain sufficient data for statistical validation. For drilling, more precise geotechnical data are needed. A systematical drilling with small spatial off-sets is required. A spare wire line system should be available in the field to ensure continuous core flow. The split liner burst at high amounts of clay minerals and the presence of water. It thus cannot be used in wet marls. While swelling clay minerals were detected (Fig. 6), kaolinite and illite (Prudhomme, 2018), were not found by SWIR. Swelling clay minerals, but also interstitial water may have induced the increase of ~10 vol.% expansion. Phase quantification by coupled XRF-XRD-Raman is thus important. During the field tests, the core scanner reached ~ 40 m/10h shift (50 % of the target: 70-80m/10h shift drill+scan). During the field tests, data superposition and data fusion software were adapted. The minivan used for the tests was a rented car, temporary equipped for the field tests. The definite SOLSA minivan will be equipped with anti-vibration technologies to avoid the effect of the drill rig and micronizer, and to achieve reliable data superposition and micronizer from the individual instruments. It was decided to install the benchtop XRF-XRD-(±Raman) in the minivan, as useful environmental data can be acquired simultaneously to drilling (e.g. drill mud, atmospheric dust). For OSD database, entry tests are ongoing to optimize interactivity and interconnectivity with the Crystallographic (COD), Hyperspectral (HOD) and Raman (ROD) Open databases (Grazulis et al. 2009, 2018; Bui et al. 2018; El Mendili et al. in press). Graphical user interfaces (GUI) are under development to facilitate operator’s work. The final system will have CLOUD data and interacting software to reach almost real-time decision making. The overall workflow was tested in the field and for the first time, the data transfer from SOLSA drill to the core scanner operated via a RFTID system on split liners. The data transfer was already performed to the core scanner system. Drill specific data which will allow conclusions on physical and mechanical parameters of the rocks will be available in future. Our results are evaluated and the next drilling test is scheduled for the beginning of April 2019 for 2 weeks at the bauxite mine. This time we will focus on the interface between marls and bauxite. The SOLSA test is on schedule and will be performed in October-November 2019 at the SLN Nickel mine in New Caledonia.

**Acknowledgements**

This project is funded by the EU H2020 project 689868 and PAIRED-X (KIC-EIT). All logistics for the field tests were provided by the bauxite mine owner SODECAPEI-VICAT. We thank all staff for help and the warm welcome.

**References**


Prudhomme, A. 2018. Characterization of a bauxite core using several field and laboratory methods. MSc Université Paris Sud – ERAMET, Eramet (SOLSA project) project, 21p.
Application of non-destructive, micro-focus X-ray computed tomographic analyses on gold occurrence and distribution in drill-core samples.

Thomas Stapley, Gillian R. Drennan, Asinne Tshibubudze, Glen T. Nwaila  
School of Geosciences, University of the Witwatersrand, South Africa

Lunga C. Bam  
South African Nuclear Energy Corporation (Necsa)

Jason D. Kirk  
Department of Geosciences, University of Arizona, USA

Abstract. Micro-focus X-ray computed tomography (μXCT) is a powerful, non-destructive technique able to produce thousands of virtual cut-through sections in a matter of minutes, closely representing data obtained through conventional, time-consuming and volumetrically limiting petrographic and SEM-based methods. μXCT as an exploration tool is currently under-utilised, partially due to the method having yet to find any adequate application in the mining industry. In this study, mineral identification through μXCT was accomplished by reconstructing grey-value attenuation coefficients into 2D grey-scale sections. By optimising the grey-value ranges for mineral identification, it was possible to fine-tune the software to pick up gold particles that were otherwise being misinterpreted as pyrite. Results from this study show that gold particles were easily identified even at a relatively “low” scanning resolution of 25 μm as gold particles occurs as > 50 μm (up to 1.5 mm in some cases). Challenges encountered during this study were related to resolution limitations, including what is termed the partial volume effect. This resulted in some fine-grained gold particles (< 25 μm) not being picked up during post-reconstruction analyses.

1 Introduction

X-ray computed tomography is a well-established and highly utilised technique in the medical industry due to its non-destructive nature (Sun et al. 2012) However, literature detailing the use and applicability of μXCT in the mineral exploration industry is relatively sparse. The application of μXCT as a method in geosciences has been well established by researchers since the early 2000’s (Carlson et al. 2000; Ketcham and Carlson 2001; Desrues et al. 2006). In more recent years, studies using the μXCT methodologies on specific ore-assemblages have been conducted, including iron ores (Bam et al. 2019) and nickel-sulphide ores (Becker et al. 2016). One in-depth study detailing the use of μXCT as an investigative method on gold mineralisation has been conducted (Dominy et al. 2011). Overall the use of μXCT as an exploration tool has still yet to gain traction in the mining industry. The aim of this research is therefore to understand how applicable such a technique can be in order to better understand gold deportment, textural characteristics, mineral associations and assemblages – which can contribute to the overall understanding of the ore-deposit at an exploration level. Ultimately, the goal is to highlight the benefits of using this non-destructive, time-efficient approach over more typical, destructive investigative methods such as optical microscopy (OM) and scanning electron microscope (SEM) petrographic analyses.

Samples have been sourced from the Gbongogo Prospect, an intrusive-hosted hydrothermal gold deposit, located in northern Côte d’Ivoire, West Africa (Fig. 1).

Figure 1. Regional geological map of the West African Craton showing the general deposit location in relation to known gold deposits with resources >1 Moz (modified after Milesi et al. 2004).

2 Micro-focus X-ray computed tomography

X-ray computed tomography is a non-destructive 3D characterisation technique allowing the visualisation of internal features such as mineralogy, micro-structures and morphology of solid samples and provides digital information on their 3D geometries (Nwaila 2014). This form of information is otherwise unobtainable using the more traditional OM and SEM-based techniques, which can only provide 2D visualisations and which require sample destruction when making thin-sections and...
polished ore-mounts prior to analysis.

μXCT records the linear X-ray attenuation coefficients of different minerals as the X-ray beam passes through the sample (Nwaila 2014). These attenuation values are primarily determined by the density and atomic numbers of substances through which the X-rays pass (Ketcham and Carlson 2001). A flat-panel detector is then used to record the attenuation values of the various minerals in an X-Y-Z coordinate system.

3 Samples and methods

3.1 Core-logging and sample selection

Core-logging was conducted over 3 weeks, and six quartered, HQ-sized (3–4 cm-diameter) diamond drill-core samples were selected from mineralised zones that contained appreciable gold-grades, as well as representative gold-grade variations as determined by fire-assay analyses. These six samples consisted of low-grade (1.3 g/t) to very-high grade (81 g/t) samples in order to get an accurate representation of the various mineralisation styles present in this deposit.

3.2 μXCT sample scanning and setup

Samples were scanned using a Nikon XTH 225L microfocus X-ray computed tomography instrument, located at the MIXRAD (Micro-Focus X-ray Radiography and Tomography) laboratory at the South African Nuclear Energy Corporation (Necsa). Scanning parameters were set to 130 keV and 63 μA in order to optimise X-ray penetration through the samples for better image quality. The diamond drill-core samples, with a height of ~25 cm, were securely mounted in a polystyrene mould in order to avoid any movement during the scanning process. Each core sample (10–30 cm) was segmented into 3 cm intervals in order to optimise the resolution (25 μm) of the scans. Automated scanning was used for each 3 cm interval in order to fast-track the scanning process, thus increasing the number of samples being scanned in a single day. This also allowed the scanning to continue over night without the involvement of an instrument scientist, resulting in a total of 66 scans being conducted within a four-day period. However, the actual scanning time was 36.3 hours.

The securely mounted specimens were placed on a rotating stage that allowed the samples to be scanned in 360°. One thousand projection images were then obtained in a 360° rotation process for each scan with a 2-sec exposure time for each image, creating ~2000 sectional 2D slices at a thickness of 25 μm. The resulting scans were then reconstructed using a Nikon CTPro software, and further analysed using VGStudio Max V2.2 (Volume Graphics, Heidelberg, Germany).

4 Results

4.1 Drill-core mineralogy and petrography

Drill-core logging highlighted that gold-mineralisation occurs in association with a distinct generation of quartz-tourmaline veining, which commonly have an albite-rich, pinkish-coloured hydrothermal alteration zone (Fig. 2). Quartz-tourmaline veins cross-cut the tonalitic host rock (Fig. 2. c, d), and gold has been observed occurring as inclusions within pyrite, or else as free-gold particles, within the host veins and alteration zone (Fig. 2. a, b).

![Figure 2. Example of the quartered core analysed in this study, showing the G1 quartz vein (highlighted in dashed-white lines), the G2 quartz-tourmaline vein (black) and the associated, asymmetric alteration zone (pink). a, b. Reflected-light photomicrographs of the gold occurrence and association with pyrite (Microsearch 2016). c. PPL photomicrograph of the tonalite (quartz-plagioclase) host-rock. d. XPL photomicrograph of the tonalite host-rock.](image)

4.2 Grey-value mineral discrimination and 2D image reconstruction

Grey-values are assigned to minerals by the attenuation responses received during the scanning process, allowing the reconstruction software to convert these values into visible grey-scales. Once reconstructed, by manipulating the brightness and contrast of the grey-scale images, it is possible to distinguish the mineralogical variations (Fig. 3. a). The host silicates (tourmaline, quartz and plagioclase), show the darkest grey-values, and the brighter the grey-value becomes, the higher the density is of that material, where gold (19.32 g/cm³) appears bright white in comparison to light-grey pyrite (5.01 g/cm³) (Fig. 3. a). Once grey-value ranges have been uniquely defined per sample for the various minerals, it is possible to isolate these ranges and assign false-colour signatures to each of the minerals (Fig. 3. b). During reconstruction of these scans, multiple coarse gold particles were identified, approximately 20–30 per scan (~0.1–0.3 mm in length), including numerous very coarse particles around 0.6 x 0.1 mm in size, and a few up to 2.0 x 1.0 mm in size.
Grey-values used to create 2D grey-scale images are not unique per mineral (although the ratios between the various minerals are), and therefore each scan needed to be calibrated to a benchmark sample in order to create a uniform grey-value range (per mineral) for all samples. By creating a histogram of the grey-values vs counts throughout the entire sample, it is possible to determine whether the calibrated grey-value ranges correspond between various sample sets (Fig. 4). In the case of the two test samples (A4 and A6), the calibration was successful as the error-range fell between 1–3% of each other. The variation in peak counts for pyrite (yellow) is due to pyrite particles being finer-grained in A6 than in A4, which increased grey-value “blending” with the lower grey-value signature of the surrounding silicates (blue).

4.3 3D image reconstruction

3D representations of the sample were created by stitching the 2000 serial 2D sections together, thereby creating a 3D volume (Fig. 5. a, b). As can be seen, the technique successfully managed to distinguish between the silicates (blue), pyrite (yellow) and gold (red). One useful aspect of reconstructing the data into 3D is that it allows one to conduct defect analyses on the particles of the various minerals (e.g. size, volume, morphology, voids), which in the case of the gold is useful to determine how much gold occurs in the overall sample volume, and where it is found preferentially occurring. The 3rd style of mineralisation identified occurs as gold veinlets cross-cutting the pyrite (Fig. 5. Bottom).

5 Discussion

Preliminary results from this study confirm that the μXCT methodology applied to gold location and distribution has been successful, picking up a significant amount of gold particles and their various styles of mineralisation - even at 25 μm resolution. The resolution was set relatively "low" in order to be able to capture the entire width of the sample during scanning.

These results highlight an alternative whole-sample analytical technique, emphasising the success of a method that is readily available to the industry, yet which is not being fully utilised. The aim was to prove that this technique can be a time-efficient means of gaining a volumetrically representative understanding and visualisation of the gold occurrence and distribution throughout the samples. An example attaining to the effectiveness that this study has managed to achieve at this preliminary stage can be demonstrated. A comprehensive, traditional OM study conducted by Microsearch in 2016, using 44 polished ore-mounts and 10 thin-sections from ten mineralised zones of the same deposit, concluded that all gold particles are <0.000625 mm² (0.025 x 0.025 mm) in areal extent. In comparison, preliminary results from this study are showing that hundreds of the gold particles are falling within 0.02–0.06 mm² in areal extent, with two grains thus far reaching up to ± 2 mm² (between 2–4 orders of magnitude larger than that of the OM study). This highlights a large discrepancy between the two analytical techniques, which could introduce complications during gold-extraction. Therefore, conducting a thorough μXCT study over a few representative samples can help improve any geometallurgical studies for optimised gold extraction.

One of the major limiting factors currently in μXCT scanning is related to resolution limiting parameters. A number of factors may play a role in limiting the resolution of the images obtained, mostly related to the overall density of the samples (and the contrast between the minerals under investigation), the size of the samples...
being scanned, and the degree of penetration achieved through the sample. In the case of the samples used in this study, the limiting factor on the resolution was sample size. The fact that the instrument is picking up this amount of gold already, suggests that a significant amount of gold should exist between the 1–25 μm range as well. Dominy et al. (2011) emphasised similar concerns, where it was discussed that any gold particles with dimensions smaller than that of the resolution used, will not be accounted for in any post-reconstruction analyses.

The Partial Volume Effect is a common artefact encountered during the μXCT reconstruction stage, as the transition, or grey value cut-off, between a two-component system with a resultant “blended” grey value (Bam et al. 2019). By incorrectly determining the blended percentages of two mineral grey-values, it is possible to “lose data”, and therefore the volume of the mineral under investigation, during analysis (Fig. 6).

6 Conclusion

μXCT scanning has proven to be a successful analytical technique for the locating of gold particles within these core samples. Even at a relatively low resolution (25 μm), scanning was able to detect a significant amount of gold in each of the samples ranging from 1.3 g/t to 81 g/t. Over 132 000 2D serial sections could be produced in less than four days which makes this method one of the most powerful available for whole-sample ore-distribution and defect analysis. This method in no-way discredits that of any SEM/petrographic methods. However, it provides an alternative, time-efficient and statistically more representative analytical approach which, when combined with the traditional methods, allows for a much more wholly-encompassing story to be understood. This study aims to showcase a technology that is currently available in the market today, without any major modifications, and determine the usefulness of this technique (including any inherent limitations) to the current exploration industry.

Follow-up work is currently ongoing, which is testing the effect that increasing the resolution (and thus information able to be extracted) will have on the results obtained - thereby quantifying any under-and-over-estimated/measured data at these lower resolution scanning phases.

Acknowledgements

This project has been made possible through funding from DST-CIMER, the Jim and Gladys Taylor Trust and Amira P934B (WAXI). Thanks goes to the Necsa Team for their assistance and support in this project. Samples were supplied, and logistical costs covered, by the former Randgold Resources Ltd, now Barrick Gold Corporation.

References

Microsearch (2016) Internal gold-deportment report commissioned by Randgold Resources Ltd.
Nwaila G (2014) Application of HPGR and X-Ray CT to investigate the potential of Witwatersrand gold ore for heap leaching: A process mineralogy approach. MSc dissertation, UCT.
Abstract. Increases in energy demands have compelled economic geology exploration into more arduous hydrocarbon targets (unconventional, deep or ultra-deep) or mineral deposits (more remote locations, deep cover). These ever-increasing difficulties in exploration require the development of new advancements in the science and economics of exploration techniques. Here we describe the development of a method to process, separate and analyze a single sample aliquot for Re-Os and Pb isotopes, PGEs and trace elements from single aliquots of aeological materials of economic interest. Obtaining geochronological and geochemical data from the same sample dissolution aliquot averts potential problems and complications inherent with the comparison of geochemical data through inhomogeneity caused by the variable effectiveness between dissolutions of different sample aliquots. Furthermore, the maximization of information that can be obtained from one sample aliquot lowers sample processing costs and time as well as affords the ability for this type of information to be determined from limited sample volumes (e.g. deep and ultra-deep petroleum systems, gold, mineral systems with low sulphide abundances, meteorite material).

1 Introduction

Instrument technologies and capabilities have provided the means to determine highly siderophile elements (HSEs) routinely since the invention of inductively coupled plasma mass spectrometry (ICP-MS) with great strides forward through determination by isotope dilution via ICP-MS at ppt levels (e.g. Pearson and Woodland, 2000). Ever expanding and focusing advances in sample preparation and element species separation techniques further compliment the continued improvements in analytical capabilities of the instruments. HSEs (Re, Au, Ir, Os, Ru, Rh, Pt and Pd) are in low abundances within the silicate earth, primarily being sequestered within cores of planets and planetary bodies (Walker, 2016). Thus, HSEs have been recognized as important tracers for a breadth of terrestrial and extraterrestrial petrogenetic processes, as well as more economical uses such as petroleum and mineral system evolution and fingerprinting that can further complement more commonly used lithophile isotope systems (Ishikawa et al. 2014).

The Re-Os system displays good affinities to organic matters because both elements are redox-sensitive and organophilic and more often enriched in related source rocks, tar sands, the crude oil itself and bitumen, providing a method of directly dating petroleum systems (Selby et al. 2007). The ability to directly date the formation, migration & entrapment of hydrocarbons within petroleum systems using the Re-Os system has limited many of the initial difficulties and uncertainties around ages from minerals of host rocks that can only provide indirect ages. However, one remaining difficulty is determining what petroleum system process the Re-Os isochron age is related to or if it is a regression line caused by mixing of hydrocarbons from multiple sources. The addition of other HSEs and trace element information to the Re-Os isotopic chronology can begin to untangle what that age truly represents by fingerprinting the oil-oil and oil-source rock correlations.

Much as with utilizing the Re-Os chronometer to the petroleum system, the direct dating of mineralization can be accomplished as well. Direct dating of sulphides can constrain mineralization age, and when combined with the ages of other mineral phases within the system and/or the surrounding rock (e.g. volcanics within a volcanic-hosted massive sulphide system) as well as potentially Pb isotope model ages and source information (e.g. Huston et al. 2014) 4D evolutionary models can begin to be constructed (Barrote et al. 2019). Furthermore, combining the age information with PGE and trace element patterns to finger different mineralization events can begin to enhanced exploration techniques for new, especially covered, mineral deposits.

To further push the science of exploration, coupling a specific fingerprint for certain mineralization events or locations with the age of mineralization greatly expands the ability of exploration particularly to undercover or deep targets. Therefore, the intention of developing a workflow to obtain Re-Os and Pb isotopes, PGE concentrations and trace element analytical information from one sample aliquot is to better understanding trace elements and HSE patterns coupled with the age. This information can then potentially pioneer not just forensic provenance studies of sulphides and gold but also constrain the source of these of interest minerals in ore deposits (i.e. a crust or mantle source for gold mineralization; and/or seawater for seafloor sulfides).

2 Methodology

Still within the early stages of development, the objective is to further the methodology pioneered by Pearson and Woodland (2000) by creating a workflow that enables Re-Os geochronology, Os isotopic ratios, PGE abundances and trace element patterns to be determined from one sample aliquot (Figure 1). The samples are initially
processed from a modified isotope dilution method via Carius tube digestion (or, potentially HPA). Once digested, the Os is extracted from the dissolved sample solution by the solvent extraction method to be analyzed by the negative thermal ionization mass spectrometry (N-TIMS) at the John de Laeter Centre (JdLC) for Isotope Research at Curtin University. The aqua regia or chromium oxide solution is then evaporated and re-dissolved in a set amount of the desired acid for anion exchange chromatography to separate the Re and PGEs from the sample matrix. However, before the column chemistry is conducted, an aliquot is removed (making note of the exact amount removed) and set aside for trace element analyses. Analyses of the remaining HSEs and trace elements are conducted using the high resolution ICPMS method, at the JdLC.

**Figure 1. Diagram displaying the workflow of obtaining with the optional addition of Pb isotopes for selected minerals.**

### 3 Prospective Applications

The intention of this methodology is two-fold: 1) to couple direct dating geochronological data of petroleum or mineral systems with forensic fingerprinting of types and sources using PGEs and trace element patterns; and 2) to provide a more cost effective and minimal sample consumption methodology for exploration.

The methodology has been implemented thus far to pyrites, gold, crude oil, and source rocks (mudstones – black shales) through two streams of digestion in Carius tubes, either reverse aqua regia (gold, crude oil, sulphides) or a chromium oxide – sulfuric acid solution (black shales, mudstones). These two-dissolution methods provide an effective attack of these materials for Re-Os and PGEs in a wide range of geological materials of economic interest without the need for HF (e.g. Ishikawa et al. 2014).

### 3.1 Petroleum System Applications

Re-Os isotope analyses of crude oil has been around for some time now, however, as discussed above, the exact meaning of the obtained Re-Os isochron age can still be difficult or even problematic to determine at times (e.g. Selby et al. 2007; Liu et al. 2019). The results from utilizing the method on two petroleum systems thus far display a wide range of HSE concentration from one system to the next (mid-ppb to high ppt levels). These results corroborate previous studies that indicate the ability to use these differences of HSEs as an oil to source fingerprinting tool (Finlay et al. 2012). Trace element analyses are able to be robustly obtained from the completely dissolved asphaltene separates providing fingerprinting trace element patterns for the crude oil system that can then be compared to potential source rock trace element pattern information separately obtained untangling not only the significance of the isochron age but also providing insight into the evolution of the system as a whole when a multidisciplinary action is taken.

### 3.2 Sulphide Mineralization Applications

This method is currently being implemented on sulphides from ore deposits located in Western Australia that have already been used for separate Re-Os isotope and trace element studies (Barrote et al. 2019). This path is being chosen to compare the results from the workflow model presented here to the more traditional methods used for these types of analyses separately.

Laser ablation-ICPMS trace element profiles and some in-situ HSE results of pyrites have been obtained from the same samples that were analyzed utilizing the presented workflow. These results as a first order investigation are being used to compare the trace element results from the in-situ method vs whole grain dissolution. Co/Ni ratios obtained using the sample digestion method are primarily greater than 1 (10 out of 14 analyses) whereas in situ Co/Ni ratios are less than one (typically in the range of around .1). However, the Zn/Ni and Cu/Ni ratios from the two methods provided similar results (all ratios from both methods are less than 1). Is this exclusively due to the digestion method attacking inclusion or black shale phases not fully removed or hidden within the picked grains or do the similarity of the Zn/Ni and Cu/Ni ratios suggest a heterogeneous distribution of the Co contents but a more homogeneous distribution of other elements such as Zn and Cu of these pyrites? As laser profiles were conducted along the pyrite grains the samples appear to be chemically constant when the average of the traverse is calculated. The Co rather is likely fractionated (due to the organic material, Moore et al. 2018) between the pyrite and another phase (in this instance the surrounding black shale) whereas the Zn and Cu are not. This would suggest that the whole grain dissolution method does indeed dissolve other phases then uniquely the pyrite and must be considered when interpreting such results.

Furthermore, Re-Os isotopic analyses of pyrite from the same sample analyzed via the two sample processing methods are also being compared. This approach is being taken due to a lack of pyrite standard material for these systems, indicating that appropriate sulphide standards need to be developed and tested.

### 3.3 Gold Exploration Applications

Pushing the method into new exploration frontiers, pilot project work has been conducted on utilizing this method with native gold. The objective is to obtain a gold trace element and PGE “fingerprinting” as a means for forensic
provenance applications and source understanding. Thus far published data on the Re-content of native gold is rare, with most studies using associated sulphides or molybdenites to infer gold mineralization. This common association of gold with sulphides, indicates that Re-Os isochron geochronology coupling native gold and another ore sulphide may be feasible.

The preliminary Re-Os work utilizing this method on native gold obtained from Paulsens gold deposit in the southern Pilbara Craton (Fielding et al. 2017) display measurable Re values of ~4 ppb and Os concentrations of ~3 ppt indicating that Re-Os geochronology is plausible with more analyses.

Trace element analyses (for proof of measurability) exhibit the ability to measure a large range of trace elements (REEs plus 26 other elements) in gold, that were below detection limits from other in situ methods (e.g. of 55 trace elements measured via LA-ICPMS of the Paulsens gold only the Ag, Hg, and Cu copper are consistently above detection limit, Hancock and Thorne, 2016). Although these initial proof of concept measurements need to be repeated for concentration information, the results display reproducible and distinct patterns when comparing the chondrite normalized REE patterns to other native gold deposits (Figure 2).

Figure 2. Preliminary REE pattern (normalized to chondrite) of native gold from Paulsens deposit as compared with native gold and host rock assemblages from gold-polysulphide-quartz, low-sulphide gold-quartz, and gold-silver deposit types (Nekrasova et al., 2010).

These first attempts at measuring the PGE contents of native gold presented promising results for the plausibility of analytical success as well as some challenges still to be addressed. Due to the high Hg content of the Paulsens gold (Hancock and Thorne, 2016) there is a significant interference on the 196Pt isotope during analyses. To solve this problem, two methods will be tested: 1) remove the Hg content during chromatography and/or 2) measuring and reducing the raw analytical results via a different Pt isotope such as 195Pt. These preliminary tests thus far do not suggest any major interferences with the other PGEs measured, however more aliquots need to be analyzed to determine if these results are robust.

This pilot study displays the ability to utilize the proposed workflow to obtain Re-Os geochronology, Os isotopic ratios, PGE abundances and trace element patterns of native gold. Even in these early stages of the project, the preliminary results display unique REE patterns of the Paulsens gold, measurable Re and Os isotopes, as well as the potential (albeit needing considerable work still) to develop the PGE analytical method of native gold. Fine tuning this method will provide the ability to fingerprint specific gold deposits potentially with the addition of direct dating, even distinguishing between different mineralization events within the same locality (the Paulsens gold deposit, for instance, is thought to include multiple gold mineralization events, Hancock and Thorne 2016).

4 Continued Work and Advancements

Although these studies have in many cases resulted in geologically meaningful results aiding in the understanding of the petroleum or mineral system of interest (e.g. Liu et al. 2019), challenges, continued advancements and improvements can still be endeavored. Complete dissolution of the gold, crude oils, and sulphides occurs using aqua regia; the chromium oxide-sulfuric acid digestion technique primarily targets organic material within the black shales and mudstones therefore samples do not obtain complete digestion. The chromium oxide-sulfuric acid solution digestion technique has been shown to be sufficient in dissolving the relevant phases for obtaining representative Re-Os isotopes and PGE concentration information via isotope dilution yet the inability for silicate phases to be digested without the use of HF results in incomplete trace element information.

Analysis of the Green River Shale reference material (SGR-1) revealed agreement with certified results for the light rare earth elements (REEs) however, displayed that the heavy REEs are sequestered within silicate phases that did not digest with the applied method (Sholkovitz 1990). The method is evolving to accommodate silicate dissolution with HF and that comparison between the effect of each dissolution phase has on the sample will be assessed fully.

Trace element determination can be obtained as a fast and cheap, almost byproduct, of the dissolution process. Although these fast results may not provide the highest precision concentration information, the trace element patterns can be geologically meaningful and important for exploration then comparing absolute concentrations, which are highly dependent on the method of analysis. A more precise trace element determination can be obtained within this method by the implementation of a series of isotope dilutions of REEs or desired trace elements on an as need-basis.

Many types of sulphides contain an appreciable amount of Pb (pyrites typically have on the order of 200-500 ppm Pb). Pb isotopes analyses of various sulphides are routinely used to determine model ages of mineralization (e.g. Huston et al. 2014, Hollis et al. 2017) or even used for Pb isotope mapping to reveal perspective locations for mineralization (e.g. Huston et al. 2019). Preliminary test demonstrates that after dissolution, another aliquot can be removed from the aqua regia solution and set aside for Pb isotope analytical sample preparation (Figure 2). From this aliquot, the sample is then processed through an anion exchange chromatography procedure and the Pb isotope analyses
are conducted using the Pb double-spike method after Taylor et al. (2015). Barrote et al. (2019) has investigated the Pb isotopes in pyrites compared with galenas from the same deposit and sample set that this workflow has already been tested (Section 3.2). Utilizing those results further work is underway to test if this modification the Re-Os isotope, PGEs, and trace element of method discussed can be successfully be applied first to sulphides and potentially expanded to other mineral systems such as gold.

5 Conclusions

These case studies presented above utilizing differing geological materials of economic interest display this methodology as a viable tool for not just obtaining complimentary geochronological and geochemical data for mineral and petroleum systems as a viable exploration tools; but also displays the ability to maximize geoscience data providing a cost-effective low sample consumption mineral or petroleum system fingerprinting and exploration workflow. Moreover, this method allows the opportunity and ability to augment or advance into further isotopic systems ever expanding the ability to provide cost-effective analyses to encourage informed exploration decisions.

Acknowledgements

The authors acknowledge: Zhen Li from the John de Laeter Centre for providing the crude oil samples and aid with the development of this method, Dr. Lena Hancock at the GSWA for providing the Paulsens gold samples, and the John de Laeter Centre, Curtin University for funding, the facilities, scientific and technical assistance.

References


Hancock E. A. and Thorne A. M. (2016) Mineralogy of gold from the Paulsens and Mount Olympus Deposits, Northern Capricorn Orogen, Western Australia. Geological Survey of Western Australia, Record 2016/14/16


Pearson D. G. and Woodland S. J. (2000) Solvent extraction/anion exchange separation and determination of PGEs (Os, Ir, Pt, Pd, Ru) and Re–Os isotopes in geological samples by isotope dilution ICP-MS. Chemical Geology 165:87-107 https://doi.org/10.1016/S0009-2541(99)00161-8


Abstract. The development of reliable geochemical indicators to guide the search for Ni-Cu-(PGE) sulfide ores associated with komatiites, komatiitic basalts and picrites has been a long-standing goal. Here we discuss the latest findings of a long-term study that tests the usefulness of laser ablation (LA) ICP-MS trace element analysis of minerals in the exploration for magmatic sulfide deposits.

We show that the Ru contents of chromite and the Cu contents of olivine empirically correspond to the sulfur-saturation state of a mafic-ultramafic host rock during chromite and/or olivine crystallization. Sulfide-mineralized systems are characterized by distinct Ru and Cu depletions relative to sulfur-undersaturated systems. The lower Ru and Cu contents of chromite and olivine, respectively, reflect the chalcophile behavior of these elements during sulfide segregation.

Our compiled data indicate that LA-ICP-MS analysis of chromite and olivine allows to predict if a system has reached sulfur saturation, and therefore is prospective to host magmatic sulfide ore, with an accuracy of >90%. These findings highlight the importance of mineral chemistry for future exploration strategies, including (1) drill core studies to develop vectors towards ore zones, and (2) stream sediment and (3) laterite/soil sampling to develop chromite-Ru and olivine-Cu heat maps to guide greenfield exploration.

1 Introduction

Over the past decades, geochemical exploration for magmatic sulfide deposits was often focused on the identification of chalcophile element variation patterns in bulk-rock samples to predict if a system reached sulfur saturation and therefore is prospective as a host for magmatic sulfide mineralization (Le Vaillant et al. 2016 and references therein). However, primary ore-forming bulk-rock signatures are readily overprinted by post-magmatic processes such as metamorphism, alteration and weathering. As a consequence, a reliable identification of primary ore-forming signatures in bulk-rock data sets may not be possible, which limits the usefulness of such an approach (Fig. 1).

Figure 1. Bulk-rock Cr-Ru variation in komatiites from the Eastern Goldfields Superterrane (Yilgarn Craton, Australia). Overlapping analyses of mineralized and unmineralized komatiites complicate use of bulk-rock signatures in exploration targeting. Modified from Locmelis et al. (2011).

Many of the uncertainties that are associated with the interpretation of bulk rock signatures can be eliminated via the in-situ analysis of primary minerals that were not...
significantly affected by postmagmatic processes. Here we discuss the latest findings of a long-term study that tests the usefulness of LA-ICP-MS analysis of minerals in the exploration for magmatic sulfide deposits hosted by komatiites, komatiitic basalts and picrites.

2 Samples

Our database comprises a globally representative suite of sulfur-undersaturated and sulfide-mineralized komatiites, komatiitic basalts and picrites. Komatiite samples were taken from the Eastern Goldfields Superterrane (Yilgarn craton, Australia), the Belingwe greenstone belt (Zimbabwe craton, Zimbabwe), the Abitibi greenstone belt (Superior craton, Canada), and the Central Lapland greenstone belt (Fennoscandian Shield, Finland). Komatiitic basalts samples were taken from the Gerry Well greenstone belt (Eastern Goldfields Superterrane, Yilgarn craton, Australia). Ferropicrites were sampled from the Pechenga greenstone belt (Fennoscandian Shield, Russia). It is noted that the komatiite samples from Alexo (Abitibi greenstone belt, Canada) and Tony’s Flow (Belingwe greenstone belt, Zimbabwe) were taken from komatiites that were sulfur-undersaturated upon emplacement; all other localities are summarized by Locmelis et al. (2018).

3 Methods

The major and minor element composition of chromite was determined using a Cameca SX-100 microprobe at Macquarie University, Australia. The trace element chemistry of chromite was determined using a Photon Machines Excite Excimer laser ablation system connected to an Agilent 7700cx ICP-MS at Macquarie University (cf. Locmelis et al. 2018). The major and minor element composition of olivine was determined using a JEOL JXA-8900R electron probe microanalyzer at the University of Maryland. The trace element chemistry of olivine was determined using a Photon Machines Analyte G2 ArF Excimer laser ablation system coupled to a Nu Instruments AttoM high resolution ICP-MS in the Planetary Environments Laboratory at NASA Goddard Space Flight Center.

4 Results and Discussion

4.1 Ruthenium in chromite from komatiites, komatiitic basalts and picrites

A recent study by Locmelis et al. (2018) investigated the fractionation behavior of Ru in chromite-saturated, high-Mg melts by analyzing the Ru contents of chromites from a global sample set of sulfur-undersaturated and sulfide-mineralized komatiites, komatiitic basalts, and ferropicrites by laser ablation ICP-MS. The data show that chromites from sulfur-undersaturated magmas generally contain between ~150 and 600 ppb Ru, whereas chromites that crystallized from sulfide-bearing magmas mostly contain less than ~150 ppb Ru. The Ru contents are independent of elements that typically document a modification of chromite, suggesting that the determined Ru concentrations are primary magmatic signatures that reflect the competition for Ru between chromite and segregating sulfides (if present).

4.2 Cu in olivine from komatiites

New data presented for olivine from komatiites show that the trace element chemistry of olivine is largely independent of the sulfur saturation state of the system during olivine crystallization (Fig. 3). One exception to this generalization are the Cu abundances: olivine from komatiite units that host significant sulfide mineralization (i.e., Betheno, The Horn and Perseverance) have overall lower Cu concentrations (< 1 ppm Cu) than olivines from sulfide-poor systems (> 1 ppm Cu), although it is noted there is some overlap between olivine from Betheno and Murphy Well (Fig. 4).

These findings are notably similar to the bimodal Ru variation in chromite shown in Fig. 2 and are interpreted to reflect the competition for Cu between sulfides and...
olivine upon sulfide segregation. In the presence of sulfides, Cu will preferentially partition into sulfides with sulfide-melt partition coefficients of ~1500 (Peach et al. 1990). In the absence of sulfides, Cu can partition more freely into olivine, albeit with low olivine-melt partition coefficients of <0.15 (Le Roux et al. 2015). Therefore, even small amounts of sulfides in the system will strongly affect the Cu contents of olivine, providing a distinct proxy for the presence or absence of sulfides in the system.

**Figure 3.** Average Bulk Silicate Earth normalized concentrations of trace elements in komatiitic olivine. Bulk Silicate Earth values are from McDonough & Sun (1995).

Although the Cu contents of olivine show promise as an exploration tool complementary to Ru in chromite, it is noted that the mineralized samples included here are from large dunite bodies, whereas the non-mineralized samples are from much thinner komatite flows. Therefore, it remains to be further tested if the bimodal Cu variation in olivine primarily reflects sulfide-saturation, or if it is also controlled by other factors, such as the silicate magma to sulfide melt ratio (i.e., the R-factor; Campbell and Naldrett 1979), kinetic effects during magma emplacement and sub-solidus re-equilibration. To further develop Cu in olivine as a pathfinder for magmatic sulfide deposits, future studies will include olivine from thin mineralized flows as well as large unmineralized dunite bodies.

4.3 Implications for exploration targeting

Our data show that low Ru contents (< 150 ppb Ru) in chromites from komatiites, komatitic basalts and picrites are indicative of systems that were sulfur-saturated during (or prior to) chromite crystallization. A similar observation is made for olivine from komatites, i.e., low Cu contents (< 1 ppm) in komatitic olivine are indicative of sulfur saturated systems. Because the Ru and Cu contents of chromite and olivine, respectively, (i) can be used to constrain the sulfur evolution of a mafic-ultramafic system, (ii) are readily determined via cost-effective LA-ICP-MS, and (iii) the results are easier to interpret than bulk-rock signatures (cf. Figs. 1 and 2), we argue that LA-ICP-MS analysis of chromite and olivine is a useful exploration tool.

**Figure 4.** Average Bulk Silicate Earth normalized concentrations of trace elements in komatiitic olivine. Bulk Silicate Earth values are from McDonough and Sun (1995).

The identification of two independent mineral-based proxies that can be potentially be used complementary to one another to predict if a system reached sulfur saturation (and therefore can host magmatic sulfide mineralization) is important because it allows to extent research to rocks where (i) only chromite or olivine exist, and/or (ii) one mineral is too small or too altered to be analyzed via LA-ICP-MS. As an example, sulfide mineralization at Perseverance is hosted by a komatiitic dunite without chromite. However, distinctly low Cu contents in olivine provide an alternative indicator for the presence of magmatic sulfides in the Perseverance komatiite (Fig. 4). Similarly, many mafic-ultramafic rocks are heavily altered and display advanced replacement of olivine by secondary minerals. Chromite, however, is more resistant to destructive alteration and therefore often exists in samples where olivine has been completely replaced. Chromite is also a widespread component of detrital heavy mineral samples and often preserved even in heavily altered terrains and/or weathered (lateritic) profiles.

The combination of Ru-chromite and Cu-olivine signatures in mafic-ultramafic systems serves as promising prospecting method to be added to the existing exploration toolbox. Three areas of future research are suggested:

1. Analysis of olivine and chromite from drill cores that intersect mineralization to test the hypothesis that systematic Ru and Cu depletion signatures provide a vector toward mineralized units.
2. Systematic analysis of Ru in chromite from stream sediments to develop Ru-depletion heat maps that may help identify undiscovered deposits in the catchment area.
3. Studies of Ru-chromite signatures in weathered profiles and/or reworked clays, thus allowing for surface prospecting in tropical regions (Perez et al. 2018).
Acknowledgements

This work was carried out as part of AMIRA Project P710A, funded by BHP-Billiton, Norisk Nickel (formerly Lion Ore), and Independence Group NL. Additional support was provided by Rio Tinto Exploration Pty Limited. The authors also acknowledge the support of the Minerals and Energy Research Institute of Western Australia (MERIWA), through grant M388, the Australian Research Council (ARC), through grant LP0669595, and the Academy of Finland through grant 281859.

References

To make better exploration tools, we first need to better understand ore deposits.

Tim Ireland
First Quantum Minerals Ltd, London, UK, and
University of Tasmania, Australia.

Robert Sievwright
First Quantum Minerals Ltd, London, UK

Adam Bath
Australian Resources Research Centre, CSIRO, Perth, Australia

Elitsa Stefanova
Geological Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria

Janharm Godfroid
First Quantum Minerals (Australia) Ltd, Perth, Australia

Abstract. In an era of industry-funded research, there is an imperative that research yields outcomes that can be applied directly, at the expense of improving fundamental understanding. Reality often proves more complex than our simplistic experiments anticipated. A summary of common experimental behaviour might be framed thus:

1. observe something of possible use
2. collect limited orientation samples
3. become enthused by early results
4. roll out the tool to genuine unknowns
5. generate abundant data with ambiguous results
6. analyse using a machine learning algorithm hoping for a miracle

This paper documents some of our recent trials and errors, mostly through application of SEM-based Tescan Integrated Mineral Analyser (TIMA) quantitative mineralogy and rock mapping, and attempts to apply mineral chemistry and chronology analysis to detrital sediment samples. We’ve learned that to improve our new tools we must:

a. expand or customise our characterisation of natural background
b. observe mineral appearance, assemblage and morphology before microanalysis
c. accept that detailed observation may demand revisions to existing models of hydrothermal mineral stabilities, and hence provoke more fundamental research
d. accept that machine learning classifications tend to be successful only when trained against local or specifically relevant orientation data

1 Introduction

This paper records some of the content discussed as the keynote to a session entitled "New Techniques for Ore Discovery". Through description of some recent attempts at applied technique development, it highlights some possible pitfalls, and one hopes, help future geoscientists design better applied research programs.

Governments have recently pushed more of the cost of research onto the companies they see as the primary beneficiaries of such research. Among many effects of this change is a drive for research to translate more or less directly into industry applications (e.g. Ahmed et al. 2019), as is the default position for research conducted internal to exploration companies. The net result is that as geologists we’re relying less on our eyes, and more on our data, while the data may not be fit for the prescribed purpose. Here we show examples that illustrate how some of our newer tools may fail in isolation; their successful application demands the combination of quantitative data with textural and mineral assemblage information in order to start to understand mineral systems.

2 Understanding background

2.1 Detrital monazite as a proxy for evaporite-related alteration in sedimentary rocks

Monazite has been described from several sediment-hosted copper deposits and appears to be especially prolific in the Kabompo Dome area of NW Zambia (Halley et al. 2016). On that basis monazite from several deposits was analysed and compiled with published data from many sources. The monazite from Zambian copper deposits and metamorphic rocks was used as a training set to derive a simple classification scheme for monazite. This approach seemed to offer the potential to distinguish hydrothermal monazite in sedimentary basins from metamorphic and magmatic monazite.

An orientation study was executed in which panned concentrates were collected from active drainages across a swath of western Zambia. SEM-based quantitative
mineralogy was applied to these samples and monazite grains were analysed by electron microprobe. We observe that monazite is in fact relatively scarce in the vicinity of some of the Zambian sediment-hosted copper deposits, and is extremely abundant in the catchments draining the basal clastic strata that experienced strong alkali alteration. The composition of this ‘salt-related’ monazite is presently indistinguishable from the monazite in the copper deposits. A far more detailed understanding of the background will be required for this to become a useful exploration tool.

In a fairly typical illustration of the tendency toward numeric, rather than visual data, the textural character of the monazite grains has not yet been investigated.

3 Textural context

3.1 Textures of detrital magnetite grains

The most basic discrimination of magnetite chemistry is based on titanium content. In sediments draining the Cobre Panama porphyry district (section 5.1), a majority of grains analysed were found to have high Ti compositions unlikely to be hydrothermal in origin. Backscattered electron (BSE) images were used to classify the grains according to the abundance and width of exsolution laminae, and the abundance and shape of fractures and non-magnetite inclusions. Grains exhibiting wavy fracturing, dark patchy texture, and/or strong trellis exsolution were found to correspond to high-Ti compositions.

3.2 Cathodoluminescent textures of detrital zircon grains

Zircon is another mineral very simply collected in detrital samples. Improvements in laboratory access and efficiency or laser ablation analysis (LA), and associated reductions in cost have meant that geochronology and zircon trace element chemistry are more accessible than previously. Typically, zircon grains are separated, mounted and polished, and cathodoluminescence (CL) images are collected under scanning electron microscope (SEM) to reveal crystal growth zones, on the basis of which spots are chosen for LA analysis.

Initially, the zircon chronology and chemistry data was interpreted in a manner similar to Lu et al (2016), i.e. we plot the data for a given rock, or a given detrital chronologic population and interpret fertility. Although the laboratory provides the CL images along with the data, frequently the individual this imagery resides on a hard disk and no effort is made to combine the crystal shape nor zoning character with the age and chemistry data. Among zircons from two different porphyry deposits in the Andes, it was observed that the grains that coincided in time with emplacement of causative porphyritic intrusions could be distinguished by the presence of distinct broad, CL-bright rims. This character occurs in the syn-mineral zircons in a Miocene porphyry Au deposit and an Eocene porphyry Cu-Mo deposit. The same character is evident in zircon imagery from El Salvador, Chile (Lee et al 2017). It therefore seems possible that in the application of detrital zircon studies to exploration, mere description of the zircon crystal zonation may improve speed and reduce cost. One may also speculate that a thick, compositionally distinct rim may render these crystals distinctive even under a conventional binocular microscope.

4 Mineral assemblages

Mineralogy imaging based on SEM technology (e.g. TESCAN) permits superior quantitative mineralogy and compositional accuracy to conventional petrography, at the expense of some textural and optical information.

4.1 Hypogene or supergene?

The Taca Taca Bajo (TTB) porphyry Cu deposit (3.086 Gt @ 0.42% Cu) comprises a subhorizontal chalcocite-bearing zone of copper enrichment located beneath a leached zone and above a domain of chalcopyrite
bearing mineralized rock associated with the lateral zonation from potassic to early phengitic alteration (Benavides 2018). Translucent yellow-green potassic alunite veins cut the chalcocite-bearing assemblages. The combination of morphology, position and association with paragenetically late amorphous alunite has been considered as evidence that chalcocite (and hence the economic elevated copper grade) formed by supergene processes that upgraded primary chalcopyrite-bearing assemblages. The combination of morphology, position and association with paragenetically late amorphous alunite has been considered as evidence that chalcocite (and hence the economic elevated copper grade) formed by supergene processes that upgraded primary chalcopyrite-bearing assemblages.

TESCAN imagery was collected on a series of samples along a vertical drillhole through the chalcocite resource, initially to inform sampling for metallurgical testwork. We had predicted that chalcocite would be intimately associated with potassic alunite, and would mostly occur as rims on primary pyrite. Rather, chalcocite mostly occurs as monomineralic grains associated with an assemblage generally considered hypogene in origin; muscovite, kaolinite, pyrophyllite, natroalunite, and woodhouseite. The abundance of hydrothermal monazite in these samples correlates closely with that of the advanced argillic minerals, and is antithetic to the abundance of apatite. We interpret therefore that primary apatite was dissolved during the chalcocite-forming event and P reprecipitated as monazite. Benavides (2018) reported a LA-ICPMS monazite age from the deposit of 29.96 ± 0.96 Ma, within error of existing zircon U-Pb and muscovite 40Ar/39Ar geochronological results for Taca Taca Bajo (Gigola 2008).

The abundance of hydrothermal monazite in these samples correlates closely with that of the advanced argillic minerals, and is antithetic to the abundance of apatite. We interpret therefore that primary apatite was dissolved during the chalcocite-forming event and P reprecipitated as monazite. Benavides (2018) reported a LA-ICPMS monazite age from the deposit of 29.96 ± 0.96 Ma, within error of existing zircon U-Pb and muscovite 40Ar/39Ar geochronological results for Taca Taca Bajo (Gigola 2008).

Figure 2. TESCAN image (CSIRO) and matching sample photos of a chalcocite-mineralised muscovite-altered granite from TTB showing primary natroalunite veins cut by veinlets of chalcocite-pyrophyllite.

TTB therefore poses a challenge to conventional models of porphyry mineralization; its morphology and position strongly support a critical role for supergene processes, whereas the quantitative mineralogy and geochronology demand that the chalcocite-bearing assemblage formed in a hypogene environment, within ~1 m.y. of crystallization of the causative intrusion. The discrepancy provokes some questions for tools used in porphyry exploration: how much emphasis need we put on the uplift and exhumation considered critical to the supergene history? If we’re to apply mineral chemistry vectors in the manner of Wilkinson et al (2015) or Urib-Mogollon and Maher (2018) is it relevant to use a calibration based on deposits without this hypogene advanced argillic assemblage? If we’re to consider the composition of resistate phases such as rutile, apatite, monazite, titanite as exploration media in detrital samples, how does the abundance and chemistry of these phases vary between porphyry systems with, and without such an acid hypogene assemblage? Our new tools are limited by our knowledge of the deposits for which we search.

5 Automated classifications

Sophisticated methods for classification of multivariate data have recently become much more accessible. These have found enthusiastic application among geologists and explorers (e.g. Kuhn et al 2018).

5.1 Detrital magnetite as a proxy for porphyry Cu

Magnetite from the hypogene alteration in porphyry deposits has some distinctive geochemical features (Nadoll et al 2015). Further, magnetite is an attractive sampling medium as it’s widespread, resistant, dense and easily collected. We therefore attempted to apply classification of magnetite chemistry to porphyry exploration via district-scale stream sediment sampling. Ideally, the characteristics of magnetite from the various porphyry-related hydrothermal environments would be distinctive, and recognisable hydrothermal grains would be sufficiently abundant to be identified further downstream than conventional fine-fraction geochemical anomalies of Cu, Au or other pathfinders.

Ideally, the chemical character of magnetites would be consistent globally from hydrothermal environments constrained for T, P, pH and redox by their shared mineral assemblages. Several different supervised classification schemes were attempted, based on a global compilation of magnetite chemistry. Of these, the random forest classification yielded the best results, insofar as the greater porphyry environment could be distinguished from background. However, under this scheme the grains from catchments directly draining the porphyry copper deposits were not distinguished from grains draining from a related laterally extensive pre-mineral granodiorite stock.

In a second experiment magnetite from the known in-situ sources was analysed and this data was used as the training set for definition of the random forest. We analysed magnetite from potassic alteration zones, alteration zones overprinted by a sericite-chlorite
assemblage, from the pre-mineral stock, from an unrelated unmineralised stock outside the mining lease, and from unmineralised basaltic andesite wallrocks. This modest collection of training data permitted far better discrimination of the detrital grains, such that the catchments draining the mineralized porphyry could be specifically identified.

Figure 3. Example of catchments coloured by the proportions of detrital magnetite belonging to each of three classes based on a random forest classification trained with a local data.

The study considered first and second order catchments of 10-40 km². The fertile signature is persistent in the larger, second order catchments, but not to third order rivers. Neither is the signal, at present, demonstrated to persist further downstream than conventional anomalism of Cu and Au. Nonetheless, in the course of the experiment, it was noted that the catchments draining the hydrothermal alteration zones contained a far broader range of magnetite textural styles than those draining volcanics and unmineralised intrusions. A future regional survey might include the combination of conventional geochemistry and BSE imagery of magnetite, such that Cu and Au anomalies can be ranked on the basis of the magnetite styles.

6 Conclusions

A well-documented decline in discovery rates means that explorers would likely benefit from new tools. However, no single tool in our current arsenal is used in isolation. As we pursue new tools, we should keep one foot rooted firmly in empirical geology, and continually ask our new tools, not to magically conjure a target, but to contribute to better all-round understanding of the geology and evolution of the target environment.

Across the world’s universities and exploration companies there are, collectively, vast amounts of data collected that would be useful if only they were published more often, and adequately compiled. On publication of industry data, one bottleneck is time, and we envisage a win-win scenario in which professional researchers collaborated more frequently with project level exploration geologists (not managers) to publish commercially insensitive data. Some of the issues outlined in this paper may have been avoided had better background data been available. To that end, centralised databases such as DateView (Eglington, 2004) and georoc (http://georoc.mpch-mainz.gwdg.de/georoc) are critical, but much more is needed. We encourage explorers and researchers to contribute more to centralised publications, such that the growing field of automated classifications has workable reference data to draw from.

Acknowledgements

The authors acknowledge First Quantum Minerals’ management, especially Mike Christie, for their ongoing support of in-house research toward exploration technology. The samples used in the examples presented were collected by First Quantum’s field teams in Argentina, Serbia, Turkey and Zambia.

References


New Techniques for Ore Discovery 1309
Hydrothermal apatite as an indicator of porphyry Cu deposit fertility

Matthew A. Loader, Jamie J. Wilkinson, Robin N. Armstrong
Natural History Museum, Cromwell Road, London, UK

Abstract. We present LA-ICP-MS and EPMA data for hydrothermal apatites from the Oyu Tolgoi porphyry Cu-Au system in southern Mongolia. The Oyu Tolgoi cluster comprises several deposits, including the lower-grade Heruga deposit (0.48% Cu) and the higher-grade Hugo Dummett deposit (1.18% Cu). Hydrothermal apatites were readily distinguished texturally from igneous apatite as they are intergrown with alteration phases including sulphides. The main difference between hydrothermal apatites from Heruga and Hugo Dummett is the concentrations of Mn and Fe, which are significantly enriched at Hugo Dummett (up to 1.5 wt. % Mn, and 0.6 wt. % Fe). These divalent cations and others (Mg, Pb) show positive correlations with apatite Cl content, suggesting a link between apatite metal contents and high fluid salinity, which have been shown to transport higher concentrations of Mn, Fe, and also Cu. We therefore suggest that the locally high Cu contents in rocks from Oyu Tolgoi, in particular at Hugo Dummett, may be explained by deposition from particularly saline fluids, which also produced Mn- and Fe-rich apatite. We conclude that hydrothermal apatite from potassic alteration zones reflects the chemistry of fluids associated with porphyry mineralisation, and may be used to assess the mineralisation potential of such systems.

1 Hydrothermal and Igneous Apatite

Apatite is the most common accessory phosphate mineral in igneous rocks (Piccoli and Candela 2002) and in hydrothermally altered rocks from porphyry systems (e.g. Bouzari et al. 2016). Apatite has the potential to record a wide range of useful information about the evolution of a porphyry magmatic-hydrothermal system, because it partitions several major and trace elements into its crystal structure in detectable abundances. These elements include Cl, F, and S (important ligands for the transport of metals in hydrothermal fluids); rare earth elements (REEs), Sr, and Y (considered to be useful in the identification of igneous rocks with enhanced porphyry ore forming potential, or ‘fertility’); and potentially redox sensitive elements such as Mn and Fe. A consistent geochemical distinction between igneous and hydrothermal apatite remains elusive, which may in part be due to the potential for the chemistry of igneous apatite to be modified by interaction with hydrothermal fluids at the magmatic-hydrothermal transition, or during lower temperature hydrothermal alteration. However, a paragenesis for apatite can be determined texturally; for example, apatite included in zircon likely records primary igneous conditions, whereas clusters of anhedral apatite crystals intergrown with (and included within) Cu sulphides in highly altered rocks may reflect the chemistry of the ore-forming fluids.

In this study, we show that the chemistry of hydrothermal apatite in low- and high grade altered rocks from a porphyry system are systematically different, and that these differences likely reflect differences in fluid salinity.

2 Oyu Tolgoi Porphyry Cu-Au (Mongolia)

Located in the South Gobi Desert, Oyu Tolgoi is a cluster of discrete ore bodies in a NNE oriented lineament ~22 km in length (Fig. 1). These deposits comprise the largest Palaeozoic porphyry mineralization in the world. Several ore bodies are present, with different metal tenors, sizes and Cu grades. Both the Heruga and Hugo Dummett deposits are of similar size (970 and 1,016 Mt respectively) but significantly different grade (0.48 and 1.18 wt.% Cu; 0.6% equivalent cut-off: Rio Tinto Annual Report 2011). These two ore bodies are within 10 km of each other, are associated with the same quartz monzodiorite intrusions, and are hosted in the same sequence.

---

Figure 1. Simplified map of the Oyu Tolgoi cluster, showing the prominent geological trend, and the major centres of mineralization. Modified after Crane and Kavalieris (2012).

Richards (2013) considered the high Cu grade at Hugo Dummett to relate to effective fluid focusing, especially in
shallower hypogene zones with hydrolytic alteration, where quartz vein density exceeds 90 vol.% (a unit referred to as "Qv90" in mine literature). However, high Cu grades also occur in much deeper potassic intervals, and local changes in grade do not correlate with quartz vein density. Sillitoe (2010) highlighted the importance of mafic host rocks in controlling the high grade at Hugo Dummett. However, the Heruga orebody is also partly hosted in the same mafic volcanic unit, and some of the highest Cu grades in the potassic zone are in fact hosted in the felsic quartz monzodiorite.

3 Analytical Techniques

A total of 296 apatites from 15 rocks were analysed in this study. Most grains were analysed from thin section, so as to retain the textural context of each grain, although some analyses were conducted on mineral separates mounted and polished in epoxy blocks. Apatites were first analysed by electron microprobe (EPMA; Cameca SX100, 20kV, 20nA) followed by laser ablation (ESI New Wave UP193FX) inductively coupled plasma mass spectrometry (Agilent 7700cs quadrupole, fluence 3.5 J cm⁻², spot size 35 - 50 µm). An attempt to mitigate against the migration of F during microprobe analysis was made by using a defocused beam (10 µm) and analyzing F first.

4 Results

4.1 Petrography

Two texturally distinct apatites types were observed in this study. In the least altered rocks, apatite is mostly associated with magnetite (hereafter, 'M-Ap'; Fig 2a), whereas where rocks show strong mineralization and potassic alteration, apatite is intimately associated with sulphides ('S-Ap'; Fig. 2b), sometimes in the groundmass and sometimes as intergrown clusters replacing a mafic phase. At Heruga, these sulphides are typically pyrite and chalcopyrite; at Hugo Dummett, bornite and chalcopyrite. S-Ap is also distinct from M-Ap due to the absence of a strong cathodoluminescence (CL) response. We consider the M-Ap to be likely igneous in origin, and the S-Ap to be hydrothermal. Given the characteristic association between S-Ap and sulphides, we suggest that these apatites attained equilibrium with the ore-forming fluids.

4.2 Trace element chemistry

S-Ap and M-Ap may be distinguished by their chondrite-normalized rare earth element (REE) patterns. Whereas M-Ap show a depletion in middle- and heavy REE and an enrichment in light REE which is typical of igneous apatite, S-Ap have flatter REE patterns, with LaN/YbN ratios <5. M-Ap also show higher Cl values than S-Ap.

There is no difference in REE pattern of S-Ap between Heruga and Hugo Dummett. The biggest distinction between these two populations is with divalent cations, especially Mn, Fe, and Pb. For each of these elements, S-Ap from Hugo Dummett is on average significantly lower than S-Ap from Heruga.
more enriched than those from Heruga, although a significant overlap in the range of data occurs. There is a broad relationship between the Mn (Fe, or Pb) concentration of hydrothermal apatite, and the Cu content of the host rock (Fig. 4), i.e. the rocks with higher Cu contain the apatite with higher Mn.

5 Discussion

Given that the S-Ap are intimately associated with the Cu sulphides, the relationship between rock Cu content and apatite chemistry suggests that hydrothermal apatite may be recording some chemical characteristic of fluids which are capable of yielding high Cu grades. Fluid composition is likely to exercise a strong control over hydrothermal apatite chemistry, because many fluid mobile components partition strongly into apatite. The observed correlations between Cl and Mn in S-Ap (Fig. 5) suggest that apatites with higher divalent metal contents were precipitated from more Cl-rich fluids.

This would imply that the fluids involved were moderately more Cl-rich at Hugo Dummett than at Heruga. Evidence from experimental studies (Ayers and Eggler 1995; Bai and van Groos 1999), and observations from fluid inclusions in mineralized granitic rocks (e.g. Audétat and Pettke 2003), have demonstrated that Cl-rich fluids are able to transport higher concentrations of cations such as Mn, Pb, and Fe, due to the greater formation of metal chloride complexes. The presence of elevated Cl in hydrothermal fluids may also increase the ability of the fluid to transport Cu (Tattitch and Blundy 2017). Thus, Cl-rich fluids, carrying elevated Mn, Pb, Fe and Cu, could account for the high Mn, Pb and Fe content of apatite in rocks with high Cu content.

Acknowledgements

We thank Paul Agnew and Alan Kobussen (Rio Tinto Exploration) for logistical and scientific support. Analytical assistance was provided in the Imaging and Analysis Centre at the Natural History Museum (London) by John Spratt and Clara Wilkinson.

References

Porphyry copper indicator minerals (PCIM) in stream sediment samples: application at the Taurus deposit in east-central Alaska with comparison to other techniques

Karen D. Kelley, Garth E. Graham

Douglas C. Kreiner
U.S. Geological Survey, Alaska Science Center

Katharina Pfaff
Colorado School of Mines, Department of Geology and Geological Engineering

Abstract. The PCIM method in stream sediment samples is a new technique that is highly effective in identifying mineralization at the poorly exposed Taurus porphyry deposit in the Yukon-Tanana uplands of eastern Alaska. The technique involves scanning electron microscopy (SEM)-based automated mineralogy of mineralized core and stream sediment samples. The primary indicator minerals in mineralized rocks include sulfide (bornite, chalcopyrite, chalcocite, molydenite) and sulfate minerals (svanbergite and jarosite); sediment samples from streams draining mineralized areas also contain most of these phases. Resistate minerals such as apatite, epidote, rutile, tourmaline, and titanite are ubiquitous in mineralized rocks and stream sediments, but preliminary chemical data for rutile and apatite suggest that a distinct population can be distinguished in the sediment samples that is linked to mineralized areas. The presence of svanbergite (aluminum sulfate phosphate) is important because (a) it is a hypogene mineral in the Taurus deposit and (b) it is found in stream sediment samples as far as ~8 km downstream from Taurus and another nearby porphyry occurrences. Hydrogeochemistry and sediment geochemistry using partial leach analytical methods also show potential as good exploration tools.

1 Introduction

Case studies, including the Pebble porphyry deposit (Kelley et al. 2011) and others in British Columbia (e.g. Plouffe and Ferby 2017) have tested the usefulness of the Porphyry Copper Indicator Mineral (PCIM) method in identifying concealed deposits in glaciated environments. More recent studies show that the PCIM method is effective when applied to stream sediment and other surficial materials in addition to till (Wilton et al. 2017). Furthermore, recent advancements in sample preparation techniques and analytical methods provide quantitative mineralogical results at high speed and low cost. Scanning electron microscopy (SEM)-based automated mineralogy combines high resolution backscatter electron (BSE) images and elemental chemistry from energy dispersive x-ray spectroscopy (EDS) and subsequent image analysis. It allows tens of thousands of grains on a mount to be analyzed in less than an hour.

The unglaciated eastern Yukon-Tanana upland that hosts the Taurus porphyry Cu(-Mo-Au) deposit and other porphyry occurrences (Fig. 1) provides a unique opportunity to test this evolving methodology and other geochemical techniques. Historic stream sediment geochemical data (minus 80-mesh, total digestion semi-quantitative analyses) show few significant base metal anomalies, even within 1-2 km of Taurus. We interpret this as the combined result of abundant ash (Richter et al. 1995) and loess (Péwé 1975) in soils and stream valleys that dilute the geochemical signal, and the low gradient that limits sediment transport. To test better ways to identify mineralization, several methods are being used as part of our study, including the PCIM method, hydrogeochemistry, and partial leach geochemical methods on stream sediments that are designed to attack selective phases. Results of the PCIM study are the primary focus of this paper with the following goals: (1) to determine indicator minerals in bedrock sources, (2) to identify and separate indicator minerals from surficial materials, and (3) to measure unique chemical compositions of these indicator minerals.

2 Regional and Deposit Geology

The Yukon-Tanana upland in east-central Alaska is characterised by sparse outcrop exposure, and is covered by residual soils and vegetation. The region is largely underlain by structurally complex metamorphic rocks that represent a variety of tectonic environments. These rocks are crosscut by Late Devonian to early Tertiary igneous suites.

Most of the porphyry-related occurrences in east-central Alaska are associated with areally extensive, volumetrically minor Late Cretaceous to earliest Tertiary granite to granodioritic stocks and dike swarms ranging from ~73-65 Ma (Allan et al. 2013; Kreiner et al. 2017). The porphyry deposits include the Taurus, Bluff, and Oreo occurrences (Fig. 1). Others in the area (Pika, Fishook, Pushbush) are poorly characterized but are most likely younger epithermal-style occurrences. The porphyry occurrences display classic porphyry-style
copper mineralization consisting of quartz-sulfide veining with sericite and biotite envelopes and disseminated Cu-Fe-sulfide minerals. Locally, tourmaline-rich assemblages and tourmaline-cemented hydrothermal breccias characterize the presumed distal and upper levels of the occurrences. At the Taurus deposit, molybdenite and gold are present locally (Kreiner et al. 2017).

3 Methods

Bulk sediment from each of 49 stream sites was sieved to obtain the 105 to 250 µm fraction. Additionally, 14 rock samples from core were collected for thin sections or to crush and process in the same manner as the sediment samples. The 105-250 µm fraction was passed over a shaking (Wilfley) table to separate lighter from denser minerals; the threshold between heavy and light minerals using the shaking table is about 2.6-2.8 g/cm³. Heavy liquid and magnetic separation techniques were not used. About 1 gram of the heavy separate was mixed with 1 gram of graphite and poured into a 25 mm diameter puck. After hardening, the puck was polished. Grains were analyzed using SEM-based automated mineralogy (TESCAN Integrated Mineral Analyzer or TIMA). High resolution backscatter electron images (BSE) were taken using a 5 µm grid with a 15 µm EDS analysis step size. Tens of thousands of grains are analyzed in about 40-60 minutes. To date, 27 of the 49 sediment samples have been analyzed.

4 Results

4.1 Previous studies

Specific indicator minerals in till down-ice of porphyry deposits in Alaska and British Columbia include gold, jarosite, andradite garnet, Mn-rich epidote, ± sulfides. Such minerals occur as far as 7-10 km from the deposits (Kelley et al. 2011; Plouffe and Ferbey 2017). Many resistate minerals (tourmaline, zircon, rutile, apatite) are present in mineralized samples from porphyry deposits, but they also occur in barren igneous rocks, and therefore their presence in till or surficial materials might not be significant. However, unique physical or chemical properties can indicate their association with mineralization. For example, epidote in mineralized rocks is typically rich in Mn and studies have shown that Mn contents in epidote decrease systematically with distance from a deposit, suggesting it is a good vector to mineralized porphyry systems (Cooke et al. 2014). Chemical differences have also been noted for apatite (Bouzari et al. 2016), titanite (Linnen et al. 2015), and tourmaline (Chapman et al. 2015).

4.2 Taurus mineralogical results

Table 1 summarizes the indicator minerals observed in core samples and stream sediment samples from the Taurus study, and Figure 1 shows the distribution of select minerals in sediment samples. Among the best...
indicator minerals in rock samples are sulfide (bornite, chalcopyrite, chalcocite, molybdenite) and sulfate minerals (svanbergite and jarosite). Some sediment samples from streams draining mineralized areas also contain sulfide minerals (bornite, chalcopyrite, chalcocite, covellite; Table 1). The low abundance of minerals such as chalcocite, covellite, and molybdenite in streams draining mineralized areas may in part be due to the breakdown of these sulfide minerals during weathering and alluvial processes. Svanbergite and jarosite are also good indicator minerals for vectoring to mineralization areas (Fig. 1). Similar to other porphyry deposits, resistate minerals in rock and sediment samples from Taurus include apatite, epidote, rutile, tourmaline, and titanite (Table 1). Their ubiquitous presence alone is not significant, but the chemistry of these phases may be used to distinguish grains associated with mineralization versus unmineralized areas (see section 4.3).

**Table 1.** Indicator minerals in drill core and sediment samples from the Taurus region. N = the number of total samples; listed in each column is the number of samples in which the indicator mineral was observed.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mineralized/ altered core samples (N=14)</th>
<th>Sediment samples (N=27)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apatite</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>Bornite</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Chalcocite</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>14</td>
<td>17</td>
</tr>
<tr>
<td>Covellite</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Epidote</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>Jarosite</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Pyrite</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>Rutile</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>Svanbergite</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Titanite</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>Tourmaline</td>
<td>14</td>
<td>27</td>
</tr>
<tr>
<td>Zircon</td>
<td>14</td>
<td>27</td>
</tr>
</tbody>
</table>

Svanbergite [(SrAl₃(PO₄)(SO₄)(OH)₆] is an aluminum-phosphate-sulfate (APS) mineral found in some high sulfuration epithermal and porphyry Cu deposits, interpreted as an alteration product of apatite during advanced argillic alteration (Stoffregen and Alpers 1987; Hedenquist et al 2017). It was identified in 5 of 14 core samples and in sediment samples from McCord Creek, the east-west trending drainage that contains the Taurus West and East deposits as well as two smaller drainages, one of which is immediately north of the Bluff occurrence (Fig. 1). Minerals associated with svanbergite in sediment samples include quartz and Al-rich clays (dickite/pyrophyllite; Fig. 2). The fact that svanbergite was detected in thin sections of core at depths below the level of oxidation/supergene processes suggests it is a hypogene mineral. It was also detected in stream sediments as far as ~8 km downstream from the Taurus and below the Bluff occurrence, and therefore is one of the best indicator minerals for identifying “Taurus-like” porphyry systems. Unlike jarosite or chalcopyrite, which both occur in samples downstream from presumably younger epithermal occurrences, svanbergite occurs only in samples related to Taurus/Bluff.

4.3 Chemical composition of resistate minerals

Chemical compositions of resistate minerals in stream sediment samples may be useful for distinguishing mineralized sources. For example, based on preliminary electron microprobe and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) results, sediment samples along McCord Creek contain two populations of rutile: one with relatively low V contents compared to the other. Those with higher values are similar to rutile from mineralized core that contain V concentrations of more than 1,300 ppm. In addition, apatite from mineralized rocks have high Cl contents (0.5 to 0.8 wt. %), high La/Sm ratios and low Mn concentrations; a population of apatite with these characteristics is observed in sediment samples collected downstream from Taurus, and is chemically distinguishable from apatite that is likely from other sources. These preliminary data suggest that distinguishing different populations of specific minerals in sediment samples is possible. Additional mineral chemistry data are needed to further document this.

5 Comparison of PCIM results with other exploration methods

Reconnaissance geochemical surveys in the Taurus area by the U.S. Geological Survey in the 1970s included analyses of minus 80-mesh stream sediments analyzed by semi-quantitative emission spectroscopy. However, few significant anomalies of Au, Cu or other base metals are indicated, even within 1-2 km of the Taurus deposit. At the time, an experimental method was also introduced (and no longer available) that utilized an oxide residue (oxalic-acid leachable fraction) of stream sediment; this leachate residue effectively concentrated metals contained in secondary iron and manganese oxides, and
greatly enhanced the level of trace element content in the sediment samples (O’Leary et al. 1976).

Our studies are designed to duplicate the enhanced trace element signatures of the obsolete oxalic leach method by testing various size fractions of sediment and partial leach methods. Results indicate that the minus 230-mesh (<63 µm) fraction using a cold hydroxylamine leach provides the greatest contrast in copper concentration and the largest footprint in and near the Taurus deposit, but evaluation and interpretation of the data are ongoing.

Results of our hydrogeochemical study suggest that high resolution analyses (ICP-MS) of stream water samples provide another promising method for detection of concealed mineralization at Taurus. Past hydrogeochemical studies at the Pebble (Eppinger et al. 2012) and Whistler deposits (Graham et al. 2015) show that in addition to Cu, low-level anomalous concentrations for some elements (e.g., Ag, Mo, Re, V) are highly effective in vectoring to mineralized areas. Our results at Taurus are similar, including Re concentrations >0.009 ppb and SO4 contents >100 ppm in all stream waters from McCord Creek and near the Bluff prospect, values that greatly contrast with background stream water values.

6 Conclusions

The PCIM method in stream sediment samples is an effective exploration tool in the Yukon-Tanana uplands, an area with abundant ash and loess in soils and stream valleys that dilute the geochemical signal, together with low gradient streams that limit sediment transport. The best indicator minerals in stream sediments are chalcopyrite, jarosite, and svanbergite because they are observed in all samples immediately downstream from the Taurus deposit, and near the Bluff porphyry occurrence. Furthermore, the chemical composition of resistate minerals such as apatite and rutile show potential for distinguishing mineralization-related grains from grains in barren rocks. The PCIM method, together with hydrogeochemistry and partial leach geochemical data for sediment samples not only identify anomalous areas but may provide information about the type of mineralization (epithermal vs porphyry) and/or alteration that is present in a given drainage basin.

Acknowledgements

We thank Kristian Price, Sarah Bala, and Kelsey Livingston for help with sample preparation and analyses. Kenorland Minerals allowed access to the property and provided information critical for interpretation of our results. We thank George Case and Bronwen Wang (USGS) for their thorough reviews.

References


1316 Life with Ore Deposits on Earth – 15th SGA Biennial Meeting 2019, Volume 3
Titanite geochronology and chlorite chemistry resolve multiple phases of propylitic alteration in the Oyu Tolgoi district, Mongolia

Lisa Hart1,2, Jamie J. Wilkinson1,2 and Robin Armstrong2
1Department of Earth Science and Engineering, Imperial College London, UK
2LODE, Department of Earth Sciences, Natural History Museum, UK

Abstract. A new frontier in exploration geochemistry is the development of techniques that detect orebodies located at depth. The propylitic halo is the most extensive footprint of porphyry systems and may be the only exposed part of a buried ore system, so is at the heart of such research. Key trace elements within propylitic minerals, such as chlorite, can vary systematically with distance from known orebodies, therefore, can be used as vectors to ore.

Porphyry systems form in active tectonic settings so alteration can be overprinted by later events, particularly in ‘older’ camps such as the Paleozoic Oyu Tolgoi deposits of Mongolia. In such complex terranes, successful exploration relies on distinguishing porphyry-related assemblages from later overprinting events.

New LA-ICP-MS U-Pb dating of propylitic titanite identified hydrothermal events occurring at approximately 370 Ma, 340-320 Ma and 290 Ma. These dates broadly match known magmatic events: Devonian porphyry mineralization; Carboniferous granodiorite intrusions; and the emplacement of the Permian Khanbogd Granite. The distribution of these dated samples suggests that post-mineralization alteration overprinted significant portions of the porphyry halo.

Using the samples with dated alteration, it has been possible to develop a geochemical classification system that can distinguish between porphyry-related chloride, and later non-porphyry chlorite.

1 Introduction

The development of new exploration tools has been a recent focus of ore deposits research as large orebodies are now more likely to be located at greater depths, and are therefore more difficult, and expensive, to find using existing techniques. The use of mineral trace element chemistry is currently being investigated as one approach to the development of such tools for porphyry exploration (e.g. Wilkinson et al. 2017).

There are two main avenues currently being researched. The first focusses on identifying trace element signals within primary or secondary minerals to understand something about the type or “fertility” of an exploration target; some key fertility indicator minerals include zircon (e.g. Loader et al. 2017), plagioclase (Williamson et al. 2016), apatite (e.g. Rukhlov et al. 2017), epidote (e.g. Cooke et al. 2014) and chlorite (Pacey 2017). The second approach addresses spatial patterns in the trace element chemistry of secondary alteration minerals as potential vectors towards ore. Minerals that have shown the best potential for this so far are epidote (Cooke et al. 2014; Wilkinson et al. 2017), chlorite (Baker et al. 2015; Wilkinson et al. 2015, 2017; Pacey 2017;) and magnetite (Sievwright 2017), all of which are commonly found in the propylitic halo, the largest and most laterally extensive alteration zone associated with porphyry deposits.

The extensive size of the propylitic halo means that it could be the only part of a porphyry system visible at surface, making it a useful guide to buried ore deposits where other evidence is lacking. The mineral indicator studies of propylitic halos published to date have been on relatively pristine porphyry systems, such as Batu Hijau, Indonesia (Wilkinson et al. 2015) and Northparkes, New South Wales, Australia (Pacey 2017), where post-mineralization events have not extensively affected the deposit. Consequently, little is known about how trace element patterns and fertility signals are affected in situations where later metasomatic or metamorphic events have extensively overprinted earlier propylitic assemblages. Understanding these effects is an important consideration in the application of these tools in older, geologically complex, porphyry belts, if such geochemical exploration tools are to function.

Dating viable propylitic minerals, such as titanite, is one way that an alteration assemblage in a rock can be linked to the porphyry mineralizing event in a district. However, the time and cost involved in such geochronological techniques preclude this as a routine tool for regional exploration applications. One way to circumvent this problem is to establish a geochronological framework in a subset of samples and then utilize the trace element signatures of other propylitic minerals in the same assemblages to define a set of multivariate signatures that are age-related. These can then be tested for using more routine mineral chemistry on a much wider suite of regional samples. This study applies this methodology to resolve and chemically characterize multiple alteration events in the geologically complex Oyu Tolgoi (OT) porphyry district, Mongolia. A total of 312 drill core and regional surface samples were collected for this study and investigated using hydrothermal titanite dating and chlorite trace element analysis.

2 Oyu Tolgoi Geology

The Oyu Tolgoi porphyry district comprises eight, closely
spaced, deposits along 26 km of the NNE-oriented Oyu Tolgoi trend. The ore bodies are associated with Late Devonian (~372 Ma) porphyritic quartz monzodiorite (QMD) stocks and dykes, intruded into calc-alkaline arc volcanics of the Lower Devonian Oyu Tolgoi Sequence (Figs. 1 and 2; Crane and Kavalieris 2013).

Mineralization occurs in a central stockwork of A-type quartz veins, and is predominantly hosted within the inferred causative intrusions themselves and the porphyritic augite basalt host rock of the Oyu Tolgoi sequence (Crane and Kavalieris 2013).

Figure 1. Geological map of the Oyu Tolgoi porphyry district showing orebody locations. Map data courtesy of Rio Tinto.

Hydrothermal alteration around the Oyu Tolgoi deposits is typical of porphyry systems, with early sodic-calcic alteration at depth in the system core that is overprinted by potassic alteration which itself grades laterally outwards into propylitic alteration. Sericitic alteration forms an upward flaring cone above the potassic zone, and can also overprint potassic alteration in the core. The propylitic halo is zoned. The innermost subzone is characterized by the presence of K-feldspar, epidote and pyrite. Beyond this is the epidote subzone, which is the most widespread propylitic zone and is characterized by the assemblage epidote-albite-calcite-titanite-andradite. The outermost chlorite subzone is rarely observed, being largely truncated by faults.

Granodiorite plutons that were intruded along major faults during the early- and mid-Carboniferous and the intrusion of the Khanbogd granite in the Permian also generated propylitic alteration in the district that overprinted the porphyry halo.

3 U-Pb Dating of Propylitic Titanite

In this study, in-situ LA-ICP-MS U-Pb geochronology of hydrothermal titanite was used to date different generations of propylitic alteration in a subset of 20 samples. Thirteen samples returned well-constrained titanite dates, with relative errors of less than 10%. Of these samples, four resolved Devonian ages, three yielded Carboniferous ages, and two yielded Permian ages; the remaining four samples produced intermediate ages (Fig. 2). Several samples yielded very large errors and did not usefully resolve any date for the alteration in those rocks.

By plotting all the titanite U-Pb data on a probability density plot, four major phases of alteration can be identified, with peaks at 370 Ma, 340 Ma, 320 Ma and 290 Ma (Fig. 3a). These dates are consistent with known magmatic events in the district (Fig. 3), corresponding to: (1) porphyry mineralization in the late Devonian; (2) the intrusion of granodiorite plutons and andesite dykes in the early Carboniferous; (3) a second pulse of granodiorite plutonism in the mid-Carboniferous; and (4) the emplacement of the giant Khanbogd Granite in the Early Permian (Fig. 3b).
4 Chlorite Chemistry

All samples containing chlorite in the alteration assemblage were analyzed by LA-ICP-MS for major and trace element concentrations. The nine samples yielding well-constrained titanite dates were grouped so that the geochemical signature of associated chlorite could be determined (see Fig. 2).

4.1 Chlorite classification

The major element chemistry of chlorite from each alteration event is distinct, with the lowest Al and Fe and highest Mg in the inferred Devonian chlorites; progressing to moderate values in the Carboniferous chlorites; and the lowest Al and Fe and highest Mg in the Permian chlorites (Fig. 4). Similarly, concentrations of several trace elements, in particular La, Zn, Ni and Co, varied significantly between the groups (Fig. 4); further evidence for multiple generations of propylitic alteration, each with a unique chemical signature.

A chlorite classification plot was then constructed using discriminant projection analysis to create multivariate parameters that incorporate all of these key elements. This plot was then used to classify the wider chlorite dataset, so that all Devonian-classifying chlorite could be interrogated for geochemical vectoring potential.

4.2 Geochemical vectoring

Wilkinson et al. (2015) devised several elemental ratios in chlorite that could be used to vector towards a porphyry deposit. In order to amplify systematic patterns in chlorite chemistry across the propylitic halo, elements were selected for the numerator that are highest in the system core and progressively decrease outwards (e.g. Ti, Mg), and elements with the opposite behavior were selected for the denominator (e.g. Sr, Ca).
Exploration techniques. Needed prior to the application of geochemical porphyry signature, and so a pre-classification step is expected that successive magmatic events obscure the therefore be reserved for complex terrains, where it is alteration may not be an issue. This work flow should necessary in younger porphyry terrains as overprinting of geochronology of co-existing titanite to filter the chlorite data prior to non-mineralized hydrothermal sources in this way is critical to the successful development and application of geochemical tools in exploration.

Now that the porphyry chemical signature in chlorite has been established at OT, the next step for regional exploration would be to classify chlorite in a regional set of samples, spanning a much wider area that could identify any undiscovered mineralized porphyry targets in the region. An important consideration when using geochemical vectors in exploration in this way, is that the trace element signatures that vector towards ore in one mineral camp, may not always be applicable in other provinces, as external factors, such as fluid chemistry, are likely to vary. For this reason, it may be feasible to extrapolate results from successful greenrock studies on a provincial or even global scale in the case of early stage target generation/greenfield exploration, where other information is lacking. However, in brownfield exploration, where there are already one or more well-tested deposits, it is far more effective to utilize all available resources, such as drill core, to first carry out an orientation study for that particular district. Such a study would identify any geochemical fertility signatures or vectors to ore within the alteration halo that are specific to porphyry mineralization at that locality. Results from such a study could then be implemented to find the most prospective targets in extensive regional exploration programs.

The initial step taken in this particular study, that uses geochronology of co-existing titanite to filter the chlorite data prior to geochemical vectoring, may not be necessary in younger porphyry terrains as overprinting of alteration may not be an issue. This work flow should therefore be reserved for complex terrains, where it is expected that successive magmatic events obscure the porphyry signature, and so a pre-classification step is needed prior to the application of geochemical exploration techniques.

**5 Discussion and Conclusions**

Through the application of hydrothermal titanite U-Pb geochronology and chlorite trace element chemistry, it has been possible to discriminate between different generations of alteration and to “see-through” overprinting assemblages in the rocks to the geochemical fertility and vectoring signals in the porphyry propylitic alteration beneath. In complex mineral camps such as OT, the ability to identify and discard unwanted alteration mineral data from non-mineralized hydrothermal sources in this way is critical to the successful development and application of geochemical tools in exploration.

Acknowledgements

This study was part of a PhD research project funded by Rio Tinto and Imperial College London. I would like to extend my gratitude to the Rio Tinto Exploration - Project Generation Group, in particular to their leader Paul Agnew and my PhD supervisor Debora Araujo for their ongoing support throughout the project. Titanite U-Pb dating was conducted at the School of Earth and Environment at the University of Portsmouth, we would like to thank Craig Storey and Stephanie Lasalle for their significant contribution to data collection, processing and interpretation. Staff in the Imaging and Analysis Centre at the Natural History Museum, in particular Olara Wilkinson, William Browncombe, Yannick Buret, John Spratt, Inja Thijssen and Elly Harman are thanked for help with SEM and LA-ICP-MS analysis. We acknowledge the extensive field support of geologists and staff at Oyu Tolgoi Ltd., in particular thanks goes to Oggy Togtokhbayar and Alan Ketaren.

**References**


Hyperspectral image analysis of Aguas Teñidas, Magdalena, Sotiel and Majada deposits: towards a drill-core scan in the Iberian Pyrite Belt

Pedro S.T. Mendes, Pierre Barnabé, Eric Pirard
Minerals Engineering, Materials and Environment (GeMMe), Université de Liège, Belgium

Juan Manuel Pons, Juan Carlos V. Vasquez
Minas de Aguas Teñidas SAU (MATSA), Spain

Carlos G. Piña
DMT GmbH & Co. KG

Abstract. Analysis of VNIR-SWIR hyperspectral images is presented to assist the development of a multi-sensor scanning system for Iberian Pyrite Belt Cu-Zn-Pb projects. Fisher Linear Discriminant and Linear Support Vector Classifier were used for supervised classification after pre-processing, spectral plotting and construction of false color composites. Validation is given by mean accuracy of confusion matrices for different scenarios considering parameters of practical applications in industrial settings. Interpretation indicates a different performance for shale and volcanic-hosted deposits. The results demonstrate the power of machine learning algorithms and hyperspectral databases applied to an automated technique to assist the traditional logging. Combined to other sensors, the methodology should be adapted to a drill-core scan delivering cost-effective and time-saving outcomes.

1 Introduction

Hyperspectral imaging (HSI) concentrates on the diversity of spectral properties inherent to each material. In other words, the light that is emitted or reflected and its variation along narrow wavelength ranges. The link between these physical properties and earth sciences has emerged to map geological parameter in different scales (Hunt 1977; Goetz et al. 1985).

The logging of drill cores has been carried out by geologists using visual inspection. Despite providing important basic information, the technique has demonstrated to be subjective. In this work, the potential of machine learning algorithms combined to HSI is evaluated as an automated logging tool by testing different supervised classification strategies. The chosen method is considered supervised because it is assisted by a previous user knowledge (Han et al. 2012).

This research aims to contribute to the classification of rocks in the Iberian Pyrite Belt volcano-sedimentary complex in a consistent manner. The work comprises a fundamental step of ANCORELOG, an EIT Raw Materials-funded project working on the development of a multi-sensor analytical drill-core scan. Finally, the new prototype will extend the functionality of DMT CoreScan System, improving utilization of ore bodies from exploration to mineral processing (Lamberg 2012).

Predictions of performance in practical applications are evaluated for the following Cu-Zn-Pb ventures: Aguas Teñidas and Patata Frita (ATE); Magdalena (MAG); Sotiel and Elvira (SOT); also, the drilling campaign of Majada (MAD). The underground mines and surface exploration areas associated to each deposit are illustrated in Fig. 1.

Figure 1. Study area (Mendes 2018).

2 Methodology

2.1 Sampling

Characterization was carried out through visual drill core logging and mine front description. The divergence between two metallonegetic environments was considered (Martin-Izard et al. 2016): Shale hosted deposits of Type 1 (SOT and MAD) and Volcanogenic Massive Sulphides (VMS) of Type 2 (ATE and MAG), where extrusives dominate.
In total 40 samples were collected following a systematic protocol to ensure representativeness of lithology, texture, alteration degree and metal grade. Chemical assays of valuable metals and penalty elements from 10 mineralized samples with cupriferous stockwork and massive cupriferous/polymetallic ore were given by ICP-OES. Main minerals are chalcopyrite, sphalerite and galena.

2.2 Image acquisition and pre-processing

The images were acquired using a Specim SWIR camera and a VNIR, which is composed by a Specim ImSpectorV10E spectrograph and a Photonfocus MV1-D1312ie sensor (Fig. 2). Both cameras are placed horizontally over a 2.5 m frame to detect the reflected light from the samples in a line pointing the conveyor belt through mirrors (Barnabé et al. 2015). The approximately 350 mm line in the field of view is placed at the focuses of extruded elliptical reflectors so it is illuminated with constant light by halogen lamps, that are situated at the other focuses.

By combining data from two sensors, the result image is composed by 323 bands of 6.25 nm and digital pixels of approximately 0.25 mm². Images were spatially cropped to keep only regions of interest, avoiding long computational time. Bands up to 500 nm were considered noisy due to the high variation of pixel intensity within the spectra, which masks mineral overtones. This wavelength range was therefore removed to avoid algorithm’s confusion regarding true classifications.

2.3 Spectral response

The mean spectrum of each sample was extracted from a random 20 x 20 - pixel window and plotted in a reflectance versus wavelength chart. This procedure along with False Color Composites (FCC) assisted interpretation of classification challenges to segregate rocks with similar spectral response.

Three bands were extracted from the SWIR database to highlight the presence of alteration minerals with deep absorption in the spectra. The 1940, 2200 and 2340 nm ranges were associated to the bands of an RGB image (Table 1), where reflectance is attenuated due to the presence of water, white mica and carbonate / chlorite / amphibole / white mica, respectively.

Since pixel intensity decreases in a specific wavelength interval when absorption occurs, the output represents relative concentrations where the target minerals are displayed by colors related to the opposite bands. White micas are normally concentrated in red-pinkish regions, water-rich material is represented by blue pixels and green areas are linked to carbonate / chlorite / amphibole / white mica occurrences and to the wooden box (GTK 2018 unpublished presentation).

Finally, saturation and contrast were enhanced to intensify local color transitions.

2.4 Supervised classification

Supervised classification was undertaken using machine learning algorithms in the perClass Library for Matlab (Fig. 3). The objective of supervised classification is to assign an image pixel to a known lithology. Dimensionality reduction with Principle Component Analysis (PCA) indicated a fall of overall performance and was initially rejected. The algorithms able to handle the dataset with satisfactory accuracy for convenient interpretation were selected: Fisher Linear Discriminant and Linear Support Vector Classifier (LSVC) (Table 2).

A total of 41 classes (samples + box) are combined to test two different strategies: First, VNIR and SWIR ranges are cropped from the dataset to evaluate the performance of cameras together and individually. Subsequently, the size of training set is modified to identify the sensitiveness of classification regarding the number of labelled pixels.
The approach represents the variation of scenarios ruled by accuracy and costs.

Accuracy is computed by the mean error over classes from a confusion matrix which shows the relationship between true labels and classifier decisions.

### 3 Results

In general, fault rocks and bright volcanics such as dacites, breccias and tuffites show similar profile due to the presence of water and OH-bearing molecules whereas calcite veins emphasize the very deep absorptions at 2340 nm (Fig. 4). The exceptions are rocks with strong silicification such as a few tuffs and the black rhyolite. Sulphides and shales display flat curves.

![Figure 4. Spectral response of Aguas Teñidas rocks (Modified from Mendes 2018).](image)

False Color Composites (Fig. 5) emphasize the difference between deposits of Type 1 (MAD and SOT) and Type 2 (ATE and MAG). While the latter display colourful regions, most of Type 1 samples contain dark pixels due to shales and massive/stockwork sulphides with lack of absorption features. Usually, volcanics have pink to greenish matrix where alumino-phyllosilicate-bearing zones are either intercalated or cut by thin veins of chlorite. The brightest green sample is the calcite vein located in the upper-right corner of ATE 2.

In addition, ATE 2 samples confirm an association of metal content and alteration aureoles in the Cu stockwork area of the deposit. As the segments move outwards from the mineralized zone, grey and greenish pixels are substituted by pink and reddish matrices. The network of thin veins of chalcopyrite immersed in a chloritic matrix decreases as the volume of barren sericite-rich material increases together with fine disseminated pyrite.

The supervised classification using both cameras and LSVC is the most consistent overall (Fig. 6). Average accuracy is close to 100% if LSVC is combined to many spectral bands. When only the SWIR data is used both algorithms show a slight increase in classification error. The incapability of LSVC of dealing within a small feature space is evident when only the VNIR camera is selected (78 bands). The algorithm loses almost entirely its capability of classification.

![Figure 5. True color composites for alteration minerals. MAD and SOT are included in Type 1 whereas ATE and MAG are Type 2.](image)

Another drawback of LSVC is time. The algorithm runs at low speed in most of the cases whereas decision time for Fisher is practically negligible in every scenario. Even though the accuracy of Fisher drops from almost 100% to 80% when only VNIR is used, the interpretation of images is still possible in this situation. In the case of SWIR by itself, time is the crucial parameter to elect Fisher as the best option.

![Figure 6. Most accurate classification scenario overall: VNIR-SWIR database, large training size and 41 class labels. LSVC performance is slightly more accentuated in this case. Accuracy for both type of deposits is close to 100% so that a comparison of misclassified pixels between them can be hardly evaluated through classified images (Mendes 2018).](image)
Overall sensitivity against training set for both classifiers is similar. However, Fisher is less accurate than LSVC at very limited subset fractions. Bearing in mind that some classes in the smallest training set (Tr4) are represented by around 5 pixels out of a test set containing 3 million pixels, the consistency of LSVC can be considered outstanding in terms of accuracy and image interpretation if applied to practical logging applications (Fig. 7).

Figure 7. Accuracy with varying training set sizes (Mendes 2018).

Performance reflects the variation of absorption features in the spectra profile, being more consistent for volcanics than fine clastics in every tested scenario of classification as seen in Fig. 8.

Figure 8. – Accuracy for the two deposit types (Mendes 2018).

4 Discussion

FCC and supervised classification reveal the ability of HSI to discriminate alteration degrees and rock types (Schneider et al. 2014). However, algorithms are dependent on investment in cameras and hardware.

Results demonstrate that reflectance and depth of absorption is extremely affected by grain size. Coarse material absorbs more radiation penetrating to the surface than fine grain size. The optical path is explained by the Labert-Beer Law (Zaini et al. 2012).

Since the diversity of lithologies increase in projects within time, the capability of both algorithms to deal with many classes is an advantage. Fisher is preferable over LSVC when time is crucial and when dealing with cameras independently. A significant increase in training set size can improve Fisher performance without compromising computational effort.

Areas at early exploration stages should consider a robust training set with a large number of classes from different parts of the IPB. On the other hand, drill holes from mine sites can count on a training set with restrict number of classes with only the known local lithologies.

5 Conclusion

A real performance can only be evaluated when applying decisions to complete drill cores on site. It should adapt the methodology to real geological sections where transitional contacts and textural variations are impractical to be sampled in a representative manner.

The analysis of spectral profiles with the support of FCC assists the re-construction of unbiased labels to define new logging classes. Automatization using HSI and machine learning can therefore simplify 3D models in the IPB. It can also save time and costs in projects where exploration rushes to find new deposits and to characterize the ore constantly feeding the plant.

This study successfully meets the first steps of ANCORELOG with promising business opportunities when applied to end-users such as mining companies and research institutes.

Future works should improve pixel-wise segmentation. Grades will be included through the fusion of HSI with the output of other sensors such as RGB camera, X-Ray Fluorescence (XRF), Laser Induced Breakdown Spectroscopy (LIBS) and time-gated Raman spectroscopy.

Acknowledgements

The authors would like to thank the involved team from MATSA and GeMMe for the constant support. Also, ANCORELOG partners, EMerald and EIT Raw Materials for the effort in education and research.

References


High-resolution short-wave infrared hyperspectral characterisation of alteration at the Sadiola Hill gold deposit, Mali, Western Africa

Semyon Martynenko, Pekka Tuisku
Oulu Mining School, University of Oulu, Finland

Frank J.A. van Ruitenbeek
Faculty of Geo-Information Science and Earth Observation (ITC), Netherlands

Kim A.A. Hein
School of Geosciences, University of Witwatersrand, South Africa

Abstract. Sadiola Hill is an ~8 Moz gold deposit located in western Mali within a ca. 2200-2050 Ma tectonic window known as Kédougou-Kénieba inlier (KKI), exposing the Western African craton. The deposit is hosted in a metasedimentary package made up of impure carbonate rocks, wackes, and arenites intruded by three distinct igneous phases. A N-S-trending Sadiola shear zone, related to the regional Senegal-Mali shear zone, and NNE-trending third order fault splays acted as conduits for auriferous hydrothermal fluid flow. The deposit has undergone a complex poly-phase alteration history. Alteration assemblages related to gold mineralization consist of biotite-carbonate-quartz-sulphide. Other assemblages include calc-silicates, chlorite, white mica, scapolite, and tourmaline (Hein and Tshibubudze 2007; Cameron 2010; Masurel et al. 2017). Current research is aimed at characterising alteration at the mineral-scale, as well as assessment of cooling trend(s) and alteration footprint(s) with high-resolution short-wave infrared (SWIR) hyperspectral scanning. In addition to detailed mineralogical classification, changes in fluid chemical parameters are determined with variations in white mica, namely, the position of Al-OH bond in the SWIR range and white mica crystallinity. Furthermore, hydrothermal fluid chemistry is assessed with Fe²⁺ content in carbonate group minerals. Protolith control on alteration expression is also investigated.

1 Introduction

Short-wave infrared (SWIR) hyperspectral imaging is a rapid and reliable technique for mineral identification. It has proven reliable at tracing hydrothermal fluid pathways in diverse range of deposit types, including orogenic gold systems in granite-greenstone terranes (van Ruitenbeek et al. 2012; Wang et al. 2017). In addition to precise identification of phyllosilicates and carbonates, SWIR spectroscopy identifies specific mineral parameters, such as Al-Si substitution in white mica, that correspond to physico-chemical changes of hydrothermal fluid (van Ruitenbeek et al. 2005). As such, it has become an effective vectoring tool in mineral exploration (Wang et al. 2017; Roache et al. 2011).

Current research investigates alteration assemblages within a world class Sadiola Hill gold deposit with SWIR hyperspectral imaging and conventional petrography. The study establishes paragenetic sequence and the number of hydrothermal events within the system. Spatial variation in the chemical composition of alteration minerals, and protolith control on alteration expression are also determined. The research is carried out on drill core samples from 6 diamond holes capturing the most representative alteration examples and is solely laboratory based. The core samples are scanned at medium (0.26mm pixel size) and high-resolution (26µm pixel size) scales. Paragenetic context of aspetral alteration mineralogy is determined with transmitted light microscopy. Spectral classes of the 26µm-pixel mineral maps are validated with petrographic observations and electron microprobe analyses.

2 Geologic setting

The West African craton exposed in the Kédougou-Kénieba inlier (KKI) is a unique Paleoproterozoic granite-greenstone belt as it contains a package of carbonate rocks of variable thickness not typical for other granite-greenstone belts worldwide. The KKI is comprised of series of volcano-plutonic belts and sedimentary basins dissected by two major regional faults, namely, the Main Transcurrent Zone (MTZ) and the Senegal-Mali Shear Zone (SMSZ). (Hein et al. 2015; Masurel et al. 2016). Previous studies have revealed that Sadiola impure carbonates are overlain by a package of greywacke. Impure carbonates and detrital sediments have been intruded by three intrusive suites: early diorite, quartz feldspar porphyry, and late diorite. The rocks have undergone a regional mid-greenschist facies metamorphism (Hein and Tshibubudze 2007; Masurel et al. 2017).

Sadiola Hill records a complex brittle-ductile history evident from 3 distinct pre- and syn-mineralization deformation events as well as two smaller scale brittle events postdating gold deposition (Masurel et al. 2017). The key structural features of the Sadiola Hill deposit include the N-S-trending subvertical to vertical Sadiola shear zone, and associated NNE-trending fault splays. The Sadiola shear zone marks the major structural break.
at Sadiola separating greywackes on the western side of the pit from marbles on the eastern side (Hein, 2008). Most notable is the D3 deformation event that resulted in sinistral reactivation of Sadiola shear zone and the NNE-trending splays and was syn-genetic to auriferous hydrothermal fluid flow along these structures (Hein and Tshibubudze 2007; Cameron 2010; Masurel et al. 2017).

Complex poly-phase alteration history at Sadiola Hill consists of ore stage K-feldspar-biotite-carbonate-quartz-sulphide potassic alteration assemblages. Other assemblages include calc-silicates related to contact metamorphism during emplacement of igneous suits into the sedimentary package, as well as chlorite, white mica, scapolite, and tourmaline (Hein and Tshibubudze 2007; Cameron 2010; Masurel et al. 2017).

3 SWIR hyperspectral imaging

3.1 Background

SWIR hyperspectral imaging uses light reflection in the 1000nm-2500nm range of the electromagnetic spectrum. Cation-OH, H2O, (CO3)2- in crystal structures reflect light in characteristic way producing diagnostic absorption features in the SWIR range (Clark 1999). White mica is characterized by absorption features positioned at 2200nm related to Al-OH bond, and 1900nm absorption feature corresponding to H-OH bond. Tschemak substitution of Al3+ by Fe2+ and Mg2+ in muscovite crystal structure shifts position of Al-OH bond to longer wavelength (Dalm et al. 2017). Illite spectral response shows a subtle difference from white mica responses, as illite also has a deep absorption feature around 2200nm related to Al-OH bond as well as OH and H-OH bonds at 1400nm and 1900nm respectively (Agus 2011; Clark 1999).

Actinolite-tremolite series are distinguished by hydroxyl stretching and bending vibrations located near 2320nm and 2390nm as well as ferrous drop (Laukamp et al. 2012). Epidote-clinozoisite series distinguished from chlorites by 1550nm absorption feature. Spectral responses of chlorite are attributed Mg-OH and Fe-OH bonds at ~2340nm and ~2250nm respectively that shift to longer wavelengths with Fe2+ substituting for Mg2+. Carbonate group minerals (Figure 2) are identified by (CO3)2- absorption band between 2300 and 2360nm combined with ferrous drop related to Fe2+ substitution into crystal structure (Clark 1999; Roache et al. 2011).

Figure 1. Sadiola Hill deposit geology after Masurel et al. (2017) Inset map shows deposit’s location near Senegal-Mali border in Western Africa.

3.2 Methodology

Hyperspectral scanning of drill core samples and offcut blocks was acquired at Faculty of Geo-Information Science and Earth Observation (ITC), University of Twente with Specim Hyperspectral camera at medium (0.26mm pixel size) and high-resolution (26µm pixel size). Data for each pixel is collected in x-, y-, and z-direction with x- and y-values of the pixel cube corresponding to length and width of a pixel within a horizontally stationed sample. Z-values represent a stack
of bands in the SWIR range with 12 nm spectral resolution, amounting for the total of 288 bands. Conversion of the raw data into calibrated hyperspectral images was done with hyperspectral python (hyppy), an in-house software developed in ITC. Calibrated images were converted into wavelength maps over 6 different ranges capturing depth and position of 1st, 2nd, and 3rd deepest absorption features. Decision trees are developed for project-specific mineralogy as matching algorithms between recorded bands to spectra from USGS spectral library. Polished thin sections were prepared from drill core samples scanned at high-resolution for one-to-one comparison of mineral maps to petrographic observations (van Ruitenbeek et al. 2017). Conventional transmitted light microscopy is added to the workflow to validate hyperspectral mineral maps and to add paragenetic constraints related to cross-cutting relationships and replacement textures to the interpretation. Exact stoichiometry of each spectral class is determined with electron microprobe.

Decision tree for muscovite and illite was constructed from combination of illite crystallinity, a ratio of depth of Al-OH absorption feature to the depth of water feature, and position of Al-OH bond. Overall, crystallinity was divided into 4 classes (>1, >2, >3, >4) based on observed variability in the samples. Position of Al-OH bond was assessed with 5nm breaks within Al-OH feature range.

Decision tree for carbonate group minerals has been developed based on Fe²⁺ drop values and presence of (CO₃)²⁻ absorption feature. Secondary Fe-OH feature near 2250nm was applied to filter out Fe-bearing phyllosilicates and epidote from carbonate classification. Position of the carbonate feature for ankerite, dolomite, and calcite were taken from the USGS spectral library and related studies (Kokaly et al. 2017).

Decision tree for classification of chlorites, calcic amphiboles, epidote and tourmaline was developed from combination of wavelength positions of the 1st and 2nd deepest absorption features in the 2100-2400nm range combined with position of the deepest features in 1850-2100nm and 1300-1600nm ranges. Ferrous drop was also utilized for tremolite-actinolite classification.

4 Preliminary results

Muscovite is more aluminous in igneous units in comparison to greywacke and impure carbonate reflecting availability of Al³⁺. In cases where Na⁺ is ubiquitous, e.g. tonalite unit, white mica composition changes to paragonite (Figure 3). Mineral-scale variations were also noted in muscovite. When muscovite replaces biotite, Al-OH feature shifts to longer wavelengths (~2210nm) consistent with incorporation of Mg²⁺ from biotite into muscovite crystal structure. Illite crystallinity has a common trend of increasing inward into a vein and is also protolith dependent, with low crystallinity illites constrained to greywacke and muscovite to igneous units and impure carbonates.
Overall, alteration mineralogy at Sadiola Hill is variable and strongly protolith-dependent evident from both white mica and carbonate chemistry. Reactive folded argillaceous laminae within the impure carbonate acted as chemical trap for gold mineralization during the D3 event. Biotite supplied iron for sulphidation reactions leading to pyrrhotite- arsenopyrite- chalcopyrite-sphalerite- pyrite- free gold precipitation (Figure 5). Dolomite-dominant laminae do not host sulphide-gold mineralization, but track CO₂ addition from auriferous fluid to impure carbonate host. Mineralization within greywacke is more sporadic with iron also sourced from biotite and is associated with patchy ferroan dolomite alteration, reflecting decomposition of silicates. Phlogopite occurs in all lithologic units in association with sulphides consistent with transition to Mg-rich silicate phase in response to ion consumption by sulphidation reactions.

Figure 5. Sample SD69 under crossed nicols showing argillaceous layer (outlined by dashed red line) within dolomitic impure carbonate unit. Note biotite-phlogopite-sulphide associations and fine-grained muscovite-dolomite aggregates. Abbreviations: Asp = arsenopyrite; Bt = biotite; Dol = dolomite; Ms = muscovite; Phl = phlogopite; Po = pyrrhotite.

5 Future work

Zonation of ore-stage carbonate group minerals and chemical variations of white mica proximal and distal to ore will be investigated further. Cross-cutting relationships and chemical composition of carbonates will be assessed with cathodoluminescence (CL). Furthermore, drill core samples scanned at 26µm resolution have been submitted for complete geochemical characterization to ALS Global (results pending). Trace element associations will compliment hyperspectral interpretation of the alteration footprint and cooling trends within the system. In addition, protolith control on mineralization and alteration expression will be further constrained.

Acknowledgements

Dr. Asinne Tshibubudze, School of Geosciences, University of Witwatersrand, is thanked for arranging funds for geochemical analyses for this project.

References


Application of ASTER Data for Exploration of Porphyry Cu-Au Deposits in the Neoproterozoic Arabian–Nubian Shield: a Case Study from Egypt

Hamdy El Desouky

Geology Department, Faculty of Science, Menoufia University, Menoufia, Egypt
Egyptian Academy of Scientific Research & Technology, Cairo, Egypt

Abstract. Porphyry deposits are the world's most important source of Cu and Mo and are major sources of Au, Ag and Sn. The deposits are characterized by widespread and distinctive hydrothermal alteration zones, which provide a useful footprint for exploration. The Arabian-Nubian Shield (ANS), the Earth's largest tract of juvenile Neoproterozoic crust, has an apparent lack of porphyry Cu-Au deposits. In this study, detailed image processing techniques were performed in ASTER satellite imagery to identify the hydrothermal alterations associated with Cu-Mo-Au mineralization in the South Um Mongul Porphyry System (SUMPS), in the northern Eastern Desert of Egypt, to enhance exploration of porphyry systems in the ANS. The hydrothermal alterations detected by the ASTER image processing techniques have shown a good correspondence with the hydrothermal alteration zones reported in the field at SUMPS. Moreover, when the techniques are expanded to cover a larger area surrounding the SUMPS, new undiscovered hydrothermal alteration zones have been detected. This implies that the applied ASTER image processing techniques are robust enough for mapping porphyry hydrothermal alterations, especially in the arid to semi-arid regions of the ANS (e.g., Egypt).

1 Introduction

Porphyry deposits are the world's most important source of Cu and Mo and are major sources of Au, Ag and Sn. They account for about 50-60% of world Cu production and more than 95% of world Mo production (Sillitoe 2010). Porphyry deposits are large, low- to medium-grade deposits, which are spatially and genetically related to felsic–intermediate porphyritic intrusions. The deposits are characterized by widespread and distinctive hydrothermal alteration zones, which provide a useful footprint for exploration (Abrams et al. 1983; Sillitoe 2010). Recent reviews of the porphyry system characteristics are provided by Cooke et al. (2005), John et al. (2010), Sillitoe (2010) and Wilkinson (2013). Because Cu porphyry deposits generally form in the upper crust, at less than 5-10 km paleodepths, in tectonically unstable convergent plate margins and are prone to erosion, more than 90% of known deposits are Cenozoic or Mesozoic in age.

The ANS, which extends from Egypt in the west to Saudi Arabia and Oman in the east and from Jordan in the north to Eritrea and Ethiopia in the south, constitutes Earth's largest tract of juvenile Neoproterozoic crust (Fig 1). The ANS has an apparent lack of porphyry Cu-Au deposits (e.g., Ahmed and Gharib 2016; Khalifa et al. 2016; Bierlein et al. 2016a,b; Abd El-Rahman et al. 2018) compared with its abundant orogenic gold deposits, which have been mined in Egypt for over 7,000 years (Botros 2004, 2015; Klemm and Klemm 2013). This lack is related either to preservation problems during tectonics or to lack of relevant exploration programs in the huge terrains of the ANS.

The recent free data availability of the remote sensing multi-spectral Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER; NASA 2001), offer geologists a potentially cost-effective alternative to expensive and time-consuming regional mineral exploration. Recent studies indicate that ASTER data can be used to map the hydrothermal alterations associated with porphyry ore deposits (e.g., Pour and Hashim 2011; Alimohammadi et al. 2015).

In this study, detailed image processing techniques were performed on ASTER satellite imagery to identify the hydrothermal alterations associated with Cu-Mo-Au mineralization in the SUMPS in the northern Eastern Desert of Egypt. The SUMPS was under exploitation for copper and gold during the Predynastic (ca. 3000 BC) and Arab (ca. 1350 AD) Periods (Klemm and Klemm 2013) and currently under development for reopening (Abd El-Rahman et al. 2018). The area has a well-defined surface geology, hydrothermal alteration and mineralization (Abd El-Rahman et al. 2017, 2018; Botros and Wietait 1997; Wietait and Botros 1997; Fig. 1). The results obtained from this test case study will enhance exploration of porphyry Cu-Au systems in the ANS.

2 Geology and Mineralization

The ANS is a north-south belt of folded, sheared, thrusted, and mostly moderately metamorphosed Neoproterozoic rocks of juvenile crust and represents an area of suturing between East and West Gondwana before the Paleozoic (Stern 1994). It formed through the accretion of numerous, mainly inter-oceanic, island arcs along ophiolite-lined suture zones and gneissic fault zones between 900 Ma and 550 Ma when the Mozambique ocean closed (Stern 1994). The basement rocks of the Eastern Desert of Egypt constitute the extreme northwestern part of the ANS.

The SUMPS is located in the northern segment of the Eastern Desert (Fig. 1a), which is characterized by lithologies with continental affinities, namely Dokhan...
Volcanics and Hammamat Sediments (Hassan and Hashad 1990), and by abundant granitic intrusions (Fig. 1b). It lacks lithologies with oceanic affinities, such as ophiolitic assemblages, which are common in the central segment of the Eastern Desert (Abd El-Rahman et al. 2017, 2018). The SUMPS is occupied by Tonian porphyritic dacite (773 ± 6.9 Ma) with continental arc tectonic setting intruded by Ediacaran post-collisional hornblende gabbro (603 ± 3.5 Ma) and monzogranite (558 ± 4.6 Ma; Abd El-Rahman et al. 2017; Fig. 1c).

According to Abd El-Rahman et al. (2018), there are two porphyry mineralization systems in the SUMPS. The older is a Cu-Mo porphyry-style, which is related temporally to the Tonain dacite (773 ± 6.9 Ma). This system is characterized by the presence of quartz-chalcopyrite-molybdenite veinlets associated with biotite-dominated potassic alteration. The younger system, which overprints the older one, is related to the Ediacaran post-collisional monzogranite (558 ± 4.6 Ma) and is similar in many aspects to the iron oxide-rich Cu-Au porphyry-style. This younger system evolved from quartz-magnetite veins with potassic selvages to quartz-spectacularite veins with more pervasive sericite-chlorite alteration (Abd El-Rahman et al. 2018).

3 ASTER Data

A cloud-free scene of ASTER Level 2 Surface Reflectance VNIR and SWIR V003 (AST_07) covering the study area was obtained from NASA (2001). The scene was acquired daytime in 29 April 2001 and pre-georeferenced to UTM zone 36 north projection using the WGS-84 datum. Radiometric, geometric and atmospheric corrections were applied on the image data. The SWIR data were further corrected for cross-talk and parallax errors due to the spatial locations of SWIR bands. The ASTER Level 2 Surface Reflectance image is composed of 9 spectral bands with different spatial resolutions (3 VNIR at 15m and 6 SWIR at 30m; Table 1; NASA 2001). Spectral resampling has been used to downscale the spatial resolution of the 6 SWIR ASTER bands to 15m resolution, then, the data has been resized to the coordinates of the SUMPS and the surrounding basement rocks (e.g., Fig. 3). The ASTER data was processed and analyzed by the ENVI (Environment for Visualizing Images) software package.

4 ASTER Image Processing

Several robust and reliable image-processing techniques, including, principal component analysis (PCA), minimum noise fraction (MNF), band ratio and band math were applied based on spectral characteristics of alteration key minerals for a systematic selective extraction of hydrothermal alteration zones in the SUMPS area and the surrounding areas. The processed images were displayed in RGB color channels to generate false color composites in order to highlight the hydrothermal alteration zones. The results of ASTER image processing were compared with the well-known hydrothermal alteration of SUMPS for validation (Fig. 1c; Abd El-Rahman et al. 2018; Botros and Wetait 1997).
### Bands and Wavelengths

<table>
<thead>
<tr>
<th>Bands</th>
<th>Wavelength (µm)</th>
<th>Description</th>
<th>Res. (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VNIR Band1</td>
<td>0.520 to 0.600</td>
<td>Visible (G/Y)</td>
<td>15</td>
</tr>
<tr>
<td>VNIR Band2</td>
<td>0.630 to 0.690</td>
<td>Visible (R)</td>
<td>15</td>
</tr>
<tr>
<td>VNIR Band3N</td>
<td>0.760 to 0.860</td>
<td>Near infrared</td>
<td>15</td>
</tr>
<tr>
<td>SWIR Band4</td>
<td>1.600 to 1.700</td>
<td>Short-wave infrared</td>
<td>30</td>
</tr>
<tr>
<td>SWIR Band5</td>
<td>2.145 to 2.185</td>
<td>Short-wave infrared</td>
<td>30</td>
</tr>
<tr>
<td>SWIR Band6</td>
<td>2.185 to 2.225</td>
<td>Short-wave infrared</td>
<td>30</td>
</tr>
<tr>
<td>SWIR Band7</td>
<td>2.235 to 2.285</td>
<td>Short-wave infrared</td>
<td>30</td>
</tr>
<tr>
<td>SWIR Band8</td>
<td>2.295 to 2.365</td>
<td>Short-wave infrared</td>
<td>30</td>
</tr>
<tr>
<td>SWIR Band9</td>
<td>2.360 to 2.430</td>
<td>Short-wave infrared</td>
<td>30</td>
</tr>
</tbody>
</table>

### PCA

PCA is a multivariate statistical technique that selects uncorrelated linear combinations (eigenvector loadings) of variables in such a way that each component successively extracted linear combination and has a smaller variance (Chang et al. 2006). A standard PCA transformation was applied to the VNIR and SWIR ASTER data.

The MNF transformation is used to determine the inherent dimensionality of image data, segregate noise in the data, and reduce the computational requirements for subsequent processing (Green et al. 1988). A standard MNF transformation was applied to the VNIR and SWIR ASTER data (Fig. 2).

Band ratio is a technique where the digital numbers (DN) of one band are divided by the DN values of another band. This technique is very useful for highlighting certain features or materials that cannot be seen in the raw bands (e.g., Inzana et al. 2003). A large number of band ratios was performed in the ASTER data, the best results include: 4/2, 4/5, 5/6 in RGB (Fig. 3); 4/5, 4/6, 4/7 in RGB (Fig. 4) and 5/6, 7/6, 7/5 in RGB.

Band math is a technique, which allow inserting the DN values of bands in mathematical formulas, e.g., to calculate the mineralogic indices of Ninomiya (2003). The performed indices include, the OH bearing altered minerals index (OHI = 7/6*4/6), the kaolinite index (KLI = 4/5*8/6), the alunite index (ALI = 7/5*7/8) and the calcite index (CLI = 6/8*9/8).

The ASTER image-processing techniques, which have shown good correspondence with field data at SUMPS were re-applied to a larger area of the basement rocks to test the technique in exploring areas with similar hydrothermal alteration to SUMPS (Fig. 5).

### 5 Discussions

The performed ASTER image processing techniques allowed detecting a hydrothermal alteration zone in the area of SUMPS (Figs. 2-4). In this zone, the hydrothermal alteration minerals are intercalated with unaltered rocks in accordance with field observations and mapping (Abd El-Rahman et al. 2018; Botros and Wetait 1997; Wetait and Botros 1997; Fig. 1c). In addition to this zone, at least two other hydrothermal alteration zones were detected at...
the north and northwest of the SUMPS (Figs. 2-4). These zones could be related to the same porphyry system or to an undiscovered epithermal system. Moreover, when the technique is expanded to cover a larger area surrounding the SUMPS (Fig. 5), more hydrothermal alteration zones with apparent similar characteristics to the zones of SUMPS have been detected. These zones could represent undiscovered porphyry systems. This imply that the applied ASTER image processing techniques are robust enough for mapping regional hydrothermal alterations, which footprint porphyry copper systems, especially in arid to semi-arid regions of the ANS (e.g., Egypt).

**Figure 5.** Band ratio composite image of ASTER bands 4/2, 4/5, 5/6 in RGB, applied to the area surrounding the SUMPS. Hydrothermal alterations similar to SUMPS are outlined by ovals.

**Acknowledgements**

The financial support of the Egyptian Academy of Scientific Research & Technology and the Menoufia University is highly acknowledged.

**References**


Structural-geochemical vectors for cost-effective targeting of unconformity-type uranium mineralization: the Maverick uranium deposit case study

Ranee E. Joshi, Irvine R. Annesley, Gautier Laurent
Université de Lorraine

Christine L. McKechnie
Skyharbour Resources

Zoltan Hajnal
University of Saskatchewan

Abstract. Bridging the gap between the increasing exploration cost, decreasing U₃O₈ spot price, and the number of new uranium discoveries, this paper presents new vectoring tools developed from an improved understanding of the Maverick uranium deposit (MUD), Athabasca Basin. These vectors include critical geochemical anomalies, structurally controlled fluid pathways, and/or structural-geochemical traps. Geochemical studies of the MUD, show a distinct zoning of alteration clay minerals around uranium mineralization. The fault damage zones can be correlated with major elements and trace elements, including Be, Ni, Zn, Rb, Nb, Ba, Ce, Sm, Eu and Tm. Gd and Tb are good vectors both in the basement and basin lithologies. Base metals are good indicators for proximity to uranium deposits, but their signatures are not evident above the sedimentary package. Sb, V, and Cd can be used to vector toward the uranium mineralization from the surface. Incorporating vectoring studies within an exploration company’s business model provides multiple advantages. In the case of the MUD, an estimated exploration cost of ~3 million US$ could have been saved by reducing costly drilling programs in the early stages of exploration and focusing on structural mapping and near-surface geochemical sampling after the initial ~40-50 exploratory/discovery holes.

1 Introduction

Uranium oxide is a radioactive, silvery-white metal (element 92 in the periodic table) that has been used as a yellow-orange pigment for coloring glass, military purposes, and for electrical power generation. In 2003, a renewed interest due to its neutral impact on greenhouse gas emissions (Lehmann 2008) caused a ten-fold price hike; reaching a maximum price in June 2007 of US$135 per pound. However, the Fukushima Daiishi accident in Japan in 2011 slowed uranium activities with spot prices approaching near historic lows (Nuclear Energy Agency and International Atomic Energy Agency 2016). At present, the U₃O₈ price is at US$28/lb, after bottoming out US$18/lb in 2016.

Unconformity-type uranium deposits, which make up a third of uranium resources, have grades 3-100 times higher than any other types of deposit (Jefferson et al. 2007). The Athabasca Basin is the main host for unconformity-type deposits and has an estimated resource more than 373,000 t U (Thomas et al. 2000). Most of the known mineralization zones are located on the eastern side of the Athabasca Basin at, above, and/or below the unconformity. The uranium grades and tonnages of the Cigar Lake (15%, 131,000 tonnes) and McArthur River (22%, 192,000 tonnes) deposits in the Athabasca are very high, giving the whole Athabasca Basin an average grade of 1.97% (Jefferson et al. 2007). Given the high uranium grade and tonnage as well as the increase in uranium demand, exploration in the Athabasca has been very active. However, many of the recent discoveries have much lower grades and tonnages, i.e. Millennium deposit (4.53%, 18,000 tonnes). Exceptions to this would be the Phoenix deposit; one of the highest grade unmined deposits, and Arrow, the largest unmined deposit.

As newly discovered uranium deposits have significantly lower grades and the U3O8 market price is much lower, the price for exploration is consistently increasing. The cost of drilling alone ranges from 100 $/m to 350 $/m. This situation calls for improvements in the exploration process, wherein the available geological information is maximized, and the costs are reduced. This paper presents geochemical and structural signatures related to potentially mineralized uranium unconformity-type zones.

2 Geologic setting

The Maverick Uranium Deposit (MUD) occurs within the eastern Athabasca Basin (Saskatchewan, Canada), a Paleoproterozoic to Mesoproterozoic sedimentary basin in northern Saskatchewan and northeast Alberta (Jefferson et al. 2007). The Athabasca Basin is estimated to have a present-day maximal depth of around 1500 m (Györfi et al. 2007; Rainbird et al. 2007; Ramaekers et al. 2007). The basin was deposited between 1.76 Ga and 1.5 Ga (Ramaekers et al. 2007) above a regional angular unconformity separating unmetamorphosed flat-lying
nearly undisturbed sediments from the highly deformed and metamorphosed basement of the southwestern Churchill Province.

MUD’s basement consists of deformed and metamorphosed Archean/Paleoproterozoic rocks of the Hearne subprovince of the western Churchill Province. The Hearne Province is separated from the Rae Province by the Snowbird Tectonic Zone (STZ), a continental scale Paleoproterozoic suture zone; the STZ is located close to the center of the Athabasca Basin (Hoffman 1988). The Hearne Province underwent high-grade deformation and metamorphism during the continent–continent collision of the Trans-Hudson Orogen (1.8 Ga) (Bickford et al. 1990; Card et al. 2007; Lewry and Sibbald 1980; among others). Structural studies of the eastern Athabasca region highlight four lithostructural domains from west to east (Annesley et al., 2005): Mudjatik Domain (MD), Wollaston-Mudjatik Transition Zone (WMTZ), Western Wollaston domain (WWD) and Eastern Wollaston Domain (EWD). The MUD straddles the transition between the Western Wollaston Domain (WWD) and Eastern Wollaston Domain (EWD) of the Athabasca Basin (Fig. 1), forming part of the former JNR Resources (now Skyharbour Resources) Moore Lakes Project.

MUD is unconformably overlain by Athabasca sandstone with a thickness about 275 meters; the sandstone on the project generally thickens from the southeast to northwest. It lies above a well-defined east-west striking (80 degrees) paleotopographic high coinciding with the subvertical to inclined, dextral D3 strike-slip Maverick structure (Figs. 1 and 2). The Maverick Structure is an inferred to be a reactivated D1-D2 thrust fault. This early thrust is characterized by a graphitic unit between two basement rocks: Archean granite in the footwall and pelitic gneiss in the hanging wall. The Maverick mineralization occurs within the dipping graphitic unit with little or no offset (i.e. strike-slip system) and the majority of mineralization occurs at or above the unconformity, with limited basement-hosted mineralization. Potential for basement-hosted mineralization is unknown, although recently Skyharbour Resources has found some.

The geochemical analysis is based mainly on JNR Resources Inc.’s geochemical and assay database, comprising historic data and unpublished assessment file data collected between 1997 and 2007. It is composed of 11956 measurements in 285 holes at and around the Maverick uranium deposit; including 252 mineralized drill holes. This unpublished data for the basin and the basement were made available from assessment file downloads by the 2nd author for the 1st author’s Master’s thesis project.

Data available

The geochemical analysis is based mainly on JNR Resources Inc.’s geochemical and assay database, comprising historic data and unpublished assessment file data collected between 1997 and 2007. It is composed of 11956 measurements in 285 holes at and around the Maverick uranium deposit; including 252 mineralized drill holes. This unpublished data for the basin and the basement were made available from assessment file downloads by the 2nd author for the 1st author’s Master’s thesis project.

The iogAS software was used for the geochemical modelling. Intensity of hydrothermal alteration zones and the degree of magmatic differentiation in the basement intrusive rocks (i.e. potential source rocks) were assessed through geochemical modeling. In addition, erratic U anomalies were correlated with minor and trace elements to vector towards mineralization.

Unconformity-type uranium vectors

Alteration mineral assemblages

The clay alteration observed in MUD is defined by distinct alteration haloes continuing to the top of the Manitou Falls graphitic pelitic gneisses are weakly to intensely altered, including within localized intervals where graphite is partially to completely destroyed and carbonaceous matter is deposited hydrothermally. Within the basin, the Maverick structure is surrounded by a damage zone which comprises intensely altered, desilicated, bleached Manitou Falls sandstone. This zone...
is strongly altered to kaolinite and dravite, and extends upwards to ~140 meters above the unconformity. In the basement, the variably altered (to clay minerals and secondary chlorite) crystalline rocks include a number of sheared, brecciated, and fault-gouged intervals. Around this highly faulted zone is a broad illite halo extending about 120 meters from the fault core. The outer shell of the alteration (i.e. the least structurally disturbed zones) changes abruptly to dickite-dominated sandstone (Fig. 3). It extends laterally throughout the Maverick structure and downward to the unconformity at about 275 meters. This suggests that the alteration feature is controlled by the orientation and dip of the Maverick structure, coinciding in part with the graphitic pelitic gneiss. The

**Figure 3.** Simplified schematic diagram showing the different alteration haloes in the Maverick Uranium Deposit.

### 4.2 Geochemical signatures

To understand the geochemical anomalies related to the uranium mineralization, the correlation between U% and major and trace elements was computed to help recognize the geochemical signature of the MUD. The data from MUD confirms expected correlation between uranium and base metals such as Pb, Co, Ni, Zn and Cu. Mineralized samples (>0.005% U) correlate with Pb, Co, Hg, Pr, V, Sm, Sc, Sn, Dy, Bi, Yb and Eu. MFa, the main host of mineralization varies well with Hg, Pr, Pb, Co, Ni, Zn, V, Sm, Dy, Bi, Th, Tb, Gd, Er. The uranium in clay varies strongly with Tb. Uranium in mineralized graphitic pelitic gneisses also varies with Sb and As.

The mineralized and fault-damaged zones can be correlated with Na₂O, MgO, K₂O, CaO, MnO, P₂O₅, Fe₂O₃, Be, Ni, Zn, Rb, Nb, Ba, Ce, Sm, Eu, Gd and Tm anomalies. The electromagnetic (EM) conductors and their associated lithologies are locally structurally disrupted, clay-altered, and anomalous in Cu, Pb, Ni, Zn and V (i.e. pathfinder elements).

Initial Principal Component Analysis (PCA) studies revealed possible pathfinder elements that are not lithologically restricted. The ranked attributes obtained are Li, Dy, Gd, Tb, Nd, Co, Pb, Cu, Zn, and Ni. These results further support uranium’s positive correlation with base metals and provide trace elements to focus on. The results show that uranium content can be best correlated with Gd content (Fig. 4). The correlation between U and Gd is 0.70. It is interesting to note that this correlation is observed both in basement and basin lithologies. Tb also showed good correlation with U (0.56). However, it could be noticed that this relationship works better for basement rocks. Other correlations can also be used (e.g. U vs Pb).

**Figure 4.** U-Gd (top) and U-Tb (bottom) molar ratio plots show that U values are well correlated with Gd and Tb both for basement and basin rocks. The correlation for Tb is lower due to its relationship with unmineralized basin rocks (red ellipse). The corresponding spatial distribution of U and Tb content in relation to the ore zone and unconformity surface.

### 5 Economic impact

To assess the economic benefits of using geochemical and structural vectors as a major step in uranium unconformity-type exploration, a comparative cost analysis on the Moore Lakes Project has been carried out. The cost analysis utilizes the following cost estimates from Lahusen et al. (2016) and McKechnie (pers. Comm.):

- Drilling speed= 4 meters/hour
- Drilling costs= $150/meter
- Fuel cost= $1/liter
- Labor cost= $50/hour
- Boron analysis cost= $30/sample
- Elemental analysis cost= $150/sample

In the conventional exploration cost analysis, it was assumed that no separate near-surface geochemistry was conducted. Instead 320 drillholes (35 exploratory drill holes for entire Moore + 285 delineation drillholes in Maverick; 100 samples per hole) in the Moore Lakes project were drilled and analyzed for U, B, SiO₂, C, S and other elements with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). On the other hand, the cost analysis for the exploration using geochemical vectoring,
uses near-surface drilling (i.e. <400 meters; U/C at ~275 meters) on the entire Moore Lakes project (Fig. 5). Using the current distribution of drillholes, it is estimated that about 50 drillholes would have covered the explored part of Moore Lakes project. From the distributed 50 holes, the Maverick zone would have been found to be anomalous and indicative for a potential deposit. Continuing with definitive drilling, the cost analysis uses 285 holes which are enclosed within the MUD. The results of this cost analysis show that the exploration costs of discovering/delineating the MUD could have been $26.4M instead of $29.5M USD; a potential cost savings of $3M USD. This supports the use and effectiveness of the geochemical vectoring tools.

Figure 5. Proposed business model incorporating usage of vectoring tools in early exploration of uranium unconformity-related deposits.

6 Conclusions and recommendations

This study encourages maximizing publicly-available data to build a geologic and geochemical model that may provide vectoring tools for unconformity-type uranium deposits. MUD provides an example of doing this and tests existing geochemical vectors. The results strongly suggest that incorporating these vectoring tools in an exploration company’s program may be one of several solutions the industry may take in bridging the gap between increasing exploration process and lower metal grades. It is important to note that although much care has been taken into verifying the data sets used to define the vectoring tools, it is yet to be tested in other nearby discovered and undiscovered uranium deposits of the eastern Athabasca Basin.

Acknowledgements

This work has been made possible thanks to the EMerald program, a 2-year Erasmus Mundus Master in Georesources Engineering. We would like to thank the host university, the École Nationale Supérieure de Géologie (ENSG), Université de Lorraine, CNRS, and GeoRessources (Nancy, France). We would also like to acknowledge the RING team lab for providing access to the SKUA-GOCAD and iogAS licenses.

References

Thomas DJ et al. (2000) Athabasca Basin (Canada) unconformity-type uranium deposits: exploration model, current mine developments and exploration directions Geology and Ore deposits:15-18
Geophysical imaging of iron-oxide apatite deposits in the eastern Adirondacks, northern New York

A.K. Shah1, R.D. Taylor1 and G.J. Walsh2

Abstract. We present results of airborne geophysical surveys, ground geophysical measurements, and laboratory analyses of rocks collected in the magnetite-apatite “Kiruna-type” deposits of the eastern Adirondack Mountains in northern New York. Airborne radiometric data mostly reflect the surface geology, but the most prominent anomalies are equivalent Th and U (eTh and eU) highs over large tailings piles, a residual of extensive mining activity in the 1800s and 1900s. These tailings piles contain rare earth element (REE)-bearing apatite, consistent with a correlation between REEs and Th in samples. Widespread K anomalies observed at iron-oxide-apatite deposits elsewhere and attributed to potassic alteration are not present, probably because of overprinting by later sodic alteration. The magnetic field is dominated by a broad high that corresponds mostly to magnetite-rich leucogranite host rock. High-pass filtering of magnetic flight line data reveals numerous anomalies associated with known magnetite deposits, although in some areas smaller leucogranite bodies are also highlighted. 3-D inversions for magnetic susceptibility show general shapes, orientation, and relative dimensions of the deposits that are consistent with published reports. Together these analyses show how geophysical surveys can be used for exploration, mapping the distribution of deposits, and as a remote sensing tool for REEs in tailings.

1 Introduction

The eastern Adirondacks in northeastern New York contain dozens of low-Ti, REE-bearing “Kiruna-type” iron-oxide-apatite (IOA) deposits that provide an excellent case study for geophysical exploration and 3-D imaging. These deposits were extensively mined for iron in the 1800s and 1900s, resulting in reasonable documentation of deposit locations and in some cases their subsurface extent (Kemp and Ruedemann 1910; Farrell 1996). Mining activities also resulted in numerous waste and tailings piles containing REE-bearing apatite, presenting a possible “recycled” resource (McKeown and Klemic 1956; Mariano and Mariano 2012; Taylor et al. 2018a). The apatite is of marked interest because it contains elevated K associated with potassic alteration (Shives et al. 2000; Sandrin et al. 2007). Magnetic and gravity data are more variable: Deposits in southeastern Missouri, northwestern Canada, Kiruna, Sweden, and Candelaria, Chile show local magnetic and sometimes local gravity highs, while deposits in the Gawler craton of Australia, which hosts the world-class Olympic Dam deposit, show gravity highs and weaker or offset magnetic anomalies (Rutter and Esdale 1985; Smith 2002; Clark 2003; Sandrin and Elming 2006; Direen and Lyons 2007; Sandrin et al. 2007; Austin and Foss 2012; Hayward et al. 2013; McCafferty et al. 2016).

In December 2015 we collected airborne magnetic and radiometric data over a 70 km by 25 km area covering dozens of magnetite-apatite deposits. Over two subsequent field seasons we measured radiometric and magnetic susceptibility on outcrops and whole rock geochemistry on samples from deposits, host rock, waste, and tailing piles. Results of these data are used to examine how geophysical methods can assist exploration, to obtain 3-D views of individual deposits, and to examine the regional geologic context of the deposits.

2 Geologic Setting

Figure 1. Simplified geologic map of the study area modified from Isachsen and Fisher (1970). Black polygon delineates the airborne geophysical survey bounds. Squares represent iron mines and prospects from the USGS Mineral Resources Database. Inset shows location in New York; yellow box shows the area of interest.
The magnetite-apatite deposits are located primarily on the northern and eastern edges of the dome-shaped Adirondack Mountains and hosted mostly in magnetite-rich leucogranite (with some exceptions). They are believed to have formed in the latter part of the Grenville orogeny during a phase of post-orogenic extensional collapse (Foese and McLelland 1995; Valley et al. 2011; Chiarenzelli et al. 2017). Other rocks in the region include a suite of anorthosite-mangerite-charnockite-granite (AMCG) and meta-sedimentary rocks, Paleozoic sedimentary cover to the east, and glacial cover in some areas (Fig. 1). We note an absence of copper and gold in economic quantities within the region indicating the deposits are more like the IOA deposits in Kiruna, Sweden (Valley et al. 2011).

Numerous deposits are present, often occurring in clusters. The largest and most productive of these are in the Mineville area with several lenticular, podlike, or tabular ore bodies whose long axes trend to the NNE and deepen to the SSW (Kemp 1898). The presence of REE-bearing apatite within the deposits is highly variable over local scales, with deposits a few kilometers apart showing very different concentrations (McKeown and Klemic 1956; Valley et al. 2011; Lupulescu et al. 2017; Taylor et al. 2018a).

3 Methods

Airborne magnetic and radiometric surveys were flown in 2015 with a line spacing of 250-m and nominal terrain clearance of 125 m (Shah 2016). Ground truth measurements of magnetic susceptibility and radiometric properties of outcropping deposits, host rock, and tailings were collected. Samples of deposits, host rock, waste, and tailings were also analyzed for whole rock geochemistry (Taylor et al. 2018b).

Exploration approaches using magnetic data are challenging in the eastern Adirondacks because the magnetite-apatite deposits are mostly hosted by larger bodies of magnetite-rich leucogranite, which can mask deposit anomalies. We thus applied high-pass filtering approaches to the magnetic data with a goal of distinguishing shallow, very highly magnetic deposits from the leucogranite. This included a simple 1-D high-pass filter on flight-line data (Fraser et al. 1966) with a window size of 150 m to capture the shortest-wavelength anomalies. We note that this window is smaller than the flight line spacing and would likely create spurious results on gridded data. A steep regional magnetic inclination of 69° indicates that reduction to the pole has a very minor effect and anomalies should be closely aligned with their sources (assuming there is no large oblique remanent magnetization component).

To image the subsurface shape, orientation, and relative extent of the deposits, we also developed 3-D inversions for magnetic susceptibility using the method of Phillips (2014). This approach inverts for susceptibility by minimizing an objective function describing the difference between the observed and calculated magnetic fields. The inversions are intrinsically under-determined so a cubic depth-weighting constraint, which mimics the falloff of the magnetic field with distance to source, was applied. We note that the solution does not include effects of remanence or demagnetization, so results have limited quantitative accuracy without external constraints, especially if those effects are dominant. Nonetheless, they can still provide a qualitative 3-D view of the various deposits and their relative differences.

4 Results

4.1 Radiometric data

The most prominent feature of the aeroradiometric maps (Fig. 2) is a set of equivalent Th and U (eTh and eU) highs from Port Henry to Mineville. These each correspond to known tailings piles. In some areas these highs continue along roads, perhaps because some tailings are used for winter road gravel. Not all tailings piles in the region exhibit eTh-eU anomalies. Geochemical analyses of materials from a subset of these piles show that the eTh-eU highs occur where REE-bearing apatite concentrations are also high, reflecting a correlation between Th and REE (see also Taylor et al. 2018a). This correlation does not appear to apply to in situ deposits, however. While eTh is elevated in locales, it is usually over a broader scale than the deposits.

The radiometric data otherwise show broad, regional trends that mostly correspond with rock type, consistent with outcrop measurements. For example, anorthosite and gabbro have low K, eTh, and eU while carbonate...
rocks are high in all three. Charnockite typically shows elevated K but eTh and eU are more variable. For the leucogranite, K, eTh, and eU are highly variable. We note that there are no regions with broad K anomalies as observed in other areas such as Kiruna and Canadian locales, attributed to potassic alteration (Shives et al. 2000; Sandrin et al. 2007). Sample analyses show that while potassic alteration has occurred, it has been mostly overprinted by sodic alteration (Valley et al. 2011).

4.2 Magnetic data

The magnetic anomaly (Fig. 3) is dominated by a broad, up to 1500 nT high near the town of Ticonderoga. The high has NNW- and W-trending branches extending towards Mineville and Skiff Mountain-Hammondville, respectively. The wider part of the high continues to the east, suggesting that the magnetic source continues beneath the Paleozoic cover. A comparison to surface geology shows that the high corresponds mostly to leucogranite (mapped partly beneath glacial cover near Mineville), consistent with leucogranite outcrop susceptibility measurements of 30-70x10⁻³ SI. There are more localized highs to the north which correspond to smaller bodies of leucogranite or gabbro (the magnetic susceptibility of gabbro averaged 1-8 x10⁻³ SI). The high also shows correspondences to major structures, with WNW- and W-trending lineaments near Hammondville and Skiff Mountain. The NNW branch towards Mineville is also notably linear.

The high-pass filtered magnetic field shows local highs ranging from about 100 to 350 nT (Fig. 3B). Most of these highs correspond to known magnetite-apatite deposits, many of which occur in clusters. Some highs are elongate, following structural trends. Some highs, however, represent narrow bodies of leucogranite against a background of less magnetic rock. In other areas the presence or absence of deposits isn’t known. Near Mineville, where the subsurface extents of some deposits have been documented (Kemp 1898), the highs follow the broad shape of buried ore bodies, noting that the bodies are narrower than the survey flight line spacing, and some might not have been fully explored (Fig. 3C).

The 3-D magnetic susceptibility inversions (Fig. 4) show higher susceptibilities where known deposits are located and suggest approximate shapes, orientations, and relative extents. The deposit with the largest volume of high susceptibilities is the Barton Hill group ore body near Mineville (Fig. 3c, 4a), which extends at depth over a kilometer, consistent with published documentation.

The magnetic anomaly (Fig. 3) is dominated by a broad, up to 1500 nT high near the town of Ticonderoga. The

Figure 3. A) Magnetic field. Faded area shows previous regional survey data; black polygon delineates 2015 survey bounds. White box shows location of panel B. T = Ticonderoga, M = Mineville, Sk = Skiff Mountain, Hv = Hammondville. B) High-pass filtered magnetic field over central part of survey area and locations of some mines and prospects. Note color scale truncates lower values. Box shows location of panel C. C) Closeup of the Mineville area mines and high-pass filtered magnetic field. Black filled polygons represent estimated ore bodies by Kemp and Ruedemann (1910). Labels note associated pits and shafts that accessed the Barton Hill group and Mineville group ore bodies.

The magnetic anomaly (Fig. 3) is dominated by a broad, up to 1500 nT high near the town of Ticonderoga. The
5 Discussion

The magnetic field highlights host rock and major structural features. A cursory consideration of the magnetic total field might suggest that individual deposits cannot be distinguished. However, application of high-pass filtering approaches can indeed highlight anomalies associated with the magnetite-apatite deposits.

For this dataset we found that filters applied to flight line data were more effective than those applied to gridded data because narrower features can be highlighted. Care must be taken with these approaches, however, because isolated magnetic bodies can appear magnetically similar to the deposits. The 3-D models, which were applied to the total field, are also able to delineate magnetite deposits, along with their general shape, orientation and relative size.

The radiometric data show eTh-eU anomalies that outline tailings piles rich in REE-bearing apatite, reflecting a correlation between Th and REEs. Local eTh anomalies do not, however, delineate in situ REE-bearing deposits, perhaps because of tremendous local variability in apatite concentrations. The deposits do not show a correlation with radiometric K, probably because potassic alteration has been overprinted with sodic alteration over much of the area. These observations thus show important differences in the way alteration history can impact the geophysical expression of IOA deposits.

Acknowledgements

The code for the magnetic susceptibility inversions was written by J. Phillips; we are grateful for his help with implementation. Margaret Goldman, Anna Klein, and Cliff Taylor provided indispensable help in the field and in the laboratory. We thank Marian Lupulescu, Paul Tromblee, and Thomas Scozzafava for facilitating visits to some of the mine and/or tailings sites. We thank A. McCafferty and J. Austin for helpful reviews. This effort was funded by the USGS Mineral Resources Program.

References


Kemp JF, Ruedemann R (1910) Geology of the Elizabethtown and Port Henry Quadrangles. New York State Museum Bulletin 138, New York State Education Department


Mariano AN, Mariano A (2012) Rare earth mining and exploration in North America. Elements 8:369–376


Insights from potential-field modeling. Econ Geol 102:1397–1414

1340 Life with Ore Deposits on Earth – 15th SGA Biennial Meeting 2019, Volume 3
New methodology of application of historical geophysical materials for the exploration of mineral deposits, as presented for the Nowa Sól area

Lidia Dziewińska
IGSMiE PAN, Cracow, Poland

Andrzej Pepel
S-Systems, Warsaw, Poland

Stanisław Speczik
University of Warsaw, Poland

Waldemar Jóźwiak, Krzysztof Zieliński
Miedzi Copper Corp., Warsaw, Poland

Abstract. The paper presents new methodology of adapting historical geophysical materials for the indication of prospective zones of Cu-Ag deposits, with the Nowa Sól exploration target in Poland used as an example. Basic gravimetric materials and transformed maps were combined to assess the tectonic structure of the region. The new method of effective reflection coefficients (ERC) allowed the application of archival seismic records for a more precise determination of the most vaguely traced interfaces within the Zechstein unit. Compared to an amplitude-based seismic section, an ERC section is characterised by its highly increased resolution of imaging.

Keywords: Fore-Sudetic Monocline, Nowa Sól exploration target, copper and silver deposits, geophysical data processing, effective reflection coefficients

1 Introduction

As the first stage of its exploration project in the Nowa Sól area, Miedzi Copper Corp. (MCC) performed extended analyses of existing historical geophysical materials. However, the quality of this abundant data did not allow its application for ore prospecting. Therefore, the use of new methods was necessary to trace the prospective zones of Cu-Ag mineralisation (Speczik et al., 2011, 2012; Dziewińska et al., 2017). The locations of prospecting boreholes were established after the reprocessing of geophysical data by means of the new methodology. The produced results compared to the effects of drilling confirmed the usefulness of the applied methodology.

2 Geological setting of the research area

The research area is located in Poland, in the southwestern part of the Fore-Sudetic Monocline, on the southern slope of the Wolsztyn High. This region is interpreted as the eastern extension of the Rhenohercynian (RH) and Saxo-Thuringian (ST) zones demarcated within the Variscan orogen of Germany, as well as the Mid-German Crystalline Rise (MGCR) (Grad et al. 2016). In Poland and Germany, these units are associated with the occurrence of mineral deposits (Wyżykowski 1971; Rydzewski 1978; Franke et al. 1993; Cwojdziński et al. 1995; Żelaźniewicz et al. 1997; Oszczepalski 1999), which justifies the performance of prospecting work.

3 An overview of current geophysical knowledge

The role of tectonic movements and the associated magmatic and hydrothermal processes as a factor destabilising the palaeo-hydrological balance in ore formation process presents a direction for geophysical research. The Cu-Ag deposits being explored are categorised as epigenetic, created due to the migration of low-temperature hydrothermal solutions. Migration pathways probably included regional and local tectonic zones. Those fractures could be considered as channels for the convection of heat necessary for mineralising processes (Speczik 1985; Piestrzyński 2007). A semi-detailed seismic image prepared for the Nowa Sól area by petroleum companies in the years 1980-1994 constitutes a grid of profiles of varying quality, 1-2 km apart from each other. Main structural objects were identified in the prospective sediments of the Main Dolomite lithostratigraphic unit. Zones of changes in the record are related primarily to changes in the lithology, facies and thickness of Zechstein cyclothsems, in particular Stassfurt and Werra, as well as the occurrence of tectonically deformed regions. Historical gravimetric surveys in the form of a semi-detailed image with the density of points of approximately 3.5 point/km² cover the whole area and its nearest surroundings. The values of anomalies are sufficient for a gravimetric study related to the rocks of Zechstein and its substrate. In terms of geology, the gravimetric image has visible high-density rocks of the older Palaeozoic or metamorphic rocks of the Wolsztyn-Pogorzela High (Kiersnowski et al. 2010). For
shallower depth intervals, the recorded residual anomalies reflect changes in the lithology and thickness of Zechstein sediments related to salts and anhydrites of varying density. The densities of P1 sediments range from 2.55 to 2.65 g/cm³. Due to their position and structure, Triassic rocks distinguished by densities exceeding 2.5 g/cm³ have no significant impact on the recorded gravimetric image. Various transformations of the image used the methods of analogue and frequency-based filtration. Along with an analysis of zones with increased gradients, this allowed tracing geological objects with elongated shapes, like faults or anticlines, as well as facial changes within analysed depth intervals. A horizontal gradient map (Figure 1) presents a zone of anomalies with a NW-SE direction, approximately parallel to the Wolsztyn High, probably indicating a tectonic zone located close to its south-western limb. The deep origins of this zone are confirmed by magnetic data and the results of seismic refraction (Dzięwieńska et al. 2017).

4 The methodology of processing ERC seismic sections

The principles of the effective coefficient method known back then as “Reapak” were developed in “Sibgeo Novosibirsk” in the 1980s (Rudnitskaya et al. 1987). This method was modified and adjusted to the lithological and tectonic variability of Zechstein sediments by the authors of the present paper (Speczík et al. 2011). The calculations used materials prepared by the petroleum industry based on historical seismic data (time records, seismic sections) retaining their original amplitudes.

The calculation of effective reflection coefficients (ERC) enables the conversion of a waveform seismic image into an impulse form of seismic record, meaning a temporal sequence of reflection coefficients presenting the subsequent layers forming a given geological structure. To this end, one of the most important features of a seismic image is used – the amplitude, its size being assumed as proportional to the reflection coefficient for a specific geological boundary. The mathematical and physical model of a geological structure is a so-called convoluted model, according to which a seismic pathway is the result of combining the pathway of reflection coefficients with elementary seismic signal. The deconvolution of an amplitude-based seismic pathway allows obtaining a seismic pathway in the form of a series of coefficients. Processing pattern includes three stages: determination of an elementary impulse, repeated mutual correlation of the impulse with the seismic pathway, as well as standardisation (horizontal and vertical addition of the individual pathways) and the use of a statistical report for the visualisation of a seismic image. The primary function of the system involves determining the shape of the elementary signal and establishing the impulse characteristics of the structure. The determination of an elementary seismic impulse proceeds by the addition of subsequent groups of reflected waves for the given pathway, presented for the same phase, and the combined time of recording. Results of the determination of elementary signal can be validated using Fourier analysis. The function of mutual correlation of elementary signal with each seismic pathway enables conversion of a wave-based seismic pathway into temporal series of zero-phase amplitudes called the effective reflection coefficients. It determines the time-based points of maximum correlation of signal with reflected waves in the form of values of the coefficient and sign of the amplitude. Sets of reflection coefficients undergo standardisation and they are presented in the form of a seismic section which shows seismic pathways converted into an impulse form. The reflection coefficients present seismic interfaces conforming to actual boundaries. This coefficient is defined by layer-related velocities and rock density above and below a given seismic reflecting interface. Assuming that changes in density are relatively small compared to changes in velocity, it is accepted that the coefficient depends mainly on the latter. This method is particularly useful when identifying thin layers, small dislocations, and tracing changes in the lithology of a given stratum, e.g. porosity, along a seismic section. Geophysical logging performed in boreholes enabled calculations of the values of parameters for strata exceeding 4 m in thickness. The values of density in individual stratigraphic units enable the construction of one averaged density model of an area. Due to the use of the attributes of an impulse section and the sign of the reflection coefficient, reflected wave intensity and the place of reflection, the efficiency of identification and correlation of seismic boundaries increases, along with simultaneous characterisation of the geometrical and physical system of strata forming a given geological structure. Evaluation of the properties of the ERC method is facilitated by comparing section TAZ20782 developed as reflection coefficients (Figure 2) to a fragment of its unprocessed version (Figure 2-A).
5 The analysis and interpretation of ERC sections for predicting ore distribution

The analysis and interpretation of results covered 9 selected seismic profiles: T0970783, TA220782, T0190790, 115-04-93K, 106-04-93K, 107-04-93K, 118-04-93K, 114-4-93K and TA230782 (Figure 3) with a total length of 82.233 km. The ultimate objective was to demarcate the probable zones of increased thickness of potential ore-bearing series. One characteristic feature is the arrangement of coefficients and zones of particular significance for predicting the occurrence of copper-bearing shales and the associated mineralised zones with the highest possible probability.

Figure 2. Time-converted seismic reflection coefficients in section TA220782 of a Zechstein deposit compared to an amplitude section (A).

On the seismic sections, particular attention was paid to the position of the boundary between Z1' and Z1. Identification of the traced stratigraphic horizons: Z4, Z3, Z2, Z1 and Z1' (see Figure 4) is analogical to what is used traditionally in the Fore-Sudetic Monocline. The nature and magnitude of reflection coefficients indicate that Zechstein sediments may be underlain by insets of rocks characterised by much higher velocity compared to sandstones. Fault zones in horizon Z1' are associated with the diverse morphology of sub-Zechstein sediments. Most faults recorded in the Zechstein extend into older rocks, evidencing their deeper tectonic origins. Zechstein sediments stand out on ERC sections due to boundaries with high values of the coefficients, documenting great lithological diversity of rocks which form series of salts, clays, as well as anhydrites and dolomites. Observed changes in the thickness of complexes between these horizons are caused mainly by changes in the thickness of the older salt of the Stassfurt cyclothem and the oldest salt and anhydrite of the Werra cyclothem.

6 Usefulness of the ERC method applied for establishing the location of boreholes

Figure 3. Location map.

Zones of lithological changes with characteristic values of the coefficients and low-amplitude faults have been recorded within Zechstein rocks and along their contact with the Rotliegend. In the Zechstein complex Z1’-Z1, there are visible interfaces originating from its individual strata. Particularly noticeable is a high-velocity complex of Zechstein sediments directly above the top of the Rotliegend. An assumption was made about the connection between the bottom part of the complex characterised by the Z1 reflective interface and the geological objective, as well as possible changes in the coefficients recorded above the Z1 boundary. Drilling results indicate that rocks associated with the orebody are several metres thick, and physical parameters characterising these sediments: velocity, density and porosity, have values similar to the highly elastic thick structure present in their overburden, consisting of limestones, anhydrites and rock salts. The presented image justified the particular attention paid to the interpretation of ERC sections for correlation between a negative reflection coefficient associated with the base of Zechstein and changes in the shape of a system of reflection coefficients present above it. Based on the arrangement of reflection coefficients, a graphical representation has been shown involving the shape of characteristic strata in the vicinity of the contact of Zechstein and Rotliegend, which are believed to be prospective in the studied area. Changes in the lithology of lowermost Zechstein sediments (interlayers and various insets) occur above the Z1’ seismic boundary as reflections with low values of the coefficients recorded in short segments of the profiles. They have been interpreted as “anomalous strata”, indicating the sites of potential mineralised zones.

Section 118-4-93K with a nearly latitudinal direction (Figure 4) is the most representative of all seismic sections selected for reprocessing. Along the Przyborów elevation and on its eastern slope, several anomalous zones were recorded at the boundary between the Zechstein and the Rotliegend, which due to the discontinuity of correlation were linked with Cu ore. Section TA220782 (Figure 2) presents an undisturbed position of seismic interfaces dipping towards the NE. The interpreted potential orebodies are situated at the SW and NE ends of the section, in the central part of the...
profile between two discontinuities delimiting a depression in the Zechstein horizon.

7 Summary and conclusions

The transformation of archival seismic data into effective reflection coefficients (ERC) enabled the demarcation of Z1'-Z4 interfaces in Zechstein rocks. It also allowed the identification of tectonic features and the characteristic zones of lithological changes near the Z1' interface, which are possible hosts to orebodies. The presented assumptions and possibilities of depicting changes in mineralised zones along ERC sections have provided information about characteristic places associated with potential orebodies. These sections enabled the indication of more precise locations for planned prospecting boreholes.

Figure 4. Time-converted seismic reflection coefficients in section 118-4-93K of a Zechstein deposit.

<table>
<thead>
<tr>
<th>Borehole</th>
<th>Correlation with ERC image</th>
<th>Seismic section</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS C1</td>
<td>YES</td>
<td>118-4-93K, 106-4-93K</td>
</tr>
<tr>
<td>NS C2</td>
<td>YES</td>
<td>118-4-93K, T9070783</td>
</tr>
<tr>
<td>NS C3</td>
<td>NO</td>
<td>118-4-93K, T9070783</td>
</tr>
<tr>
<td>NS C4</td>
<td>YES</td>
<td>TA220782, 115-4-93K</td>
</tr>
<tr>
<td>NS C11</td>
<td>NO</td>
<td>114-4-93K</td>
</tr>
<tr>
<td>NS C12</td>
<td>NO</td>
<td>TA220782, 114-4-93K</td>
</tr>
<tr>
<td>NS C13</td>
<td>YES</td>
<td>118-4-93K, 107-4-93K</td>
</tr>
<tr>
<td>NS C14B</td>
<td>YES</td>
<td>TA220782</td>
</tr>
<tr>
<td>NS C16</td>
<td>YES</td>
<td>TA220782, TA30782</td>
</tr>
<tr>
<td>NS C17B</td>
<td>YES</td>
<td>115-4-93K, 114-4-93K, 106-4-93K</td>
</tr>
<tr>
<td>NS C22</td>
<td>YES</td>
<td>118-4-93K, T9070783</td>
</tr>
<tr>
<td>NS C33</td>
<td>YES</td>
<td>118-4-93K, T9070783</td>
</tr>
</tbody>
</table>

Borehole C17B described as negative reflects the lack of characteristic anomalies associated with potential mineral series on three interpreted ERC sections. Summarising the produced results, for twelve prospective boreholes drilled, nine remain in compliance with the ERC image and three (C3, C11, C12) present a negative result of correlation. This proves the high validity of the performed interpretation of seismic sections in relation to drilling results and justifies the adopted course of research. Boreholes drilled close to or along the interpreted seismic sections confirmed the effectiveness of the ERC method in approximately 75%. Prospective boreholes planned near the slope of a zone of higher gradients in the substrate of Zechstein proved to be located properly in terms of suggested relationship of mineralised zones with Zechstein base morphology. The completed drilling operations also confirmed the assumption about the position of lower Zechstein copper orebodies, forming a rather wide strip (5-10 km) placed in a zone extending NW-SE along the eastern range of the Zielona Góra oxidised area (Zieliński and Speczik 2017).

The presented results have been produced based on historical documentation, with relatively low financial expenses and with no need for costly on-site work. This study also has a methodical nature, showing the ability to use the impulse form of a seismic record for the identification of prognostic Cu and Ag resources, as confirmed by the results of prospecting drilling.

References


Implicit model creation for the application of geophysical inversion and forward modelling; drill target generation for undercover ore deposits

Daniel Gerger, Patrick Ledru, Dwayne Kinar, Grant Harrison
Orano Canada Inc., Saskatoon, Canada

Gabriel Courrioux
BRGM, Orléans, France

Charles Gumiaux
University of Orléans, ISTO, Orléans, France

Abstract. Exploration for undiscovered uranium deposits within the Athabasca Basin, Saskatchewan, Canada is complicated by a thick sedimentary cover, masking the geophysical expression of the basement-sandstone unconformity interface that provides a favourable pathway and trap for mineralizing fluids. Zonal alteration associated with uranium deposition disrupting the regional distribution law of density and resistivity must be identified and parsed from the primary controls on the geophysical response; geological and structural form of the underlying strata. Provided a solid understanding of the geological context, these secondary disruptions can be identified and targeted for diamond drilling investigation through inversion processing of the geologic model.

A 3D block model of an exploration zone has been created through implicit modelling from sparse drill-hole data to aid in three-dimensional visualization, inversion modelling and resulting target optimization. When combined with an ‘expert-driven’ approach to data analysis regarding principal metallogenic guides within the geological context of the exploration area, identification of zones of physical property variation unaccounted for in the primary geological conditions can be used to vector towards zones of interest for improved drill targeting of deeply buried ore deposits.

1 Introduction

The advancement of successful geoscience targeting in an efficient manner continues to become more difficult as near-surface deposits that can be easily identified are increasingly rare to discover. This is true across most mineral commodities and is particularly significant for high-grade uranium deposits endemic to the Athabasca basin in northern Saskatchewan, Canada. Recent discoveries in the most explored districts, with a few exceptions, are confined to several hundred metres below the topographic surface and as such are termed “blind” deposits due to the nature of the technically difficult exploration that must be undertaken. Application of geophysical methods reconciled with known geological constraints can aid in the reduction of uncertainty inherently associated with exploration at depth.

The Athabasca basin is a district of significant economic interest as it is known to host many of the world’s largest and highest-grade uranium deposits (Card et al. 2007). The metallogenic model follows the precipitation of uranium in the form of pitchblende or uraninite during low-mid temperature redox reactions at the discordant contact between Archean to Paleoproterozoic metamorphic basement gneisses and the Paleoproterozoic Athabasca sedimentary sequence (Jefferson et al. 2007). Deposit formation is typically associated with steeply dipping, structurally re-activated shear zones acting as fluid flow conduits within high metamorphic grade, graphite-bearing paragneisses. Graphitic horizons are identified through electromagnetic (EM) geophysical methods and have historically been used as a first-order exploration guide. As graphitic horizons are wide-spread across the basement of the Athabasca basin, various other geophysical methods can be used to infer the changes in the spatial distribution of physical rock properties that may be indicative of uranium precipitation, to help narrow down areas of exploration interest. The most utilized methods apart from EM include DC resistivity, magnetics, and gravity. Alteration associated with uranium deposition is hydrothermal; generally argillic to propylitic in nature and as such significantly reduces the density and resistivity of the country rock (Hoeve and Quirt 1984; Quirt 2003).

This study focuses on the effects of density variation as it pertains to the gravity response across known areas of alteration within a uranium exploration project, Getty Russell, operated by Orano Canada Inc. in partnership with Cameco Corporation, along the Wollaston-Mudjatik Transition Zone in the Athabasca basin (Fig. 1). Using the 3D Geomodeller (Intrepid) software, a 3D block model has been created within the exploration project area with the goals of better imaging the structural geometry of the basement geology, mapping known alteration corridors, and using geophysical inversion methodology to identify areas of anomalous petrophysical property variations that could be associated with alteration. The geophysical signature will be dominantly controlled by the geology and structure of the underlying strata and consequently alteration zones act as discreet and difficult to determine
contributions. These alteration zones must be considered as secondary effects on the overall geophysical response that can be quantified through the inversion workflow.

Identification of areas of physical property variation not currently accounted for within the geological model, which may be related to alteration haloes associated with uranium mineralization, facilitates exploration by concentrating efforts towards zones with the highest potential prospectivity. Diamond drilling is an expensive but necessary method of exploration for buried ore deposits (Doney et al. 2015); through cross-validation and reconciliation of all available data, innovative approaches can be developed to lessen this expense and better focus exploratory efforts.

2 Methodology

For the most consistent elimination of ambiguity and to decrease uncertainty as much as possible within the original 3D geological model before inversion processing, data associated with the original model must be interpreted and cleaned as much as possible (Gerger 2018). Comprehension and simplification of heterogeneous geological units, examination of regional alteration that will have an effect on gravity modelling, examination of the available geophysical data and its use and integration in geological interpretation, application of GIS tools that can aid in the modelling process, and assumptions made going forward with regional scale 3D models, including geological, structural, and geophysical criteria must all be reconciled to create a stepwise approach to this case study:

1) Construction of an unconformity plan geology map respecting all available geophysical interpretations, project geological data and interpretation, and drill-hole constraints.

2) Define a stratigraphic pile in Geomodeller that is reflective of the stratigraphic relationships between present lithologies (Calcagno et al. 2008). The interpolation is dependent upon the choices made with respect to these interpreted relationships and therefore all observed field relationships between differing rock layers must be considered.

3) Import drill-hole constraints to the Geomodeller database after simplification to make the logged geology comprehensible at a regional scale. Respect contacts, generalized lithologies, and orientation data where available. Adjust and re-interpolate the model based on drill-hole importation and/or update with drilling progress and new information.

4) Create regional and grid scale cross-sections orthogonal to geology and structure in order to assess behaviour of the model at depth. Use existing cross-sections and orientation data to add constraints to the shape and trend of interpolated geology.

5) Introduce alteration envelopes into the model and discretize based on the parent lithologies overlapped by the alteration (Fig. 2).

6) Analyze and input physical property data into the different units of the 3D model, constructing a density block of the petrophysical property distribution across the project area. Statistical distribution of the density loss due to alteration must originate from field information (Fig. 3).

7) Forward model the response of the 3D geological model iteratively throughout the modelling process. Correct and reconcile to obtain a best-fit for the observed potential fields.

8) Continue with inversion modelling in Geomodeller to obtain areas of exploration interest not currently accounted for by the distribution of physical properties across the geological block model.

This process requires a significant amount of data to be used from a variety of sources. The most relevant sources are: digital terrain map of the project area, magnetics maps, gravity surveys (Fig. 4a), EM surveys, logged geology, geochemical data, interpreted unconformity map, historical interpretations of the area (Annesley et al. 2005; Tran 2006; Jeanneret et al. 2016), drill-hole intersections, and petrophysical property data. Forward modelling is the critical step to create a reasonable block model before going forward with inversion and target acquisition.

3 Forward and inversion modelling to characterize and target alteration zones

3.1 Alteration characterization

Forward modelling of known drilling intersected alteration zones is used to characterize the overall effect of uranium associated density loss on the gravity potential field (Fig. 4). Using the generalized alteration envelope (200 x 1500 x 400 m) it is apparent that for an alteration corridor of the approximately necessary size for an economic uranium deposit, the gravimetric response will be in the order of 0.4 mGal. The overall range of gravimetric values for the vertical gradient in the observed geophysical response is ~3.9 mGal. Using the assumption that the larger effect of the main alteration envelope (C2 alteration corridor, Fig. 4c) is under-represented in the geological model as it is solely constrained by drilling, it can be said that the effect of a large alteration corridor might represent a 10% effect on the overall gravity response in this particular geological setting. Through this workflow it is evident that the effect of a large alteration zone is discreet when several hundred metres from surface and that it acts as a secondary contributor to the overall geophysical response. Therefore, the identification of unknown zones of alteration could be aided by geophysical inversion as many discreet alteration bodies will be difficult to distinguish from the bulk gravimetric response by eye alone.

3.2 Inversion modelling for target advancement

Inversion modelling across the geological model has been carried out using both lithology inversion and density inversion workflows that allow the inversion to change the lithology or the density, respectively, to best fit the observed gravimetric response. An understanding of the geological and structural conditions associated with
uranium mineralization in the Athabasca basin such as graphitic metasediments, reactivated basement structures, and their intersections at the unconformity surface must be kept in mind when analyzing which areas of low density are the most interesting from a targeting perspective. Historic metallogenic guides across the eastern Athabasca basin indicate the importance of graphitic horizons and metasediments for uranium deposition. The inversion has therefore to be limited to add or change alteration only in the vicinity of prospective lithologies, leaving the remainder of the block model static. The effect of a large basement alteration zone is discreet at the depth of the unconformity-basin interface. However, through processing and knowledge-based analysis target areas can be identified.

This type of ‘expert-driven’ approach to analysis of the inversion results with respect to the accepted metallogenic guides can aid in vectoring towards zones indicative of possible low-density anomalies in the subsurface currently unaccounted for in the geological model (Fig. 5). The Getty Russell project area primarily targets basement mineralization as the dominant mineralization style intersected to date is of the ‘ingress-type’. Therefore, efforts have been concentrated on the basement intersection with characteristic narrow alteration corridors.

4 Perspectives and conclusion

Results from the attempts to model and reconcile the project scale geology with the geophysical response indicate that through successive stages of workflow, difficult buried terrains can be modelled with reasonable results. Uranium exploration concentrated along defined graphite-bearing corridors significantly narrows the areas of interest while searching for anomalies in the results of the density inversion. This particular research has focused on uranium exploration set under the cover of several hundred meters of sandstone and Quaternary sediment cover (Ramaekers et al. 2007); however, this methodology could be applied to any type of sub-surface mineral deposit that has associated hydrothermal or propylitic alteration haloes that affect the density of the surrounding strata. Through the interdisciplinary approach looking at available geophysical, geological, geochemical, and spectral data sources, complications can be limited, yet room for advancement in the detail and scale of methodology remains.

Obvious gravimetric anomalies can be used as control zones to determine validity of the model and inversion. Density variations shown in the inversion can however be re-joined to the geological model and target areas identified from zones less characterized by historical drilling.

This workflow through forward modelling and inversion processing works based on the assumption that the first-order controls on the geophysical response of the project area are based on the geological and structural form of the underlying strata. Through geological modelling it can be demonstrated that hydrothermal alteration haloes can be contributing effects to the overall gravimetric response, yet are minor in comparison to the overall effect caused by the base geology and structure. Forward and inversion reconciliation between the predicted geological model based on field observations and the observed geophysical response can help to vector towards these discreet zones of physical property variation potentially associated with low-density alteration corridors.

New Techniques for Ore Discovery 1347
Figure 3. Statistical histogram distribution of density data for all basement lithologies. Blue represents unaltered lithologies; green represents logged alteration.

Figure 4. Project gravimetric response. a observed, b a priori, c individual contribution of the largest alteration zone intersected within the project boundaries.

Figure 5. Queried alteration voxets showing inversion-predicted alteration zones. Coloured lines indicated lithological boundaries at the unconformity surface.

References

Prospecting strategy for deep sediment-hosted Cu-Ag ore deposits in Poland

Stanisław Speczik, Tomasz Bieńko, Alicja Pietrzela
Miedzi Copper Corp., Al., Poland
University of Warsaw, Faculty of Geology, Poland

Krzysztof Zieliński
Miedzi Copper Corp., Al., Poland

Abstract. In 2011, Miedzi Copper Corp. initiated an exploration programme focused on deep Cu-Ag deposits in the Fore-Sudetic Monocline. The exploration target initially comprised 21 concessions. Their boundaries were based on known prognostic areas in the vicinity of palaeo-elevations and contacts between oxidised and reduced facies. During the first stage of the exploration programme, historical drill cores were analysed and samples were collected for further examinations, including organic geochemistry and the Rock Eval method. In some regions it revealed so-called strong Rote Fäule, a facies usually associated with high grade copper mineralisation. Also, geophysical data reprocessing was performed using an innovative method of effective reflection coefficients. Due to the results of this stage, the number of concessions was reduced in order to focus on the most promising areas. The drilling programme started in 2013. After its initial results, the operations continued in 6 concessions with the highest grade of ore. The exploration programme has led to the discovery of three deep Cu-Ag deposits in the Fore-Sudetic Monocline: Mozów, Sulmierzyce and Nowa Sól. The performed economic analyses proved that profitable mining operations in all three deposits are possible using modern extraction technologies.

1 Introduction

Copper supply from easily accessible deposits is recently decreasing due to the depletion of shallow, high grade reserves, both in porphyry and sediment-hosted deposit types, and due to the growing costs of copper extraction (Zieliński and Speczik 2017). Moreover, technological progress enables major companies to perform successful mining operations at greater depths (Addison et al. 2012, Zieliński et al. 2017). With growing demand for copper, it is much more justified to extract higher grade ore from deeper deposits, than lower grade ore from the shallower ones. For that reason, the exploration begins to target deeper mineralisation which in the near future will be a subject of economically reasonable extraction.

Therefore, in 2011 Miedzi Copper Corp. started a greenfield exploration programme in the northern part of the Fore-Sudetic Monocline in SW Poland. Copper-silver deposits in this region are of the stratiform sediment-hosted type, occurring in a contact zone between the continental red beds (Rotliegend) and Zechstein marine sediments. The ore-bearing series consists of white sandstones (Weissliegend), Kupferschiefer shales and Zechstein limestones (Oszczepalski 1989). The central part of the Fore-Sudetic Monocline is a well-known mining area (the Legnica-Głogów Copper District) where operations focused on deposits at depths between 700 and 1000 metres below ground level. However, deeper Cu-Ag mineralisation, occurring up to 1300 meters below ground level, have recently become a subject of interest. Miedzi Copper Corp. is focusing its exploration programme on targets where the ore occurs deeper than 1500 metres, with the potential for future extraction of rich deposits (Speczik et al. 2013; Zieliński et al. 2017).

2 Assumptions of the exploration project

The occurrence of Cu-Ag ore in deep parts of the Fore-Sudetic Monocline was noted for the first time in 1956; however, at this time the possibility of its development was not considered. Further investigation based on the re-examination of core samples and drilling data from deep oil and gas wells ultimately allowed the demarcation of Cu-Ag prognostic areas within deep parts of the Fore-Sudetic Monocline (Oszczepalski and Speczik 2011; Oszczepalski et al. 2012).

Miedzi Copper Corp.’s programme was focused on deep parts of the Fore-Sudetic Monocline, which had not previously been an object of interest of other companies (Zieliński et al. 2017). In 2011, Polish Ministry of Environment granted the company 21 prospecting concessions on the Fore-Sudetic Monocline. The concessions were selected based on several criteria, most importantly the vicinity of Permian palaeo-elevations (Wolsztyń and Szprotawa domes) surrounded by contacts between oxidised and reduced facies. High grade copper mineralisation is very likely to occur in places where transgressive, epigenetic and oxidising Rote Fäule facies contacts reduced sediments (Oszczepalski and Rydzewski 1997; Pieczonka et al. 2007). The areas with prognostic copper mineralisation demarcated by the Polish Geological Institute (Oszczepalski and Speczik 2011) were also considered while establishing the boundaries of exploration targets.

3 Investigation of historical data and geological materials

The first stage of Miedzi Copper Corp.’s exploration programme involved the examination of historical drill
core samples. These studies were carried out in core repositories of the National Geological Archive and PGNiG – Polish oil and gas company, and included the review of rock material from a total of 411 boreholes. Samples from 216 selected boreholes were a subject of extensive laboratory examination. Miedzi Copper Corp. collected 2559 samples for lithogeochemistry analyses and 1081 samples for petrological and mineralogical studies, with simultaneous examination of organic matter geochemistry. This constituted the first research-based determination of future copper and silver drilling targets in deep parts of the Fore-Sudetic Monocline.

In addition, the company performed the reprocessing of geophysical data, which involved examining 24 000 gravimetric points and more than 1700 km of seismic sections. Seismic data was reprocessed using the method of effective reflection coefficients (Speczik et al. 2012). It allows transforming a conventional seismic image into an impulse form of seismic records, meaning a temporal sequence of coefficients, whose sections can be correlated with the logs of historical boreholes in order to trace the course of lithological series. This method is useful for establishing the location of major structural features like faults, which are the crucial components of a mineralising system. The identification of certain major tectonic deformations forced the company to modify its exploration programme for the first time, in order to focus on zones where the probability of finding abundant mineralisation was higher.

Moreover, in two of its concessions the company carried out experimental field studies using the magnetotelluric method, with a total profiling length of 27 km. The results of magnetotelluric surveying were not accurate enough to trace the macro trends of copper mineralisation at depths exceeding 1500 metres. For this reason, the company decided to discontinue the use of this method.

4 Results of geochemical analyses

The analyses of archival core samples included a wide range of specialised examinations of organic matter. Their results show positive correlation between the occurrence of orebodies and pervasiveness of the alteration of organic matter in rocks hosting the ore (Oszczepalski and Speczik 2009, Zieleański et al. 2017). Oxidised rocks are depleted of organic carbon and exhibit a lower hydrogen index, while their vitrinite reflectance index, thermal maturity and oxygen index are elevated (Table 1) (Sawłowicz 1993; Speczik 1994). Moreover, dominant components of organic matter in copper-bearing shale include macerals from the liptinite group, with vitrinite and inertinite group macerals occurring in minor amounts (Speczik and Pütmann 1987).

Furthermore, Miedzi Copper Corp. performed organic matter decomposition tests on the collected core samples using the Rock-Eval pyrolysis. Results showed the presence of strong Rote Fäule in prognostic and prospective areas. High grade copper mineralisation is usually directly correlated with strong Rote Fäule zones (Oszczepalski and Speczik 2009), thus the identification of such alteration became a strong argument in favour of further exploration in selected areas.

5 Drilling programme and its results

Based on the results of the above-mentioned analyses, more precise boundaries of prospective areas were established (Oszczepalski et al. 2016). Furthermore, Miedzi Copper Corp. amended some of its concessions before the initiation of drilling operations. The company decided to resign from areas where the base of Zechstein was particularly deep and initial investigation of mineralised intervals indicated low grades. Before the commencement of drilling, the only available data about Zechstein base in deep parts of the Fore-Sudetic Monocline originated from oil and gas wells. Of the 32 holes drilled in the years 2013-2019, 24 produced positive results in terms of Cu-Ag grade. Moreover, all boreholes led to more precise identification of boundaries between major oxidised fields and reduced zones. After the initial phase of drilling, certain concessions were reduced in area in order to focus on the richest, the most prospective parts – the so-called “sweet spots”. Effectively, the operations continued in 6 most promising concessions (Nowa Sól, Wilcze, Zatonie, Jany, Mozów-1 and Sulmierzycze). As a result of its drilling operations, Miedzi Copper Corp. has discovered 3 stratiform Cu-Ag deposits in Poland – Nowa Sól, Mozów and Sulmierzycze, lying within the boundaries of all six aforementioned concessions.

6 Geology – new aspects

The drilling results indicate that the general ore distribution and zonation are similar to the Legnica-Głogów Copper District, with the ore-bearing zones being adjacent to oxidised fields. The biggest differences involve narrow zones of very intense mineralisation, as well as the fact that areas with elevated Pb-Zn content are more extensive. Furthermore, in numerous holes lead and zinc minerals occur at the same depths as copper and silver, instead of forming a separate layer above them like in the mining district. This is caused by the presence of two sources of mineralising fluids: the
Szprotawa and Wolsztyn elevations, which resulted in the mixing of brines and a more polymetallic nature of mineralisation. An example of this can be seen in Figure 1, which shows selected core samples from the Nowa Sól C14B hole, along with the results of chemical analyses of the whole ore-bearing interval.

6.1 The Mozów deposit

The Mozów deposit is characterised by the deepest mineralised interval that occurs at the depth from 2100 to 2700 metres below ground level. The location of the deposit is shown in Figure 2A. Currently, the estimated resources are 4.4 million tonnes of Cu and 7.3 thousand tonnes of Ag in Polish category C₂ (an equivalent of indicated resources), with average thickness of 2.45 metres and average copper content amounting to 2.42%. Additional resources in category D₁ (inferred) are 8.4 million tonnes of Cu and 11.9 thousand tonnes of Ag.

Despite the depth, according to a technical report prepared by Runge-Pincoc-Minarco, mining operations in this deposit are economically justified. The estimated production costs are US $2705 per 1 tonne of copper with underground milling or US $2765 per 1 tonne with conventional milling (Goodell et al. 2017). All calculations for this and the following deposits are based on an expected average copper price of US $3 per 1 pound in a 10-year period.

6.2 The Nowa Sól deposit

The Nowa Sól deposit partially overlaps 4 concession areas: Nowa Sól, Jany, Zatonie and Wilcze (Figure 2A). The depth of the mineralised interval in that deposit varies from 1500 to 2400 metres below ground level. The demarcation of this deposit was a true greenfield discovery, as there had been no historical boreholes in the Nowa Sól concession, with no archival cores to examine before the initiation of Miedzi Copper Corp.’s
drilling programme. Currently, the estimated resources in categories C₁+C₂ (indicated and measured) are 7.0 million tonnes of Cu and 17.8 thousand tonnes of Ag, with average thickness of 3.40 meters and 1.40% of copper. Additional 4.5 million tonnes of Cu and 11.0 thousand tonnes of Ag are calculated in category D₁ (inferred). According to the technical report, mining operations in this area are also possible from an economic point of view. The estimated production costs are US $ 2698 per 1 tonne of Cu with underground milling or US $ 2698 per 1 tonne with conventional milling (Goodell et al. 2017). Geological documentation of the Nowa Sól deposit fulfilling the requirements of Polish law is in the final stage of preparation and it will be presented to the Minister of Environment in 2019. After the Minister’s approval it will be possible to apply for a mining licence.

6.3 The Sulmierzyce deposit

The mineralised interval of the Sulmierzyce deposit lies between 1400 and 2000 metres below ground level. The location of the deposit is shown in Figure 2B. The current estimated resources in categories C₁+C₂ (indicated and measured) are 4.7 million tonnes of Cu and 10.5 thousand tonnes of Ag with average thickness of 1.87 metres and 2.93% of copper. Resources in category D₁ (inferred) are 5.4 million tonnes of Cu and 13.2 thousand tonnes of Ag. According to the technical report, future mining operations are also economically justified. The estimated production costs are US $ 2429 per 1 tonne of Cu (Bohnet 2017). Geological documentation of this deposit is also in preparation and it will be conveyed to the Minister of Environment in the middle of 2019.

7 Summary

Calculations have proved that mining operations in all deposits discovered by Miedzi Copper Corp. are economically profitable for the assumed average copper price of US $ 3 per 1 pound. Underground extraction should focus on copper ore of the best quality and highest grade. Currently available mining techniques are sufficiently developed to meet the challenge of building a deep copper and silver mine on discovered new Polish deposits of the Fore-Sudetic Monocline. The construction of mines in these areas is determined by the introduction of modern mining techniques of shaft sinking, waste management and air conditioning (Addison et al. 2012; Bohnet 2017; Goodell et al. 2017; Zieliński and Speczik 2017). Miedzi Copper Corp.’s drilling operations are currently continuing in the Nowa Sól area with the purpose of increasing the amount and accuracy of resources which will be disclosed in the annex to the geological documentation of this deposit.

References


Bohnet E (2017) Technical Report on Miedzi Copper’s Sulmierzyce Project, Poland


Miniaturised Gravity Sensors for Geophysical Monitoring

Institute for Gravitational Research, University of Glasgow, UK

D. J. Paul
School of Engineering, University of Glasgow, UK

Abstract. A miniature gravity sensor is being developed that utilises the fabrication techniques used to make mobile phone accelerometers. These devices will be significantly cheaper than existing commercial gravity sensors used in geophysics. This reduced cost means that networks of gravimeters will be feasible, providing greater spatial resolution to gravity surveys. Here, the latest iterations to the prototype are outlined. A measurement of the Earth tides is presented, demonstrating the sensitivity, and long-term stability of this sensor. The device is shown to have a sensitivity of less than 10 μGal/√Hz (i.e. 10^{-7} m/s^2 in an integration time of one second).

1 Introduction

Gravimeters are used for various applications within geophysics; prospecting (Barnes 2012), volcanology (Carbone 2017), and hydrology (Naujoks, 2008) being three examples. They can be used to infer subterranean density variations, and hence gather information difficult to find by other means.

Gravimetry has also been used in the mineral exploitation industry (Martinez 2013), but its use has been somewhat limited. Mosher and Farquharson (Mosher 2013) state that one reason for this is the size of existing devices. They explain that borehole gravimetry is of particular use for mineral exploration, but that the size of existing equipment means that this can only be done in holes of a large bore. The development of miniaturised devices could therefore enable wider usage of borehole gravimetry in the industry.

Commercial gravimeters cost upwards of fifty thousand pounds, and generally weigh at least five kilograms. The size and cost of these devices has limited their widespread usage. One exception is a borehole gravimeter developed by Scintrex (Nind 2007), but this device is not available for purchase (only for surveys conducted by the company), and it is not fabricated in a way that enables mass production.

Mobile phones utilise MEMS (micro-electro-mechanical-systems) accelerometers for various purposes. These devices can be mass produced in great numbers. They do not, however, meet the sensitivity requirements of a workable gravimeter by four orders of magnitude; nor would they be stable enough to make long-term measurements over day to week timescales, another essential criterion of commercial gravimeters.

Utilising experience within the gravitational wave community (Abbott 2016), researchers at Glasgow created the first MEMS gravimeter (Middlemiss 2016). This device capable was of long-term measurements, and with a noise floor within an order of magnitude of commercial gravimeters. Since this work was published in 2016, several iterations have occurred in the design of the sensor (Middlemiss 2017; Bramsiepe 2018); each making the device smaller, more rugged, and more sensitive to gravitational acceleration.

This manuscript outlines the significant changes made to the latest design of this device, and a demonstration is made of the current sensitivity of the device.

2 System Description

The MEMS gravimeter is comprised of a mass suspended from four geometrical anti-spring flexures (Acernese 2015). This entire structure is etched monolithically from a single piece of silicon using standard photolithography techniques. As a mass-on-spring system, this structure has a mechanical resonance, which occurs at a frequency of 7.3 Hz. Beneath this resonance peak, the device has a constant relationship between displacement and acceleration. This means that by measuring the displacement of the mass on the springs, one can make a direct measurement of the local gravitational acceleration. This displacement is measured using a capacitive method. Metal electrodes are patterned on the surface of the silicon mass. A second (fixed) plate is then fixed above the mechanical structure. Another set of electrodes are patterned onto this second plate. A sinusoidal signal is driven to the electrodes on the mechanical structure, and the second plate is used to measure the current variations caused by mutual capacitance variations as the mass moves. The mechanical device can be seen in figure 1, with the metal electrodes visible on the surface of the suspended mass.
Complications are inevitable when constructing a device for such precision measurements. As with any other relative gravimeter (so called because it makes measurements relative to a spring whose spring constant can vary); parasitic signals are a problem. The Young’s modulus of silicon varies with temperature (Hopcroft 2010); changing the spring-constant of the flexure; and thus the measurement of gravity. For this reason, it is essential to control the temperature of the structure to within 1 mK using precision measurement and control loop feedback. This is achieved using nested temperature control enclosures. A metal box is controlled at a set-point around five degrees Kelvin above ambient temperature. The MEMS package is enclosed within this box; separated by a peltier device. The peltier allows a second level of thermal control. To further reduce the effect of long-term drifts, it is necessary to use a lock-in amplification technique (Scofield 1994).

The functionality required to implement the signal processing outlined above can now be carried out using a custom-built FPGA (field-programmable gate array) electronics board (Monmasson 2011). This board can be programmed to input multiple data-streams, feedback control signals to maintain temperature, and carry out a lock-in amplification process.

3 Results

To demonstrate sensitivity of the device and its capacitive readout, the system was left in a basement lab for one week. During this time the MEMS did not experience temperature variations larger than 1 mK. The output of the system was monitored continuously. This output was converted into unit of μGal (a unit commonly used by the gravimetry community, where 1 Gal is equal to 1 cm/s²).

Figure 2 is a time-series of the data recorded during this week-long period. The light grey series is the raw signal (with a polynomial drift removed), the black series is the same data with a running average applied, and the yellow series is the theoretical Earth tide signal, as predicted for our location in Glasgow by the T-Soft software (Van Camp 2005). The Earth tides are periodic fluctuations in the elastic crust caused by tidal forces within the Earth-Moon-Sun system (Farrell 1973). These crustal fluctuations change the distance between the crust, and the centre of the Earth, and thus the surface value of gravity. A clear correlation is seen between the measured data and the theoretical Earth tide signal. Unlike data previously published, these data have not been processed using regression analysis; yet the signal is still clearly observable.

To ascertain the noise floor of the system (when controlled using the FPGA board), an amplitude spectral density was plotted (Fig. 3). This figure demonstrates that the device can measure the primary and secondary microseismic peaks (Peterson 1993). In addition to this, it demonstrates that the noise floor of the system lies beneath 10 μGal/√Hz.

4 Conclusion

A device capable measuring variations in gravitational acceleration beneath 10 μGal, with a small size/cost will change the way in which gravimetry is carried out, and the people who can do it.

A dramatic cost reduction in gravimeter technology will mean that networks of gravimeters can be placed in an array over an area of geophysical interest, providing increased spacial and temporal data. Work is already underway to do this at Mt Etna Volcano in Sicily, as part of the NEWTON-g H2020 consortium.

The reduced weight of these devices means that they can be flown in drones, to conduct airborne gravity surveys. Work is also underway on a device that can be
drone-mounted.

More generally, by reducing the size/cost of gravimeters, the field of gravimetry can be democratized; gravity surveys will no longer solely be the remit of oil and gas multinationals or large academic consortia. The mineral exploration industry – which has only used gravimetry sparingly in the past - will be a clear benefactor here.

Acknowledgements

We would like to thank Kelvin Nanotechnology for fabricating the MEMS devices used to gather the data presented in this manuscript. We also wish to thank the staff and users of the JWNC for their support in the development of the MEMS fabrication process.

References


Low volume solution ICP-MS: achieving high-precision geochemical analysis of small amounts of sample

Lewis A. Banks  
British Geological Survey and University of Leicester

Simon R. Tapster, Matthew S.A. Horstwood, Simon R. Chenery  
British Geological Survey

Daniel J. Smith, Tiffany L. Barry  
University of Leicester

Abstract. There is a need to improve geological models for ore deposits. This requires the analysis of ever smaller amounts of material and element, to either increase the spatial (and hence temporal) resolution of the study or bring novel minerals into the realms of analytical capability. The precision and accuracy of these measurements must be sufficient to resolve the geochemical variation required, e.g. across an orebody. Here we show the application and potential of the novel method of low volume sampling for geochemical measurements, by solution mode ICP-MS. Through the analysis of U-isotopes, we demonstrate that by changing the way solutions are introduced to ICP-MS instruments, comparable precision to that achieved using conventional measurement techniques, can be attained by the low volume method, yet utilising ten times less material. This method yields a 2.5 times improvement in measurement precision over the conventional method, for 2 ng U. The analytical time of 10 minutes shows a threefold reduction compared to conventional methods. The potential of low volume sampling greatly improves the analytical efficiency, the spatial resolution of a study or opens novel minerals to routine analysis.

1 Introduction

The challenge facing the progression of analytical geochemistry, and therefore the understanding of ore deposits, is the inability to measure finite amounts of element contained within the volume of a single crystal. These are inaccessible due to instrumental detection limits, impacting the precision of the analysis. This renders small variations in the target system unresolvable.

Inductively coupled plasma mass spectrometry (ICP-MS) is a widely used tool for trace element and isotopic analysis. This is due to its low backgrounds, the ability to ionise most elements, and its adaptability to analytical requirements. This study presents the application of the Teledyne-CETAC MVX 7100 µl Workstation (MVX) to solution ICP-MS. This aims to bridge the gap between conventional solution ICP-MS and laser ablation ICP-MS.

This new method of solution ICP-MS analysis targets and overcomes the inefficiencies of conventional ICP-MS sample introduction. This method relies on the relative preconcentration of the element of interest in the solution to yield an increased signal to noise ratio (SNR; Bauer and Horstwood 2018).

Integrating the ability to achieve high-precision elemental and isotopic analyses on low amounts of sample with petrographic, tracer and geochronological records will better constrain the timing and the sources of the formation of an ore deposit. This will enable a deeper, and higher resolution understanding of their genesis. This method will use geological materials that have previously been impossible to analyse, advancing the understanding or ore forming processes.

2 Sample introduction for solution ICP-MS

Figure 1. The analytical setup of the low volume method. The green square identifies the sample introduction mode. This can be a conventional autosampler, a laser ablation system or the MVX for example.

Conventional solution sample introduction to ICP-MS instruments (Fig. 1) is a significant source of inefficiency to the analysis, both in terms of time and wasted sample. Long sample grow in and washout times can lead to significant amounts of the sample not being utilised in the sample measurement. This creates both wasted time and wasted sample.

Another source of wasted sample by conventional sample introduction for ICP-MS is that generally only part of the sample is utilised, e.g., 1500 µl of sample is prepared and only 1000 µl is aspirated. This therefore results in 500 µl of remaining sample solution.

There is also a relatively ‘low and long’ signal profile when measuring conventionally as the sample solution is dilute. This results in a low SNR whereby the baseline and/or background make up a significant proportion of the total signal intensity.

Beam stability for conventional analyses relies on the stability of the Ar stream aspirating the sample. Fluctuations can lead to variations in signal intensity, which yield inaccurate results if obtaining ratios by some single collector (SC) instruments, whereby spectral skew can be an issue.
3 What is low volume sampling?

The low volume solution sample introduction method aims for a square-wave signal profile whereby the sample grow in and washout are minimised. This leads to more of the sample being used in the analysis, therefore leading to less wasted sample and time.

The low volume method only utilises 100 µl of sample solution, facilitated by relative preconcentration. This method also aspirates the whole sample, so wasted sample is negated.

Contrary to the ‘low and long’ signal profile of conventional methods, the low volume method utilises a ‘high and short’ peak signal due to the relative preconcentration of the element of interest. This higher signal intensity results in an increased SNR. As the baseline and background provide less of the total signal intensity with the low volume method, more of the sample contributes to the final measurement precision.

The MVX is a syringe driven autosampler which actively pushes the sample into the ICP-MS. Therefore, any effects of a variable Ar stream affecting the beam intensity are reduced, reducing the chance of spectral skew effects.

4 Example: Uranium isotopes in geological samples

Understanding U-isotopes is a fundamental aspect of geochronology as they underpin U-based dating methods. A well constrained U-isotope value in the sample will provide a more accurate age determination (Hiess et al. 2012; Tissot and Dauphas 2015). The U-isotope value of the sample determines the relative abundance of radiogenic Pb in the sample by which it is dated. Therefore, understanding the U-isotope ratio is imperative to an accurate age determination.

Low volume sampling demonstrates the ability to gather high-precision data on 2 ng of natural U with a 2.5 times improvement in measurement precision (Fig. 2) over conventional methods. This amount of element is in the realm that is present in single crystals for monazites and large zircons. The ability to measure single crystal U-isotope compositions allows a unique U-isotope value to be applied to measurements, allowing the most accurate age determination possible.

Although 2 ng U may not be enough material to resolve variation in U-isotopes in zircons, the measurement precision achieved facilitates resolving the larger range of variation in $^{235}U/^{238}U$ present in nature, at a higher resolution than the conventional method, when using 2 ng.

Monazite is a REE-phosphate accessory mineral found in igneous and metamorphic rocks. It can also be formed by hydrothermal processes and is found in some orogenic Au deposits. Fig. 3 shows analysis of three single crystal fragments of this mineral by the low-volume method. Stern is a common reference material used during monazite analysis, making full characterization important. Not only does Fig. 3 show that this method is appropriate for this type of measurement, but that the Stern monazite is homogenous at this scale (see Fig. 3 caption). This information was previously outside the realms of analytical capability due to the amount of material required to yield this level of precision.

Further work to characterise a suite of monazite reference materials will establish the homogeneity of U-isotopes within crystals and crystal fragments of the commonly used reference materials. Again, this work will have significant implications to U-based geochronology, whereby the starting U-isotope composition is imperative to an accurate date (Hiess et al. 2012). Also, heterogeneity in reference materials introduces a fundamental limitation to uncertainty. For example in laser ablation analysis, there is a fundamental limitation on the uncertainty of monazite reference materials of 1% (2σ). This limits the resolving power of an analysis. Subsequent geochronological measurements will facilitate a better constrained ore deposit genesis at a
higher resolution (Fig. 4) than is previously possible.

5 Advantages of low volume sampling to industry and academia

The low volume sampling method increases the overall efficiency of the measurement by measuring as much of the sample as possible. This results in significant advantages over the conventional method.

For the measurement of U-isotopes, it is shown that a tenfold decrease in sample size is required to achieve the same precision by the low volume method, as would be achieved using the conventional method (Fig. 2). This decrease in sample size required has far reaching effects in geochemistry, namely, the spatial resolution of geochemical analysis by solution ICP-MS is greatly increased (Fig. 4). For example, conventional analysis will require a bulk dissolution of ten crystals to yield the amount of U required for the precision needed to resolve variation in the samples. This results in an ‘averaging’ of the potentially different values in the crystals, yielding one homogenised result. Using the low-volume method however, this can yield ten, single crystal analyses at the same precision as the bulk dissolution, therefore greatly increasing the spatial resolution of the study. It can also bring novel minerals into the realms of analytical capability. These minerals can have concentrations of element previously too low to measure. The advancements facilitated by this new technique will further our understanding of ore deposit genesis by creating a higher resolution model. This is achieved by both low-volume, single crystal analysis of orthodox minerals and routine analysis of novel minerals by the same method.

Further to this, if measuring the same amount of element as the conventional method, but running by low volume, the increase in precision will yield a higher resolution of the study. This means that smaller variations in elemental and isotopic ratios can be defined.

Furthermore, the time taken for the complete sample run by the low volume method is three times faster than that of the conventional method. This means that the throughput of samples for the low volume method is increased over the conventional method, creating a higher efficiency method overall.

The low volume method also produces negligible waste per sample. This results in less potentially hazardous waste being produced, therefore also making this method cheaper and safer.

Acknowledgements

This study is being undertaken with funding by a NERC CENTA studentship. This is a CASE award with Teledyne-CETAC. Thanks to Pete Winship, Niel Williams and Damon Green from Teledyne-CETAC.

References


Biogeochemical surveys for epithermal Au-Ag exploration in New Zealand

Anthony B. Christie
GNS Science, PO Box 30-368, New Zealand

Colin E. Dunn
Colin Dunn Consulting Inc., North Saanich, British Columbia, Canada.

Abstract. Biogeochemical orientation surveys were undertaken at epithermal Au-Ag deposits in the Coromandel Volcanic Zone – Hauraki Goldfield (CVZ) and Taupo Volcanic Zone (TVZ), and at the Waiotapu geothermal area in the TVZ. Several plant types were sampled including pine tree bark and needles, tree fern fronds and tea tree foliage. The ferns had the most consistent occurrence and were easiest to sample, although tea tree was the main sample medium at Waiotapu. Sampling at the three CVZ Au-Ag prospects, Luck at Last, Pine Sinter and Ohui, was on previous soil geochemistry grids. The biogeochemical element anomalies successfully highlighted most known quartz veins and provided additional anomalies for further investigation. The latter were in many cases not spatially coincident with similar soil geochemical anomalies and these spatial differences are attributed to deeper penetration by the plants or soil creep downslope. At the Goldmine Hill Au-Ag prospect in the TVZ, highest Au, Ag, As and Al in ferns correlated well with the elevated Hg reported previously in soils from this area and with anomalies of pathfinder elements in reconnaissance rock chip geochemistry. At the Waiotapu geothermal area, significantly higher concentrations of Ag, Au, Sb, As, Cs and Rb were present in samples close to Champagne Pool than elsewhere confirming its location as the main outflow source of precious metals and their pathfinder elements.

1 Introduction

Exploration of late Cenozoic, volcanic-related, low sulphidation epithermal Au-Ag prospects in the North Island of New Zealand typically involves soil geochemical surveys as a primary method for siting drilling in areas with sparse outcrop. Between 2013 and 2017, biogeochemical orientation surveys, predominantly sampling ferns (Fig. 1), were carried out in the Hauraki Goldfield - Coromandel Volcanic Zone (CVZ) and in the Taupo Volcanic Zone (TVZ) to test the method as an alternative to soil surveys (Fig. 2). Three Au-Ag prospects were sampled in the CVZ, Luck at Last, Pine Sinter and Ohui, and one in the TVZ, Goldmine Hill (Fig. 2). Additionally, in the TVZ, sampling was carried out in the Waiotapu geothermal area, famous for its Champagne Pool and surrounding Au-As-Sb-Tl-bearing sinter sheet that is used as a modern analogue of epithermal mineralisation processes (e.g. Rowland and Simmons 2012).
2 Analyses

Samples of plant material were oven-dried and the foliage separated. Some sets of samples were processed as dry tissue, whereas others were ashed by controlled ignition at 485°C for 24 hours. The samples were analysed at Bureau Veritas Laboratories in Canada by method VG104-EXT (52 elements) plus 12 of the REE elements not included in the standard suite, to give a total of 64 elements. The material was digested in aqua regia (HNO₃-HCL-H₂O at 2:02:02) and analysed by inductively coupled plasma emission spectroscopy (ICP-ES) for Ca, Mg, Na, K, and Fe, and inductively coupled plasma mass spectrometry (ICP-MS) for Ag, Al, As, Au, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, La, Li, Lu, Mn, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr. For most elements there are little or no losses during ashing and for others there are small losses (e.g. As and S), and complete loss of Hg. The elements that partially volatilise typically exhibit a consistent loss provided consistent ashing conditions in the laboratory are maintained, and so the patterns of element distributions are meaningful (Dunn and Christie 2014). Ashing concentrates fern tissues by approximately 10 to 15-fold and by determining the ash yield of each sample, the data can be levelled to a dry weight basis.

The QA/QC protocols followed were:

- Control SF1 (swordfern ash) was inserted at irregular intervals throughout the analytical sequence at a frequency of 1 standard per 20 samples.
- Field duplicates were inserted at the same frequency as the control SF1.
- The geochemical laboratory inserted 3 analytical duplicates at a frequency of approximately 1 per 40 samples.
- The laboratory also inserted several of their own controls and blanks at a frequency of approximately 1 of each per 40 samples.

3 Hauraki Goldfield, CVZ

3.1 Luck at Last

At the Luck at Last prospect, west of Whangamata, underground mining over a vertical extent of ~108 m, from 1896 to 1929, produced 13,176 oz of Au-Ag bullion from quartz veins in hydrothermally altered, flow-banded rhyolite and andesitic tuffs. The biogeochemical survey used a previous soil geochemistry sampling grid and sampled pine tree bark and needles, and several fern species at or adjacent to the previous soil sample sites (Dunn and Christie 2014; Dunn et al. 2017). Silver fern (‘ponga’) proved to be the most widespread and diagnostic of the several species tested. Concentrations of Rb and Cs were elevated near the mineralised vein, but the highest levels of Au and Zn occurred near the eastern margin of the survey area and around the disturbed ground in the west previously occupied by the stamp mill battery. At the latter site, analysis of adjacent ‘ponga’ and ‘wheki’ (rough tree fern) showed that ‘ponga’ is considerably more enriched in most elements – with the notable exception of Ba being higher in the ‘wheki’. Several elements such as Ag (Fig. 3) exhibited anomalies associated with both the quartz veins and the eastern area. The eastern anomalies lie along a northeasterly trend east of the main quartz vein and mine and provide new targets for future exploration.

3.2 Pine Sinter

The Pine Sinter prospect is a recent discovery and has had no previous mining. A rhyolite dome is overlain by a sequence of rhyolitic tuffs and breccias, and andesitic flows and pyroclastic units. Remnants of a sinter sheet are present on the surface. To the east, the sequence is overlain by post-mineral andesite. Following the positive experience with ferns at Luck at Last, only ferns were sampled at Pine Sinter and they were collected on a previous soil geochemistry sampling grid. Results showed that silver ferns have slightly anomalous Ag content in a north-trending zone located near and parallel to the post mineral andesite contact (Fig. 4). Several elements (Ba, Ca, Sr, Se and REE) are elevated in a parallel trend but ~100 m to the west. All Au levels were low and no definitive trends were obvious.
Figure 4. Pine Sinter – contours of ppb Ag in silver fern. Sample points are shown by the black triangles, the thick black line in the top left is a road and the blue line is a stream. Grid spacing is 100 m.

3.3 Ohui

At Ohui, shallow underground mining from the 1890s to 1910 produced 234 oz of Au-Ag bullion from quartz veins hosted in andesite and rhyolite. Ferns were sampled on a previous soil geochemistry grid. The Phoenix and Staircase vein areas are defined by elevated Ag and Sb in the ferns (Fig. 5), but not by Au (Dunn et al. 2018). The Staircase veins also show some weak enrichment of As, Nickel, Co, and to a lesser degree S, Ca and Ag (Fig. 5) define a north-easterly trend between the Phoenix and Staircase areas, providing secondary exploration targets. Earlier soil surveys showed enrichments of Au, As, Sb and Hg near the Great Mexican fault, but these signatures are either not present in the ferns where sampled, or the weak signatures are laterally displaced. A large part of the area of interest was not available for sampling because the vegetation had been cleared by logging operations (shown by area of ‘No samples’ in Fig. 5).

Figure 5. Ohui – contours of ppb Ag in silver fern. Grid spacing is 100 m.

4 Taupo Volcanic Zone

4.1 Goldmine Hill, Puhipuhi

At Goldmine Hill, east of Rotorua, alteration and mineralisation occur in close spatial association with dacitic intrusions, breccias and flows of Pleistocene age (Fig. 6). These rocks are intruded into and erupted onto Okataina Group rhyolitic volcanic and volcaniclastic rocks. They are transgressed by northeast-trending faults. Exploration to date has been of a reconnaissance nature and there has been no past mining or drilling.

Reconnaissance sampling of pine bark and needles, and ferns, on road and stream traverses showed that wheki is the dominant fern species, but there were sufficient ponga and mamaku (Fig. 1) to establish that they absorb substantially different amounts of elements, with wheki having lowest concentrations of most elements. However, the spatial distribution of elements is of greater significance than absolute concentrations, and highest Au, Ag (Fig. 6), As and Al in wheki correlated well with the elevated Hg reported previously in soils from this area and with anomalies of pathfinder elements in reconnaissance rock chip geochemistry (Dunn and Christie 2017).

Figure 6. Goldmine Hill, Puhipuhi – ppb Ag in wheki at sampled locations. Grid spacing is 100 m. Base geology map modified after Corbett (2015).

4.2 Waiotapu

The Waiotapu active geothermal area is characterised by a large area of steaming ground and fumarolic activity. Vegetation in the area is dominated by two types of tea tree – Kanuka and Manuka. Kanuka has higher concentrations of the epithermal related elements Ag, Au, Sb and As than Manuka, especially close to Champagne Pool (Fig. 7) where the deep
geothermal alkali chloride water flows out to surface from a hydrothermal eruption crater. The sample taken near Champagne Pool is growing in soil developed on a hydrothermal eruption breccia, although the metal enrichment in the Kanuka is probably also in part a result of precipitation from the metal-enriched mists emanating from Champagne Pool (Dunn et al. 2018).

5 Discussion

5.1 Fern versus pine geochemistry

At Luck at Last, a comparison of median concentrations of elements in ferns, pine bark and pine needle litter showed that many elements were considerably more concentrated in the ferns than in the other media – notably Al, B, Ce, Cr, Cs, Cu, Ga, K, La, Mg, Mn, Mo, Na, Ni, P, Rb, S, Sc and Y (Dunn and Christie 2014). Elements consistently enriched in the pine bark were As, Au, Pb, Ti, and Bi. Pine needles had the highest concentrations of Ag, Ca and Zn.

5.2 Fern versus soil geochemistry

Many of the biogeochemical anomalies were away from known sources (veins, breccia, sinter) and some of these were not spatially coincident with similar soil geochemical anomalies. These spatial differences are attributed to deeper penetration by the plants, or soil creep downslope, with contributions of elements migrating vertically from concealed mineralisation.

5.3 Selection of sample media

A major factor in selecting a suitable plant species to sample is its distribution in the survey area. The plant species must be commonly present and occur throughout the area. It must also have a good response to the elements of interest so that concentrations are significantly elevated above the lower level of detection. This can be improved by ashing to concentrate the elements, but at the loss of Hg. In the epithermal Au-Ag prospect areas sampled here, ferns proved the most useful sample medium.

6 Conclusions

Biogeochemical orientation surveys carried out in New Zealand show that common plant species exhibit anomalous element concentrations in the vicinity of Au-Ag deposits. Different species have different responses and therefore care must be taken in the species selection, preferably through an orientation survey in the exploration area and employment of samplers that are trained in identification of the selected species. Surveys to date have assembled a reference biogeochemical database of common species to assist in future mineral exploration surveys.

Acknowledgements

Access to Luck at Last, Ohui and Pine Sinter was provided by Newmont Waihi Gold and OceanaGold, and facilitated by Rick Streiff, Lorraine Torckler, Rob Theron and Robert Schoonderwoerd. Access to Goldmine Hill was provided by Silver City Minerals and facilitated by Chris Torrey and Gordon McLean. Jenny Black, Holly Harvey-Wishart, Chris Town, Gordon McLean and Rob Theron provided field assistance and John Simes provided laboratory assistance. Jenny Black drafted Fig. 1. Funding was provided by the New Zealand Government and by Silver City Minerals for the analyses of the Goldmine Hill samples.

References


Troubleshooting hydrogeochemical sampling in grassroots mineral exploration: a Case Study from central Australia’s Western Amadeus basin

Jennifer A. Roskowski
Generative Exploration Group, First Quantum Minerals Ltd., West Perth, WA, Australia

Nathan Reid
CSIRO Mineral Resources, Kensington, WA, Australia

James Kidder
Department of Geological Sciences, Queen’s University, Kingston, ON, Canada

Ryan R.P. Noble
CSIRO Mineral Resources, Kensington, WA, Australia

Abstract. Early-stage exploration for ore deposits has historically included reconnaissance sampling of solid media. Sampling of natural waters for mineral exploration has been increasing since its initial adoption in the 1970s but has not yet become a standard greenfields exploration tool despite increased commercial availability of low detection limit water analyses. A practical field sampling methodology was developed by the CSIRO, and interpreting results appeared fairly straightforward after initial literature review. However, the practicalities of analyzing hydrogeochemical data from real-world mineral exploration samples has led to important learnings regarding the assessment of metal anomalism in natural waters. We present an example of highly base-metal anomalous samples from saline groundwaters in Australia. Several phases of water sampling across different seasons followed by pump testing of the anomalous water bore revealed that the extremely elevated copper anomalism was related to downhole equipment rather than a buried mineral system. We outline the evolution of field work and data interpretation that led to this conclusion as well as share guidelines for how to mitigate the effects of potential downhole contaminants to produce viable, geologically meaningful water sampling results for reconnaissance mineral exploration.

1 Introduction

Geochemical footprints of ore deposits are detectable in groundwaters on a larger scale than is typically visible in solid media (Leybourne et al. 2007). With the advent of lower detection limits in commercially available analytical techniques, hydrogeochemical sampling can now reliably detect and map kilometre-scale footprints of both ore and pathfinder elements (Eppinger et al. 2012). The ability to detect mineral system footprints from farther away or under deeper post-mineral cover is becoming increasingly important in modern-day mineral exploration.

Reconnaissance hydrogeochemical sampling was employed during an initial field program in the Amadeus Basin of arid Western Australia. The Amadeus Basin is a Neoproterozoic to Devonian intracratonic basin formed during the breakup of the supercontinent Rodinia (Walter and Veevers 2000). The Amadeus Basin covers an area of approximately 180,000 km² along an E-W axis, and sediment thickness reaches in excess of 12km (Edgoose 2013). Much of the basin lies in the Northern Territory, but the western extent of the basin traverses into Western Australia and is interpreted from regional magnetics to exist under thin cover in an approximately 40,000km² area. Copper shows and prospects are known in the eastern and central Amadeus basin, where these Neoproterozoic strata outcrop extensively.

2 Exploration Program Overview

The Amadeus Basin is broadly coeval in time and tectonic setting with the well-endowed Central African Copperbelt, and the western extent of the basin was selected for on-ground exploration for large sediment-hosted copper deposits following desktop review. The western sub-basin was interpreted to contain shallow to outcropping Neoproterozoic strata obscured by a thin veneer of desert sand and has had relatively little historic exploration due to its remoteness and the challenging access conditions.

The presence of relatively thin (generally less than 50m) transported, post-mineral cover on conceptually prospective sedimentary rocks made the western Amadeus a prime location for a wide-spaced, reconnaissance-style hydrogeochemical sampling campaign. Initial levels of base metal anomalism in water samples were very encouraging. Repeat sampling of the most anomalous bore continued to indicate elevated levels of base metals at the site; however, traditional reconnaissance geological mapping and sampling in the region was not compelling.

Before proceeding with more substantial on-ground expenditure, robust evidence supporting a direct relationship between the strongly base-metal anomalous water bore and buried mineralisation was required. Due
diligence work was conducted to assess whether the metal anomalism of the borehole could be due to contamination at the site.

Several types of contamination were hypothesized including historic leaded petrol spills, downhole industrial detritus, sample acidification with contaminated acid, and metallic downhole gear. Re-assay and re-sampling of several bores in the region ruled out any issues with sample preparation or assay laboratories. Hydrocarbon sampling of bore waters ruled out the current presence of any type of hydrocarbon at the site, and Pb isotope sampling was proposed as one possible avenue to test for spills of historic leaded petrol.

However, after correspondence with James Kidder at Queen’s University, it became apparent that the suite of anomalous metals and their relative levels of anomalism were very similar to waters measured from various household and industrial water taps with brass fittings. With this information in mind, the downhole gear became the prime suspect for base metal contamination in the water bore. A water bore pump test was designed with input from the CSIRO team in Perth and executed by FQM personnel and contractors.

Details of sampling campaigns, methodology, and results are elucidated below.

3 Initial Reconnaissance Water Sampling

3.1 Overview

A helicopter-supported, sub-basin wide water sampling program was conducted in collaboration with Indigenous Aboriginal Traditional Owners and anthropologists during October-November 2013. Sample spacing was entirely dependent on the location of existing surface and subsurface water sources in the region; approximate sample spacing was on the order of 30km.

Knowledge of the location of available water sources was derived mainly from consultation with Ngaanyatjarra Land Council anthropologists and Traditional Owners. Water sources included traditionally known soaks, seeps, and springs; locally administered water bores; and historic gold exploration drill holes. Water bores typically contained varying types of irretrievable downhole equipment. Several of the water bores were ~1950s-60s era hand pump bores.

Sample collection was conducted during the drier months of the year.

3.2 Methodology

Samples were collected according to the procedure in Noble et al. (2011). Samples were stored at camp in an air-conditioned trailer for the duration of the 3 – 4 week program. Samples were sent to ACME Labs in Canada for acidification and low-level hydrogeochemical analysis; however, significant dilution of the salty, Australian cation samples was required at this lab in order to maintain the instrument quality for use on very fresh Arctic waters. This and other analytical challenges prompted FQM to send a split of the cation samples to ALS Chemex Minerals lab in Vancouver for verification purposes. Reassay of cation samples at ALS confirmed anomalism and generally reproduced the ACME results.

Water sample assays were placed into aquifer groups determined by their physicochemical properties and each aquifer group was assessed separately for anomalism. Metal anomalism was evaluated with respect to the pH, Eh, and salinity of the water in question.

3.3 Results

The 2013 water sampling campaign resulted in several Cu anomalous samples; these samples tended to also have high Pb and Zn and variably elevated V, Cd, and U. In both locations with exceedingly anomalous base metal enrichment, the samples were serendipitously collected as field duplicates. The fact that the anomalous metal concentrations were broadly repeatable in field duplicates increased confidence that the metal anomalism was genuine.

Background levels of copper in water for this region are ~30ppb Cu. The highest copper assay in water was 954ppb Cu with a similarly high but slightly depressed duplicate sample; this bore was also strongly anomalous in Zn (3869ppb), moderately anomalous Cd and V, and had concerningly elevated Pb (49.5ppb) given that the water source was a hand pump bore occasionally used for drinking water by local residents during hunting trips.

All other base-metal anomalous water samples were determined to lie broadly along the NaCl - metal enrichment trend, thus downgrading the significance of their high metal content.

Figure 1. Location map of water samples in western Amadeus Basin. Raw copper values (ppb) on satellite imagery.

4 Re-assay Water Sampling Campaign
4.1 Overview

After significant delays in on-ground access due to protracted negotiations, the field area was again accessed in March 2016. During the execution of an Aboriginal Heritage Cultural Clearance Survey on this tenure, repeat duplicate samples were collected from the anomalous water bore and a background-level water bore also within the license area.

Samples were collected during the wetter part of the year.

4.2 Methodology

Samples were collected according to the procedure in Noble et al. (2011). Samples were stored in a camp cooler in the shade for several days before being transported to Perth via aircraft. Cation samples were acidified at the CSIRO lab in Perth with 1mL clean nitric acid; no substantial precipitate was noted in the samples.

Samples were submitted to ALS Perth for shipment to ALS Chemex Minerals Lab in Vancouver for analysis by high resolution hydrogeochemical package. Duplicates, blanks, and standards were included in sample submittal for lab and method verification.

4.3 Results

Re-assay of both water bores showed similar patterns to the initial assays. Duplicates were reasonably consistent though did show a tendency to have slightly varying levels of metal anomalism between field duplicates.

Whilst water samples from both re-sampled bores showed similar patterns to the 2013 samples, the absolute values of nearly all elements were suppressed by approximately half. This pattern conformed to expectations, as these samples were collected during a wet time in the region whereas the previous sampling campaign was conducted during a dry season.

One exception to this pattern of absolute value suppression was the Pb concentrations. In both bores the Pb values from the 2016 samples were equal to or higher than the Pb values from the 2013 samples. For the background bore this discrepancy could be attributed to a slight change in lab methodologies between the two sample batches; however, one of the samples from the anomalous bore had twice the Pb levels of the initial sample: 98.4ppb Pb. Pb is not particularly soluble in surface waters in similar hydrogeochemical regimes in Australia, so these increasingly high levels suggested Pb contamination (Gray 2001). There was not substantial evidence at this time to suggest contamination of Cu, Zn, or other metals.

5 Pump Test of Anomalous Bore

5.1 Overview

In late 2017 an on-ground work program was conducted within the license area containing the anomalous bore. Rock chip sampling and geologic mapping were conducted on exposed rocks, and systematic surface sampling of solid media completed.

Results of the surface sampling and geologic investigations were interesting but not compelling. A final test of the water bore was planned to determine unequivocally whether the anomalous metal values were related to a mineral system or due to contamination.

In February 2018 a field team conducted a campaign involving a thorough investigation of the bore itself and collection of water samples from the bore by several methods. During on-country work it became apparent that the downhole equipment at the anomalous bore had been removed and replaced; the change in gear reportedly occurred in 2014 or 2015, meaning that the downhole gear in place during the first year of sampling and during the re-sampling campaign in 2016 were not the same.

5.2 Methodology

Upon arrival to the site a water sample was collected with a plastic bailer while the downhole gear was still in place. After the downhole gear was retrieved using a block and tackle set up, a plastic waterline connected to a pump at the surface was snaked down the borehole.

Two stages of pump testing were conducted consecutively: 30 min at 0.5L/s and 3.5 hours at 1.5L/s flow rate. Physicochemical measurements were taken at regular intervals throughout the pump tests, and water samples were collected at one times the bore volume (1000L), three times the bore volume (3000L), at a spike in TDS around the 100 minute mark, and at the end of the pump test (7500L).

Following the pump test, the downhole gear was reinserted into the bore. Hand pump apparatus was worked vigorously and a water sample was taken once the water was clear of significant sediment. The bore was allowed to rest overnight. The following morning two samples were collected: the first water from the hand pump which contained some sediment, and a sample of clear water after renewed pumping.

Downhole gear was tested with a Niton portable XRF. Footer valve, actuator arm, pipe fittings, and outflow pipes contained percent levels of Cu, Zn, and Pb and up to 100s - 1000s ppm of Cr, V, and Ag. Sediment retrieved from the footer value was anomalous in Cu, Zn, Pb, V, Cr, and Au.

5.3 Results

Results are shown in Figure 2. Samples taken with the hand pump show extremely elevated levels of copper, while all other methods show background levels. It is
unclear why this particular hand pump is substantially more anomalous than any of the other hand pump bores sampled. High levels of metals may be due in part to fairly saline water conditions. Very low throughput of water from the bore – due in part to its saline nature and in part to its remoteness on a lesser used side track – could contribute to accumulation and precipitation of metals into the lower portion of the water column and into the sediment that has settled there.

Figure 2. Copper concentration in groundwater samples from single ‘anomalous’ bore. Note the very high concentrations of Cu in samples collected using the hand pump apparatus. Bailed sample and samples from pump test contain Cu values near regional background. With repeated flushing of hand pump, Cu levels appear to be dropping off to background levels suggesting high base metals in this bore were from downhole contamination.

6 Recommendations

Following multiple hydrogeochemical orientation studies and exploration programs, several guidelines regarding use and interpretation of water sampling data for mineral exploration can be delineated:

1) Cation species important in base metal exploration such as Cu, Pb, and Zn are more prone to influence from contaminants in surface waters than oxyanion species like Mo, U, V.

2) Data interrogation of linked anomalous elements may prove useful. A strong association of cation species in broadly neutral waters can suggest contamination while an oxyanion association with occasional cation spikes may indicate a mineral system.

3) Some elements in a sample or data set may show order of magnitude contamination, e.g. Cu, Pb, Zn. Other pathfinder elements in the same data set may show no or low-level contamination and can thus still be used in the exploration assessment; Co and Cr in this study experience only minor ppb-level shifts.

4) Flush as much water through the sampling apparatus or system as possible to ensure a clean sample. This is not always possible in early-stage surveys, but data assessment methods can mitigate these relatively rare risks.

5) Take two aliquots of water for cation analysis at every sample location. Acidify and store this back-up sample safely for up to a year.

Contamination in hydrogeochemical sampling is a minor concern in most large data sets but can become critical to the success of wide-spaced, reconnaissance-level surveys. An awareness of metal associations and characteristics of potential downhole contaminants can adequately mitigate risk to exploration interpretation. As hydrogeochemistry becomes a more widely used tool, technical teething issues such as the one presented here will become better known and more routine to manage.

The more we use and troubleshoot robust techniques like hydrogeochemical sampling, the more reliable the technique becomes and the more confidence explorationists will have in the consistency and practical utility of this geochemical method.

Acknowledgements

Many thanks to David Gray from CSIRO and Michelle Carey at IMDEX for constructive discussions regarding hydrogeochemical data analysis and potential contaminant test designs.

Pump testing would not have been possible without the Pumps United team in Perth and the multi-faceted expertise of field specialist Geoff Nicholson. Expert field support provided by XM Logistics.

All on-country work was made possible by the collaborative and welcoming spirit of the Ngaanyatjarra Land Council and Tjami Tjamu Traditional Owners and staff. Special thanks to anthropologists David Brooks and Bryony Nicholson.

References


Application of synchrotron X-rays to ore geology research

Bjorn P. von der Heyden
University of Stellenbosch, South Africa

Abstract. Ore mineralization genetic models, which strongly guide exploration efforts, rely heavily on a full and fundamental scientific understanding of the exposures provided by known ore deposits. To this end, synchrotron-based X-ray techniques represent an emerging class of research technologies that can be used to augment traditional ore geology studies. These techniques provide a unique set of affordances that include micrometer- to sub-micrometer chemical mapping (synchrotron X-ray fluorescence mapping), as well as detailed insights into chemical valence states and local coordination using X-ray Absorption Spectroscopies (XAS). In this contribution, the unique insights provided by synchrotron X-ray techniques are highlighted by referring to their applicability to studying ore fluids, trace element distributions in ore minerals, and supergene/surficial ore-forming processes. As synchrotron science and technology continues to evolve, particularly to include high-resolution three-dimensional capabilities, high brilliance X-ray techniques are expected to play an increasingly important role in ore geology research, ultimately benefitting the efficiency of exploration and mining activities.

1 Introduction

Rampant technological advancements over the last twenty years have seen the emergence and proliferation of third and fourth generation synchrotron light sources (e.g., Ice et al. 2011). Correspondingly, ore geology researchers have increasingly found novel and effective ways in which to apply synchrotron X-rays towards advancing this important field of earth science (Fig. 1).

Relative to standard bench- or laboratory-scale X-ray sources, synchrotron X-rays are characterized by a much higher brilliance, are more energetic, have significantly smaller spot sizes (<10 nm), and can be fine-tuned to provide exceedingly good energy resolution in measured spectra (e.g., 0.05 eV (Merkulova et al. 2019)). These superior X-rays interact with the electrons in the orbital structure of matter (including ore metals) and thus give rise to a host of highly specialized techniques for understanding molecular-scale to sub-micrometer scale properties of ore mineralization (Brugger et al., 2010). These techniques include: X-ray Absorption Spectroscopies (XAS) which probe local coordination (e.g., XANES: X-ray Absorption Near-Edge Structure) and bonding interactions (e.g., EXAFS: Extended X-ray Absorption Fine Structure); synchrotron X-ray Fluorescence (sXRF) used to quantify and map chemical distributions at sub-micrometer resolutions; and synchrotron X-ray Computed Tomography (sXCT) which provides 3D insights into ore parageneses. A limited number of researchers and research groups are currently applying these techniques towards understanding the controls and characteristics of ore mineralization. The aim of the present contribution is to highlight to the broader research community how these techniques can and have been utilized toward enhancing our understanding of the fundamental aspects of ore formation. Results derived from future synchrotron studies are anticipated to result in continuous and incremental improvements in the scientific strength and accuracy of the ore mineralization models that are produced and which are ultimately used to advise minerals exploration.

2 Chemistry of ore-forming fluids

Synchrotron X-rays have been central to two key study methodologies which focus on the chemistry of ore mineralising fluids, viz. fluid inclusion studies and metal complexation studies in experimental fluids. The former approach was pioneered in the 1980’s (e.g., Frantz et al. 1988), albeit with large spot sizes and limited detection of chemical concentration. In the last few decades, these two parameters have been significantly improved, and synchrotron XRF (sXRF) is now a quantitative characterisation technique which can be successfully applied to fluid inclusions as small as ~10 - 30 µm (e.g., Cauzid et al. 2006; Berry et al. 2009). Furthermore, recent sXRF fluid inclusion studies are combining element quantification with chemical insights from XANES and EXAFS which reveal the valence and coordination chemistry of metals within mineralising fluids (Berry et al. 2009; Richard et al. 2013). These insights will be particularly important for understanding ore deposit formation, especially those in which reactions between the wall-rock and the chemical moieties in hydrothermal
solution give rise to metal precipitation.

A growing body of experimental work on aqueous metal complexes complements the fluid inclusion analyses described in the previous paragraph. These studies utilise especially-designed high-pressure and high-temperature cells (e.g., Testemale et al. 2005) that enable model aqueous hydrothermal fluids to experience temperatures of 30 – 600 °C and pressures ranging between 0.1 and 200 MPa. These experiments commonly pair quantitative sXRF (for concentration and solubility data) with XANES and EXAFS (for coordination chemistry insights); and often couple these experimental insights with ab initio molecular orbital calculations. A recent synthesis of metal coordination chemistry in these model systems highlights the role that temperature-dependent coordination changes play in metal fractionation in natural hydrothermal mineralising systems (Brügger et al. 2016).

3 Speciation and distribution of contained trace metals

The economic viability of an ore deposit is often strongly influenced by the presence of sought-after by-product metals that enhances the economic viability of the deposit, or the presence of deleterious trace elements which detract from the viability of an ore deposit. The affordances of sXRF as a micrometer-scale chemical mapping technique is gaining prominence over LA-ICP-MS mapping (which has a poorer spatial resolution), and SEM-WDS and electron microprobe mapping (which have inferior chemical detection limits). Recently, the temporal scales for collecting sXRF mapping data have been greatly enhanced by the development of multi-detector arrays such as the Maia detector at the Australian Synchrotron (Fisher et al. 2015; Li et al. 2016).

The chemical speciation of contained trace metals has important implications for the ultimate ore processing (i.e., it impacts the metallurgical extraction from the host mineral). The mineralogical siting, valence state designation, and identity of adjacent atoms in the bulk lattice structure are parameters which are best probed using XANES and EXAFS spectroscopies. For example, two recent papers by Bonnet et al. (2016) and Belissont et al. (2016) investigate the speciation of germanium in natural sphalerite minerals sampled from two different ore deposits. Germanium was identified in three different coordination environments, viz. Ge$^{2+}$ in tetrahedral coordination to sulphur, and Ge$^{4+}$ in octahedral coordination with oxygen ligands (Fig. 2). The differences between the two studies are tentatively attributed by Bonnet and coworkers (2016) to the controls of Fe on oxygen fugacity within the mineralising system.

![High iron sphalerite](image1)
![Low ion sphalerite](image2)

**Figure 2.** Chemical coordination environments of Ge in sphalerite identified for high Fe sphalerite (Belissont et al. 2016) and low Fe sphalerite (Bonnet et al. 2016).

4 Mineralization in low temperature environments

Low-temperature biogeochemical mineral transformations and precipitation reactions generally give rise to small and poorly-crystalline mineral assemblages. One such example is the mineralogy of laterite deposits (important for Al, Ni and Cr resources), which have thus far received significant attention from ore geology-focussed synchrotron user bases. Studies of these deposits include EXAFS finger-printing of Ni speciation with depth into the laterite profile (Dublet et al. 2012), and mechanistic insights into the adsorption of Ni to highly-adsorptive oxide surfaces (Robbins et al. 2015; Hens et al. 2019).

Poorly crystalline precipitates also form actively during the growth of ferromanganese nodules on the sea-floor. These nodules represent rich resources of Mn, and are associated with the presence of adsorbed (and then included) trace metals such as Co, Cd, Zn, Ni and PGE (e.g., Manceau et al. 2014). Synchrotron XRF and XANES and EXAFS studies respectively help to identify the distribution of these trace metals and the local bonding coordination associated with relevant adsorption reactions. Finally, a growing body of work is focussed on the mineral-microbe interactions which primarily take place in low-temperature surficial environments (e.g., Yang et al. 2014, Shuster et al. 2015, SGA 2019 (this conference) session: ‘Coevolution of Life and Ore Deposits). These interactions take place on exceedingly small scales and involve complex biogeochemical
transformation reactions, thus requiring the small spot size and chemical characterisation capabilities enabled by synchrotron techniques.

5 Conclusions and envisaged future directions

Because of their high tuneability, excellent spatial resolution, sub-ppm detection limits, and provision of chemical insights into molecular level bonding environments; synchrotron X-rays have found fruitful application to several specialised aspects of ore geology research. Most of these applications have been constrained to two spatial dimensions (e.g., detailed chemical mapping on the Maia detector). Recent studies, however, have highlighted the power of mapping chemical distributions and speciation across three dimensions (e.g., Sayab et al. 2016). 3D studies provide much clearer insights into the chemical, mineralogical and textural associations within ore parageneses. Studies conducted over higher-order dimensions also include those that evaluate temporal timescales (e.g., to evaluate reaction kinetics), and those that track geochemical changes across temperature and pressure dimensions (e.g., using experimental P-T cells). These high-level affordances all ensure that synchrotron science will continue to contribute meaningfully to the development of ore geology as a science in which micro- and sub-micrometer scale observations help to explain macroscale phenomena. Rigorous scientific contextualisation and grounding of mineralisation models will in turn lead to more tightly constrained and efficient minerals exploration undertakings.

Acknowledgements

This work was supported by the National Research Foundation (NRF Grant number 106006) with additional support from NRF-DST CIMERA. The African Lightsource (AFLS) organisation is also acknowledged for the useful discussions that served to motivate for this review.

References


Garnierite characterisation for open data bases for nickel laterite exploration

Nicolas Maubec, Pierre Gilles Blaineau, Cédric Duée, Anthony Da Silva Alves, Xavier Bourrat, Guillaume Wille  
BRGM, 3 avenue Claude Guillemin, BP 36009, 45060 Orléans Cédex, France

Beate Orberger  
GEOPS, Université Paris Saclay, Bât 504, 91405 Orsay Cedex, France  
CATURA Geoprojects, 2 rue Marie Davy, 75014 Paris, France

Monique Le Guen  
ERAMET IDEA, 1 avenue Albert Einstein, 78190 Trappes, France

Cristina Villanova-de-Benavent  
Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Geologia, Universitat de Barcelona (UB), C/Marti i Franquès, s/n -08028, Barcelona, Spain

Abstract. In order to develop a mineralogical and chemical database, which will be associated with an on-line on mine instrument, for nickel mining exploration, several garnierite samples were studied in laboratory. The collected samples are Ni-bearing laterites from New Caledonia and Dominican Republic and are mainly composed of serpentine-like and/or talc-like and/or sepiolite-like phase. These three types of phases are clearly differentiated by X-ray diffractometry (XRD). The presence of Ni within the crystallographic structure of these phases can be observed from the infrared or Raman spectra, where the effect of Mg/Ni substitutions causes shifts in some bands. The relative intensity of these bands can be correlated with the Ni content. These different parameters are a reliable indicator to define the nature of garnierite and to have an indication on the Ni content.

1 Introduction

On-line–real time drill core scanner may comprise sensors such as Red – Green – Blue (RGB) cameras, profilometer, X-Ray Fluorescence (XRF) and hyperspectral cameras, X-Ray diffractometer (XRD) and Raman spectrometer. The analyses are performed on-line, and data interpretation relies on data bases with accurate and precise analyses on reference samples. Some data bases are available via the USGS Spectral Library (Kokaly et al. 2017) or CSIRO Mineral Spectral Libraries (Laukamp et al. 2019). However, these databases are not necessarily suitable for mining industries that need custom databases tailored to their specific ore types.

Nickel laterites are the most important Nickel source for the industries. It represents 60-70% of the total nickel resource in the world (Dalvi et al. 2004). They are complex soils with heterogeneous grain sizes (nanometric minerals to centimetric large aggregates or concretions). Nickel is present in several types of phyllosilicates (serpentine, chlorite, clay minerals and talc), which are sometimes agglomerated to garnierite (Gleeson et al. 2004; Soler et al. 2008).

The SOLSA project develops a coupled expert system comprising a sonic drill module, a core-scanner including RGB camera, profilometer, a XRF spectrometer and VNIR and SWIR cameras, and a XRD-XRF-Raman-benchtop system. The core scanner will define regions of interests (economic or for processing designs), while combined XRD-XRF-Raman will only analyze the regions of interest.

In this paper, we present detailed analyses on garnierites from different laterite sites in the world with the aim to calibrate and evaluate optical, chemical and mineralogical characteristics of the garnierite varieties, and to quickly categorize it for mining and processing purposes. All analyses will be entered in the Open Data Bases developed in the frame of the SOLSA H2020 project (www.solsamining.eu), and available for mining companies.

2 Sample material

A set of representative Garnierites of different facies and mineralogies from New Caledonia and the Dominican Republic were used for this work (Fig.1).
Three samples, referenced NC1 to NC3, are from New Caledonia (Fig. 1A-C). Samples NC1 and NC2 are characterized by the occurrence of green veins (dark green for NC1, blue-green for NC2) surrounding darker grains. The third sample (NC3) does not have veins but has a blue-green matrix associated with brown regions. Samples DR1 and DR2 are from the Falcondo deposit in Dominican Republic (Fig. 1D-E). Sample DR1 features green blocs within bulky lighter grains while sample DR2 displays light blue fibbers.

3 Methodology

3.1 Sample preparation

The samples were analyzed by electron probe micro-analysis (EPMA), XRD, Fourier Transform, Infrared (FTIR) and micro-Raman spectroscopies for their chemical and mineralogical characterizations. Raman spectroscopy and EPMA were performed on polished thin sections, representing the different areas of interest (garnierites and associated phases). The XRD and FTIR analyses were carried out on powders. Because of the heterogeneity of the samples, it was decided to hand-pick a few tens of milligrams from different areas of each sample, in order to obtain “pure” phases. The targeted areas were greenish veins and matrices, as well as dark grains. The powder samples were ground in an agate mortar and sieved to 63 µm.

3.2. Analytical methods

Quantitative electron probe microanalyses were performed with a Cameca SX5 electron microprobe equipped with five vertical spectrometers. The analyses were performed on carbon-coated (20 – 30 nm) polished thin sections using a 15 kV acceleration voltage, 20 nA probe current and 1-2 µm spot size. For each sample, the chemical composition was obtained from about ten measurement points.

The XRD analyses were performed on randomly oriented samples. For each sample, tens milligrams of powders were set on a zero-background sample holder. The diffractograms were acquired with a Bruker D8 Advance DA VNC110 diffractometer equipped with a CuKα source (λ = 1.5406 Å), operating at 40kV and 40mA, and a LYNXEYE XE 1D detector with a 3.3° opening. The XRD patterns were measured in continuous scan mode over the 4-75°2θ range with a step size and a measuring time of 0.03°2θ and 576 seconds per step, respectively.

FTIR spectra were obtained using a Bruker Equinox 55 FTIR spectrometer, equipped with a middle-infrared (MIR) source and a KBr beam splitter. For each sample, 30 scans in the 4000-400 cm⁻¹ spectral range were recorded with a resolution of 4 cm⁻¹. The analyses were carried out on pellets discs consisting of a mixture of 0.5 mg of sample and 150 mg of KBr. Before being analyzed, the pellets were stored at 60°C to minimize the absorption of water on KBr and on the sample.

Raman measurements were performed with a Renishaw InVIA Reflex microspectrometer coupled to a DMLM Leica microscope. Three different lasers were used (λ = 514.5 nm; 633 nm and 785 nm). The analyses were carried out using thin-sections observed with a x100 objective (NA = 0.90) or x50 objective and exposed to a laser beam with a power of around 1 mW at the sample surface. The Raman spectrometer was operated using continuous scanning mode with large spectral windows from 100 to 4000 cm⁻¹. Acquisition times (generally over 10 seconds) and accumulations of spectra vary depending for instance on the mineral type.

4 Results

The chemical compositions of the different samples, obtained by EPMA, are presented in Table 1. Each sample is mainly composed of Si, Mg, Ni. These are the main elements of the silicate phases found in garnierites. Only NC1 dark grain and NC2 brown grain contains some percent of Fe.

From a mineralogical point of view, the clay minerals found in garnierites form solid solutions by substituting Mg with Ni. The Ni(Ni+Mg) ratio gives an indication of these substitutions. In the present study, this ratio varies from 14% to 97% and indicates a fairly wide diversity in composition from one sample to another. It is also interesting to note that for samples that come from the same piece, such as NC1 and NC2, the Ni content is much higher in the veins than in the grains.

Table 1. Average composition of samples measured EPMA

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂ %</th>
<th>Al₂O₃ %</th>
<th>MgO %</th>
<th>Cr₂O₃ %</th>
<th>MnO %</th>
<th>FeO %</th>
<th>CoO %</th>
<th>NiO %</th>
<th>Total</th>
<th>Ni(Ni+Mg) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC1, dark</td>
<td>0.49</td>
<td>0.09</td>
<td>23.73</td>
<td>0.02</td>
<td>0.05</td>
<td>2.41</td>
<td>0.11</td>
<td>0.34</td>
<td>85.73</td>
<td>27</td>
</tr>
<tr>
<td>grain_1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NC1, green</td>
<td>0.61</td>
<td>0.03</td>
<td>21.63</td>
<td>0.01</td>
<td>0.10</td>
<td>0.56</td>
<td>0.56</td>
<td>0.84</td>
<td>86.91</td>
<td>97</td>
</tr>
<tr>
<td>vein_2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NC2, brown</td>
<td>0.77</td>
<td>0.01</td>
<td>34.62</td>
<td>0.00</td>
<td>0.56</td>
<td>0.63</td>
<td>0.47</td>
<td>82.32</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>grain_3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NC2, green</td>
<td>0.52</td>
<td>0.04</td>
<td>23.11</td>
<td>0.03</td>
<td>0.14</td>
<td>0.01</td>
<td>0.61</td>
<td>83.06</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>vein_4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NC1, matrix</td>
<td>0.61</td>
<td>0.01</td>
<td>19.88</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>18.97</td>
<td>93.52</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>NC3, matrix_5</td>
<td>0.77</td>
<td>0.01</td>
<td>11.41</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>1.70</td>
<td>93.73</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>NC1, green</td>
<td>0.93</td>
<td>0.01</td>
<td>5.61</td>
<td>0.00</td>
<td>0.11</td>
<td>0.02</td>
<td>4.16</td>
<td>88.52</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>DR1, green_5</td>
<td>0.70</td>
<td>0.02</td>
<td>0.76</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>1.20</td>
<td>88.65</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>DR2, green_7</td>
<td>0.75</td>
<td>0.02</td>
<td>0.80</td>
<td>0.00</td>
<td>0.02</td>
<td>0.02</td>
<td>1.33</td>
<td>88.65</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

Mineralogical analyses obtained by XRD allow identifying the main mineralogical families featured into garnierite. These families are often defined according to their basal d₀₀₁ reflection: “serpentine-like” phase (7Å), “talc-like” phase (10Å) as well as “sepiolite-like” phase (12 Å) (Villanova-de-Benavent et al. 2014). In the present study, the three families are detected by peaks located at 7.3 Å, 10.2 Å and 12.1 Å (Figure 2). The two powders obtained from NC1 sample are mainly composed of serpentine-like minerals. Between the two diffractograms (NC1 dark grain and NC1 green vein), only a difference in peak width is visible. This difference is probably related to the significant presence of Ni into the veins in contrast to the grain.
The two samples taken from the NC2 sample have a different mineralogical composition. NC2_brown grain is mainly composed of serpentine and quartz, while NC2_blue green vein is a mixture of talc-like, serpentine-like phase and quartz and probably also sepiolite-like phase. The NC3_green matrix sample is a relatively pure sample of talc-like phase with only traces of quartz detected. As for the NC2_blue green vein sample, the characteristic peaks of talc-like phase are broad. The DR1_green matrix sample has a complex composition consisting of the three types of clay minerals (serpentine-like, talc-like and sepiolite-like) as well as quartz. According to EPMA analyses, Ni is very abundant in relation to Mg and can be located within the crystallographic structures of the three clay phases. The DR2_green matrix is a pure sample of sepiolite-like phase characterized by a main peak at 12.1 Å.

The spectra obtained by FTIR, on the spectra ranges between 3000-3800 cm⁻¹ and 500-1200 cm⁻¹ (Fig. 3).

Each spectrum shows three series of absorption bands; one between 500 and 700 cm⁻¹, the second between 900 and 1100 cm⁻¹ and the third between 3500 and 3700 cm⁻¹. Between 500 and 700 cm⁻¹, the results show that there are similarities between the samples NC1_dark grain and NC2_brown grain. For these two samples, there are two absorption bands located around 550 cm⁻¹ and 605 cm⁻¹. The similarity between these two samples is consistent with the previous data indicating that they are Mg-rich serpentines. On the other hand, the comparison with a Ni-rich serpentine, such as that present in the NC1_green vein sample, shows a difference in the position of these bands. For this sample, the bands are around 660 cm⁻¹ and 610 cm⁻¹. In the case of a sample rich in talc-like phase (NC3_green matrix), there is a characteristic band centered around 665 cm⁻¹ with a shoulder towards 610 cm⁻¹. These are the same positions as those observed for the Ni serpentine. This similarity is certainly related to an environment around Ni that is comparable between the two clay structures. Compared to the other samples, sepiolite-like phase (DR2_green matrix) is characterized by two bands of low intensities at 643 cm⁻¹ and 670 cm⁻¹. For samples consisting of phase mixtures, the bands are relatively broad and poorly resolved. They consist of the association of the different absorption bands that characterize the different clay minerals. In the 900-1100 cm⁻¹, the spectra have very similar characteristic. Except for sepiolite-like phase, the samples are characterized by an asymmetric band with a maximum located between 950 and 975 cm⁻¹, and a shoulder around 1080 cm⁻¹. In this absorption domain, it is the vibration modes of the SiO₄ tetrahedra that are at stake (Suarez and Garcia-Romero 2006). Only sepiolite is distinguished by the presence of two well-defined bands at 974 cm⁻¹ and 1002 cm⁻¹. These bands are perceptible in DR1_green matrix which also contains sepiolite. The 3500-3800 cm⁻¹ range is characteristic of the vibrations of hydroxyl groups associated with R-(O,OH) octahedra (where R = Mg or Ni) (Baron and Petit 2016; Suarez and Garcia-Romero 2006). The position of the bands will depend on the Mg/Ni substitutions. This is particularly the case when comparing the spectra between the Mg-rich serpentines (NC1_dark grain or NC2_brown grain) and the Ni-rich serpentine (NC1_green vein); the bands present at 3687 cm⁻¹ and 3646 cm⁻¹ shift towards lower frequencies in the presence of Ni (3646 cm⁻¹ and 3608 cm⁻¹, respectively). In the talc-like sample (NC3_green matrix), there are similarly located bands. The difference with serpentines comes from the presence of very broad bands between 3100 and 3500 cm⁻¹ attributed to the vibrations of the water molecules present in the structure (Gerard and Herbillon 1983). The sepiolite-like sample (DR2_green matrix) differs from the other samples by the presence of two well-defined bands at 3628 cm⁻¹ and 3569 cm⁻¹ in addition to broad bands due to water molecules.

In addition to FTIR analyses, Raman spectroscopy makes it possible to differentiate between the different types of clay minerals (Figure 4).
Serpentine-like sample (NC1_dark grain and NC2_blue-green vein) are characterized by four main bands in the range 200 - 1200 cm\(^{-1}\), located around 230 cm\(^{-1}\), 675 cm\(^{-1}\), 3633 cm\(^{-1}\) and 3500-3800 cm\(^{-1}\) spectral ranges. Compared to serpentine, talc-rich samples (NC2_blue-green vein and NC3_green matrix) are marked with a main band at 675 cm\(^{-1}\). Bands with low intensity around 380 cm\(^{-1}\) and 870 cm\(^{-1}\) may also be visible. In the 3500 - 3800 cm\(^{-1}\) range, the two samples are characterized by a well resolved band at 3678 cm\(^{-1}\) accompanied by a broad band centered at 3632 cm\(^{-1}\). The only visible difference between these two samples is the intensity ratio between these two bands (\(I_{3632}/I_{3678}\)). This ratio is higher for the sample with a higher Ni content, namely NC3_green matrix (Table 1). Sepiolite minerals (DR2_green matrix) are clearly distinguished from other samples by the presence of four well-defined bands located at 3633 cm\(^{-1}\), 3651 cm\(^{-1}\), 3669 cm\(^{-1}\) and 3686 cm\(^{-1}\). Most of these bands are found in the DR1_green matrix sample but with different relative intensities.

4 Discussion and conclusions

A set of Ni-bearing laterites samples from New Caledonia and the Dominican Republic representative of the diversity of Ni-bearing clay minerals has been characterized using different analytical techniques (EPMA, XRD, FTIR and Raman micro spectroscopy).

The garnierites characterized in this study are composed of either serpentine-like, and/or talc-like and/or sepiolite-like phase(s). These three types of clay phases (serpentine-like, talc-like and sepiolite-like) can form series of solid solutions by substituting Mg for Ni (Gleeson et al. 2004). The presence of nickel is first visible to the naked eye where the areas enriched in this element tend to be green or blue green. Then, in analytical point of view, the effect of the substitutions of Mg by Ni generates a structural disorder which results in the broadening of diffraction peaks (Baron and Petil 2016). This is the case for Ni-rich serpentine (NC1_green vein) and talc-like phase where Ni is important. Then the presence of Ni within the crystallographic structures induces differences (peak shift) on the spectra obtained by FTIR and Raman spectroscopy. The observed shifts are due to the nature of the cations (Mg\(^{2+}\) or Ni\(^{2+}\)) which will have an influence both on the environment of the SiO\(_4\) tetrahedra and on the properties (lengths, forces) of the R-O,OH bonds, where R = Mg or Ni (Baron and Petit 2016; Petriglieri et al. 2015).

All these data are important because they are indicators to define the nature of garnierite and to have an indication on the presence of Ni into the samples. These data are entered into the SOLSA Open data bases, which will be online by the end of the SOLSA project 2/202 and will be able to assist mining and metallurgical companies in exploration and mining exploitation.

Acknowledgements

This study received grants from the EU H2020 project SOLSA N°689868. Samples were provided by ERAMET, BRGM and University of Barcelona.

References


It’s not easy being green – detecting arc-related mineral system fingerprints using mineral chemistry in ‘propylitic alteration’ in a Cambrian arc terrane Victoria, Australia

Rob Duncan, David Taylor
Geological Survey of Victoria, Melbourne, Victoria, Australia

Sebastien Meffre, Ivan Belousov, Leonid Danyushevsky, David Cooke
Centre for Ore Deposit and Earth Sciences, University of Tasmania, Hobart, Australia

Abstract. Epidote and chlorite compositional data were collected using laser ablation inductively-coupled mass spectrometry (ICP-MS) on samples from two mineral prospects in the Cambrian Stavely Arc, western Victoria. The aim was to distinguish between regional metamorphic and hydrothermal alteration origins for epidote-chlorite-bearing assemblages. At the Thursday’s Gossan Porphyry Cu(-Au-Ag) Prospect, chlorite signatures are similar to both propylitic hydrothermal and regional metamorphic origins, however, elevated Zn and Sr contents are associated with the former. Application of the chlorite proximitors (predicted distance to a hydrothermal centre) identify a likely hydrothermal centre at depth. At the Eclipse Cu-Zn(-Au) VHMS Prospect, epidote As and Sb and chlorite Zn, Cu and Pb contents are consistent with propylitic alteration in most samples. Systematic variations in chlorite Cu and Pb and As and Cu in epidote contents identify a portion of the prospect for follow-up exploration. This study demonstrates that even a limited epidote-chlorite mineral chemistry dataset can provide fertility and vectoring information for mineral exploration targeting. These data are consistent larger-scale geochemical data and geodynamic models that predict the Stavely Arc has significant arc-related mineral system potential.

1 Introduction

Hydrothermal alteration patterns in mineral systems have long been used in mineral exploration. Visibly altered rocks extend beyond the mineralized footprint, and recent efforts have shown geochemical anomalies in epidote and chlorite extend even further than whole rock geochemical anomalism and can also be used to predict the location of hydrothermal deposit centres (e.g., Wilkinson et al., 2015). As part of an effort to de-risk mineral exploration in the, largely covered, Stavely Arc of western Victoria, epidote and chlorite geochemical analyses were undertaken on ‘green rock’ samples from two mineral prospects. The aim of this work was to use these data to assess mineral system fertility and prospect-scale mineral exploration vectors.

2 Geological setting

Arc-related mineral systems formed in the Stavely Arc during the ~525 to 495 Ma collision between the Palaeo-Pacific Plate and the eastern margin of the Proto-Australian Continent (e.g., Schofield et al., 2018). Originally, the Stavely Arc consisted of four sub-parallel volcanic belts (~1,200 km in total strike length) that contain Cambrian low- to high-K boninitic, tholeiitic and calc-alkaline volcanic and intrusive rocks separated by panels of Cambrian metasedimentary rocks – these rocks record a transition from a thinned continental margin through to a more Andean-style tectonic environment (Cayley et al., 2018).

The Stavely Arc was affected by two major structural rearrangements; D1a related to sinistral transpression (pre-505 Ma – Delamerian Orogeny) and D4 related to dextral transtension (~400 Ma – Bindian Orogeny). These events are responsible for the current distribution of volcanic belts (Fig. 1). Sinistral transtension (D1b) during the Delamerian Orogeny (post-505 Ma) was accompanied by porphyry intrusion emplacement into (D1b) thrust-bound arc-slices. Mineral occurrences of porphyry-, epithermal-, and volcanic-hosted massive sulphide-(VHMS) affinity have been identified in the Stavely Arc in small portions of (poorly) exposed Cambrian bedrock, although the majority (>99%) of Cambrian rocks are concealed by younger cover. ‘Green rock’ mineral assemblages have been recognized at numerous mineral occurrences in the Stavely Arc. It is unknown if these occurrences are related to propylitic hydrothermal alteration or low-grade regional metamorphism. Material for this study was collected from the Thursday’s Gossan and Eclipse prospects (Fig. 1).

2.1 Thursday’s Gossan Porphyry Cu-Au(-Ag)

Thursday’s Gossan is located at the northern end of the exposed Stavely Belt (Fig. 1) and is hosted by andesitic to rhyolitic volcanic rocks, volcanioclastics and sedimentary rocks that have been intruded by a series of dacitic to tonalitic sub-volcanic porphyry stocks (Buckland, 1987). An inferred, supergene resource of 28.1 Mt at 0.4% Cu at 0.2% cut-off grade has been estimated (Stavely Minerals, 2019). Supergene mineralization is thought to be associated with hypogene porphyry-style mineralization at depth. A series of nested hydrothermal alteration zones are present at Thursday’s Gossan – the largest is a ~8 km² propylitic assemblage (chlorite-epidote-calcite±zeolite-sericite-illite-pyrite) which envelopes a 3 km² phyllic assemblage (quartz-sericite-illite-pyrite) and a 0.5 km² central advanced
argillic assemblage (kaolinite-dickite-quartz). Mineral exploration is on-going at Thursday’s Gossan and has intersected wide zones of M-veins veins, potassic assemblages and chalcopyrite-bornite mineralization associated with D-veins (Stavely Minerals, 2019). Significant intersections, such as 952 m at 0.23% Cu, 283 m at 0.16 % Cu and 124 m at 0.35% Cu and 0.18 g/t Au (Stavely Minerals, 2019) demonstrate the porphyry potential at Thursday’s Gossan. Timing of mineralization is best constrained by Re/Os molybdenite model ages of ~503 to 501 Ma from chalcopyrite B-veins – these accord with ~505 to 501 Ma U/Pb zircon ages for pre-mineral diorite and dacite porphyries (Schofield et al., 2018; Lewis et al., 2016).

Figure 1. Map to show location and distribution of volcanic belts that comprise rocks of the Stavely Arc, western Victoria, ~250 km west from Melbourne. Only small portions of the Stavely Arc are exposed at surface, mostly southwest of Thursday’s Gossan and east of the Eclipse prospects.

Figure 2. Examples of chlorite and epidote alteration assemblages in Stavely Arc rocks analyzed during this study. (A) to (B) Chlorite-epidote-pyrite assemblages in volcanic rocks from Eclipse. (C) to (D) Chlorite-bearing assemblages in porphyritic phases and greywackes. (E) Epidote-chlorite assemblages from heterolithic volcanic rocks far removed from known mineralization. Annotation shows drillhole and downhole depth – scale bars are 1 cm.
2.2 Eclipse Cu-Zn(-Au) VHMS

Eclipse is located at the southern portion of the exposed Black Range Belt (Fig. 1). No resource has been estimated. Supergene copper mineralization is partly covered by post-mineral cover and has developed above an intense phyllic (quartz-sericite-pyrite) zone that hosts massive, stratabound chalcopyrite-sphalerite-pyrite and later quartz-calcite-sulfide veins in dacitic to rhyolitic volcanic and volcaniclastic rocks (Navarre Minerals, 2014). Laterally the phyllic alteration transitions to a chlorite-sericite assemblage. Significant intersections include 267.1 m at 0.3% Zn, 2 g/t Ag and 0.1 g/t Au from 1.3 m (including 6 m at 1% Zn, 1 g/t Ag, 1 g/t Au from 147 m depth) and 5 m at 0.2% Cu, 3.9% Zn, 2.7 g/t Ag and 1.4 g/t Au (Navarre Minerals, 2014). The age of mineralization is unresolved but is likely >503 Ma based on the U/Pb zircon age of the similar unit that hosts similar style mineralization in the Stavely Belt (Fig. 1).

3 Materials and methodology

Polished rock mounts of propylitic alteration assemblages from eight (four from each prospect) diamond drill core samples were prepared and imaged using scanning electron microscopy (SEM) to: examine textural and paragenetic relationships; determine potential intra-grain epidote and chlorite group mineral compositional variations; and identify included mineral phases. Materials from Thursday's Gossan (Fig. 2) consists of two equigranular, porphyritic, feldspar-phyric intrusive phases and two medium-grained greywackes – chlorite in these samples is typically fine-grained and intergrown with quartz in the groundmass and no epidote is present. Materials from Eclipse (Fig. 2) consists of dacitic to andesitic coherent lavas with variable grain sizes – chlorite and epidote are typically intergrown with each other and sericite-pyrite. The samples were analyzed for major, minor and trace elements using LA ICP-MS with New Wave™ 193 nm solid-state laser coupled to an Agilent 7500cs quadrupole mass spectrometer housed at The University of Tasmania (CODES). Calcium for epidote and Al for chlorite data derived from SEM energy dispersive spectra were applied as internal standards to convert the laser ablation data.

4 Results and interpretation

Forty-eight epidote and 122 chlorite analyses were undertaken. Filtering using in-house tolerance parameters removed complete (or portions) of contaminated spectra generated by mineral intergrowths and/or micro-inclusions. Filtering removed more chlorite than epidote analyses – 25 out of 60 Eclipse and 26 out of 62 Thursday’s Gossan chlorite analyses were acceptable compared with 41 out of 48 Eclipse epidote analyses. This highlights the potential issues of applying this technique in fine-grained rocks. Limitations of this data include: the relatively small dataset; a lack of...
regional metamorphic background epidote and chlorite benchmark data; and the lack of chlorite-epidote data from VHMS systems worldwide. Selected elemental results are plotted here (Fig. 3).

4.1 Thursday’s Gossan – chlorite only

Chlorite from Thursday’s Gossan are similar to both copper-gold porphyry-related and regional metamorphic compositions. Elevated Zn (510 to 806 ppm) and Sr (2.2 to 32 ppm) in two samples are indicative of hydrothermal chlorite compositions – the other two samples have <350 ppm Zn and <2 ppm Sr (Fig. 3). Arsenic in all chlorites is relatively low compared with porphyry-related chlorites worldwide. Applying the chlorite proximitor (Wilkinson et al., 2015) yields conflicting results from the sample position relative to a predicted hydrothermal centre – in this case, typically 800 to 1600 metres. This could reflect the presence of several discrete hydrothermal centres or may result from the heterogeneous rock package (e.g., ultramafic rocks may locally buffer Ni, Co and V in chlorite) – the original proximitors were developed in a largely heterogeneous rock package. A comparison of the proximitors derived from two samples from within a single drillhole indicate that the deeper sample is relatively proximal to the predicted hydrothermal centre – this indicates a vertical temperature component to the hydrothermal system. This observation accords with the notion that porphyry mineralization was post-thrusting and no significant vertical rotation has occurred since mineralization (Cayley et al., 2018), and is supported by mineral exploration at Thursday’s Gossan that continues to intersect relatively thick zones of mineralization at depth (Stavely Minerals, 2018).

4.2 Eclipse – epidote and chlorite

The Eclipse epidote-chlorite data are interpreted in the context of data available from copper-gold-porphyry systems – notwithstanding that the mineralization at Eclipse is of VHMS affinity. Epidote and chlorite from Eclipse share similarities with porphyry and metamorphic-related compositions. One sample contains <3.6 ppm Sb and <2.6 ppm As is metamorphic in origin, the other epidotes are classified as hydrothermal in origin and contain up to 18.7 ppm Sb and 97.9 ppm As (Fig. 3). Within this hydrothermal group decreasing As and Sb values (Fig. 3) related to increasing proximity to the predicted hydrothermal centre – as increasing sulfide contents partition Sb and As over epidote. The hydrothermal epidotes are elevated in LREE, Y and Pb and Na-Mg (and low in Mo) compared with mineralized porphyry compositions. The significance of this is unclear but may be result from enrichment in some Stavely igneous rocks (Schofield et al., 2018) and may be important for fingerprinting VHMS-style mineralization. Chlorite is typically elevated in Sr (>5 ppm) compared with regional metamorphic chlorite – indicative of a hydrothermal origin (Fig. 3). Chlorite from the sample with metamorphic epidote, is also likely metamorphic in origin due to low As and Zn contents (<1 ppm and <300 ppm, respectively (Fig. 3)). Systematic variations in Cu, Pb and Zn in the hydrothermal chlorites can be used to interpret relative sample position with respect to mineralization (Fig. 3) – this identified a (relatively) poorly explored area of the Eclipse Prospect for follow-up mineral exploration.

Mineral exploration significance

The Stavely epidote-chlorite dataset, albeit relatively small, has provided spatial information to assist in mineral exploration decision-making. The data accord with pyrite LA ICP-MS data (Steadman and Large, 2015) that reveal: a transition from oscillatory zoned, Co-Ni-Se associated with relatively high temperature magmatic fluids through relatively lower temperature magmatic-hydrothermal fluids characterized by deposition of a Cu-Sb-Zn-Au-Ag-Bi-Mo assemblage at Thursday’s Gossan; and a VHMS-like assemblage of Mn, Hg and Tl (along with relatively high Au) in pyrite at Eclipse. More broadly, in terms of fertility, a series of Cambrian intrusions across the Stavely Arc have Sr/Y and V/Sc (relative to SiO₂ content) that typify relatively hydrous magmas that contribute to the significant metal endowment in large porphyry systems worldwide (Loucks 2014). Additionally, portions of the Stavely Arc volcanic rocks yield major and trace element ratios (e.g, Zr/Nb, Nb/Y, La/Yb(cm)) associated with productive VHMS elsewhere (Piercey, 2010). Early thrusting that generated significant dislocation of original volcanic belts during the Delamerian Orogeny, explains why porphyry and VHMS mineral systems appear to be closely associated spatially in the Stavely Arc.

References


New Techniques for Ore Discovery 1377
Remote sensing based geological mapping and mineral exploration of the area of North Waziristan Pakistan

Adil Nawaz
Faculty of Geology Geophysics and Environmental Protection, AGH University of Science and Technology, Poland

Janusz Magiera, Dr. Inż.
Akademia Górniczo-Hutnicza im. Stanisława Staszica Krakow, Department of Economic and Mining Geology, Faculty of Geology, Geophysics and Environmental Protection

Abstract. In mineral exploration, remote sensing tools are important and cost effective. Minerals occur in a variety of genetic associations but commercial deposits of minerals are limited in genetic types and modes of occurrences which forms the basis of modern concept based prospecting and is also responsible for the significant role of remote sensing in exploration. Remote sensing data can help to differentiate melogenic provinces/belts/sides and mineral guides in a larger terrain. Keeping in view the importance of RS Tools, digitally enhanced OLI Landsat 8 images are applied to find alteration zones and for geological mapping of North Waziristan Pakistan. The territory is rough with sparse vegetation; the exposure of the Waziristan ophiolite, related sedimentary-igneous lithologies and inaccessibility to the area made the utilization of Landsat information helpful in this investigation. Spectral signatures recorded by Landsat 8 data were used to differentiate different rock units and alteration zones. RS tool i.e. band ratios, band combinations, principal component analysis and image classification are helpful in this regard; multispectral images were prepared and investigated for this study. Final detection of the lithology and alteration zones is based on correlation between classes generated in the thematic map and the referenced geological map. On the basis of the image classification techniques; unsupervised classification, band ratios, five principles lithological units and alteration zones with highest percentage of clay and iron ratios are identified which are giving satisfactory results with overall accuracy 63.07 % in comparison with referenced geological map using confusion matrix analysis. The results are subject to discussion and need to examine about the utility and confines of remote sensing strategy on the investigation zone.

1 Introduction

Waziristan is situated close to the intersection of the western edge of the Himalayan orogeny and western transpressional margin of the Indo-Pakistani craton. Due to security reasons and lack of infrastructure, access to this territory is difficult. This area is globally always under discussion due to geostrategic and geo environment position. In view of economic geology, region held unprecedented mineral resources. According to FATA research center so far 19 minerals including Gypsum, Iron Ore, coal, limestone, marble, lead, barite, emerald graphite, Soapstone, dolomite, feldspar, quartz, silica sand, bentonite and marl have been reported here. Region includes west and south-west of Peshawar between the Kurram River (Tochi River) toward the north and the Gomal River toward the south, bordering some portion of Pakistan’s Federally Administered Tribal Areas (FATA). Study zone lies in North Waziristan with path 152 and row 37. Zone has been portrayed as a place where there are high and troublesome slopes with deep and rough terrains. Exposures of Cretaceous and early tertiary structures like Main Waziristan thrust and stratigraphic connections in the zone are noticeable however not obvious in numerous different territories of the Asian intersection zone, mainly in parts of the ranges of the North Himalayan mountain chain. In North Waziristan, mountains are geographically isolated from the larger mountain frameworks of Koh-e-Sufaid in the North and Koh-e-Sulaiman in the South. The normal stature of the slopes in Waziristan is 1,500– 2,500 meters (4,900– 8,200 ft.) above ocean level.

Study area is characterized with dry climate, almost no vegetation cover, vast and clear exposures of rocks and sediments are being a good subject to remote sensing spectral analysis. The aim of the project is remote sensing based mineral exploration and to create a map of lithology of rocks, sediments and their residuals exposed on the land surface. The new map which depends on unsupervised classification and color composite studies, expands limited mapping of the ophiolite, approves and enhances past general conclusions and uncovers new prospects in the territory. The use of multispectral imaging to remote district, for example, northwest Pakistan makes the construction of definite geologic maps economical and efficient. The use of appropriate band Rationing and Principal Component analysis is part of examination which permits auxiliary and lithologic information to be extrapolated from the ground. Modified map is verified with available referenced data; including geological map published by geological survey of Pakistan, high resolution airborne ortho photomap and different field reports.

2 Research problem and methodology

The study goes in four stages. First three stages are iterative.

a. Creating updated lithological map with the use of image processing and analysis
b. Highlighting alteration zones.
c. Rectification of the map obtained by comparison and statistical validation with referenced data.
d. Modification of processing parameters.
e. Final rectification of the map.

The ophiolite belt of Waziristan is economically potential for certain type of ore deposits, consisting VMS type of copper deposits, podiform chromite & banded manganese. Remote sensing tools are being applied on target area to identify VMS type deposits. The occurrences of these deposits in the ophiolite belt of Waziristan was first reported by Asrarullah of Geological survey of Pakistan, Taher Kheli, Aftab Ahmed (1959), Afzal (1970). A number of principal geological criteria, which are helpful in this study, have been setup for mineral prospecting (McKinstry 1948; Peters 1978; kreiter 1968) that can be observed on remote sensing data including: 1-statigraphical–lithological, 2 Geomorphology, 3-Structural, 4-Rock alterations, 5-Geobotnical etc. (Gupta 1991)

3 Regional geology and tectonic setting

Indo Pakistani landmass is encased by two giant global alternatives; Indian Ocean and the Himalayas having standard origin. Northern most region of the Pakistan lies in Tethyan domain and delineates a troublesome geology while southern part has a place with Gondwana area and is supported by Indo-Pakistani crustal plate. Around 130 million years back, The Indo- Pakistan sub- continent isolated from the motherland Gondwana (Jhonson et al. 1976). The study area (Survey of Pakistan topographic sheet No. 38-H/13) falls in the North Waziristan agency and is a part of the Federally Administrated Tribal Area (FATA). The average rainfall is 250 mm per annum. The area is covered by igneous and sedimentary rocks and can broadly be divided into two distinct tectonic blocks:

• Shelf slope sediments of the Indian plate, Waziristan Kurram Block (WKB)
• Waziristan Ophiolite (WO)

4 Methodology

Seven clear, cloud free Landsat-8 images were downloaded from online repository of the USGS (United States Geological Survey) in tiff format, the study area (Path/row-152/37) is captured by Landsat 8 scenes acquired on 15 May, 2016. Figure 1 shows the Landsat image of the study area representing band ratio in the area. Geology and alteration zones’ interpretation is based on the following remote sensing techniques; color composites, Band ratios for quantitative analysis (clay, iron-oxide, NDVI and its derivatives). To classify multispectral images, unsupervised classification (ISOCLASS) is applied with 70 number of classes and different classification parameters; results are verified visually and statistically with reference data, color composites and band ratios.

Composite in Figure 2 shows false colour RGB 653 which creates an enhanced image with strongly green vegetation, blue or black water and red-to-brown rock or soil. RGB 753 and 652 are alternatives of this combination. Quaternary fan deposits are clearly visible in brownish colour, Red to brown or purple colour shows barren earth.

In NDVI (Bannari, 1995) b5/b4 band is used while In PC1 Mudrova, M. 2010) bands from 1-7 are used. Clay ratio (figure 3) is produced through the combination of b6/b7 bands. Clays, carbonates and micas can produce the light grey to white zones in greyscale images. In pseudo color, clay with red colour is showing maximum value which is 1.65. It can be due to the reason that hydrous minerals or alteration zone have high absorption as compare to band 7.

Figure 1: Colour Composite created through Band Ratio with B7/B6 in red, B6/B5 in Green and B2/B3 in Blue.

Unsupervised classification is executed using Iterative Self Organizing Data Analysis Algorithm Technique (ISODATA) (Tou & Gonzalez, 1974). In this classifier we don’t use training samples data as a base for classification. Instead, these classifiers involve algorithms. Undefined pixels are analyzed by these algorithms in the image and collect them into number of classes established on the natural clusters or grouping present in the image values. Geological referenced map is reclassified in ER mapper using algorithms.
Colour composites; false or true colour, are created to differentiate geological zones. The false colour display assignment can be done in an absolutely random way for any band of a multispectral image so that the colour of a target in the displayed image does not show any resemblance to its actual colour. The resultant image is known as a false colour composite. However, some methods can be more appropriate for the detection of certain features in the image. False colour composite schemes for exhibiting a Landsat 8 OLI multispectral image used in this research are RGB 653 and RGB 543.

5 Result and discussion

The purpose of the study was to generate a revised Map of the rocks revealed on the surface in geologically Complex area and to identify VMS type deposits using RS tools. Geological referenced map was having 20 major lithologic units; JUM, QFD, JPS, JUM, JWV, QFD, QTG, JSD, DOLORITE DYKE, KML, JVV, JG, QRS, JPG, ZEF, TKF, JAF, JZF, TRF and QAL (See end page for details). 5 potential areas are identified using RS tools and a revised map is setup (fig 4) having uniform distribution of 5 major lithologic units. Study showed that on a broad scale, the use of 70 classes in unsupervised classification produced more precise distribution of lithology. The result of study are satisfactory enough to apply remote sensing as a tool to differentiate lithological units and marking alterations zones. Within the ophiolite complex different igneous rock types like gabbroic rocks, ultramafic rocks, and the sheeted dike complex are differentiated on the basis of spectral ratios, false color composites, ISO classification and PCs. Error (Confusion) Matrix (Awad, N.M.A., 2011) analysis allows for quantitative estimation of the overall accuracy of classification and this analysis is giving us quite satisfactory result ~73%. Alterations zones are identified by using Clay ratios and iron oxide ratios (fig 1 and 3) in the rocks, such alterations zones could be perspective zones for minerals occurrences. The reference data used in this study was the geological map of North Waziristan on the scale 1:50,000. For further studies and to minimize uncertainties caused by vegetation, complex geologic history and local landscape evolution events, it would be valuable to use other data (field data, geophysical data) for reference purposes. Keeping in view the complex geological history of the area, I suggest that a combination of remote sensing with sampling on ground and geophysical data; magnetics and gravity could produce more accurate results. Information could be changed due to geomorphic processes and different factors; erosion and deposition, so evaluating the accuracy of unsupervised classification, results of Landsat 8 OLI data through error matrix and kappa hat shows that remote sensing using digital image processing techniques can generate moderate to high level results
In lithological mapping and finding alteration zones especially in arid regions.
Figure 4. ISO reclassified thematic map 9-JAF: Jurassic Alexandra Formation, 12-TRF: Triassic Raghazii Formation, 19: JUM: Ultramafic Rocks, 21-JPS: Pelagic Sediments, 26-QFD: Quaternary Fan Deposit.

Abbreviations

Raghazai Formation (TRF Triassic)
Kishai Formation (TKF Triassic)
Zebe Formation (JZF Jurassic)
Alexandra Formation (JAF Jurassic)
Zargar Khel Formation (JAF Jurassic)
Mami Rogha Limestone Formation (KML Cretaceous)
Waziristan Ophiolite (WO)
Ultramafic rocks (JUM)
Gabbro (JG)
Plagiogranite (JPG)
Sheeted dyke complex (JSD)
Vizhada sar volcanic (JVV)
Wala Volcanic (JVV)
Terrace deposit (QTG)
Fan deposit (QFD)
Quaternary alluvium (QAL)
River bed QRS

Acknowledgements

I am grateful to all faculty Professors for providing assistance during my studies. I am thankful to my supervisor Dr. Janusz Magiera for his understanding, endless support and encouragement.

References

Badshah MS (1985) Development of Waziristan. FATADC, Record 3:15
Lithium prediction using reflectance spectroscopy in Jiajika area of western Sichuan province, China

Jingjing Dai, Denghong Wang, Hongzhang Dai
MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences

Abstract. The Jiajika ore deposit has become one of the areas with the richest Li resources in China and even in the world. Based on the spectral measurement of representative drill hole ZK1101 in X03 vein, the spectral characteristics of spodumene, pegmatite containing spodumene, pegmatite without spodumene and surrounding schist were analyzed. They indicated that the spectrum of spodumene had three absorption at 1413 nm, 1910 nm, 2207 nm, and the discrimination of these three kinds of rocks can be achieved using the 1910 nm spectral absorption feature. Then a quantitative estimation model was built based on the correlation analysis between absorption depth on 1910 nm and content of lithium which reveals that they were linear positive correlated with $R^2=0.75$. It will provide spectral basis for prediction of lithium in the feature.

1 Introduction

Reflectance spectroscopy is a rapidly advancing technique used to acquire spectral reflectance data in the visible-near infrared (VNIR) and short-wave infrared (SWIR) wavelength regions (0.35-2.5 nm) for material characterization (Van der Meer 2018). The spectral reflectance method as an analytical tool has such advantages as rapid data acquisition, non-destructive sample measurement and low operational cost. Electronic transition and charge transfer processes associated with transition metal ions cause absorption of incident light in the visible and infrared region, producing diagnostic spectral features (Clark et al. 2013). Much research has been taken on the spectral characteristics of altered minerals such as muscovite, chlorite, alunite and kaolinite with regards to their application in hydrothermal deposits exploration (Biel et al. 2012; Carrino et al. 2015; Mathian et al. 2018). Lithium is currently an important rare metal due to the increasing demand of emerging industries (Wang et al. 2018). However, little research has been undertaken on the diagnostic absorption features of lithium, and few data has been published on the relationship between absorption features and chemical composition of lithium. In this paper, spodumene from the Jiajika area of western Sichuan province, China was studied using reflectance spectroscopy to provide theoretical principles for lithium prediction.

2 Geological setting

Jiajika lithium-polymetallic ore is located at the junction of kangding, Yajiang and Daofu county, which is on the southeast margin of Tibetan Plateau (Liu et al.2017). The main stratum in this area is sandy shale of Triassic Xikang Group, which is converted to biotite schist, xantholite schist, andalusite schist, cordierite schist by regional and contact metamorphism. Two-mica granite shaped like a horse neck is the main metallogenic rock in this area, with numerous pegmatite veins around it. Among these veins, the X03 vein, known as the “new No.3 vein”, is the most important vein with regards to the Li2O resource with up to 643100 tons, much higher than that of the No.3 vein in Keketuohai, Xinjiang (Wang et al. 2016). The main Li-bearing mineral is spodumene, including comb-like spodumene type, micro-crystalline spodumene type, hair-like fine grain spodumene type and giant crystal column spodumene type (Fu et al. 2015). Drill hole ZK1101 in new No.3 vein with depth of 126.49 m was chosen for our study.

3 Spectral measurement

The spectral reflectance data were acquired using an ASD FieldSpec-4 portable spectroradiometer in a darkroom. The FieldSpec-4 spectroradiometer measures dispersive reflectance at wavelengths from 0.35 nm to 2.5 nm. For reference, a Spectralon plate was measured every ten minutes. A 8° field-of-view fore optics lens was used for spectral data acquisition. Five spectral scans were repeated for each sample and an average spectrum was recorded.

4 Discussion

4.1 Spectral analysis

The spectral characteristics of rocks and minerals including biotite schist, xantholite schist, cordierite schist, andalusite schist, granite, pegmatite containing spodumene, pegmatite without spodumene, spodumene, aquamarine were analyzed. The spectra of surrounding rocks including biotite schist, xantholite schist, cordierite schist, andalusite schist had no diagnostic absorption features with the lowest recorded reflectance. The spectra of spodumene samples had three absorption at 1413 nm, 1910 nm, 2207 nm which was coincident with the USGS spectral library (Fig.1), and the spectral characteristics of pegmatite containing spodumene was similar to the spectra of spodumene (Fig.2). The pegmatites and granites without spodumene and granites showed two deep absorption features at 1413 nm, 2207 nm and a weak absorption feature at 1910 nm whereas mineralized pegmatite showed a deep 1910 nm
absorption feature. Therefore, the absorption at 1910 nm could discriminate ore-bearing or ore-barren (Fig.2).

![Figure 1](image.png)

**Figure 1.** The photo and spectral characteristics of spodumene mineral

![Figure 2](image.png)

**Figure 2.** The spectral characteristics of pegmatite containing spodumene, pegmatite without spodumene and surrounding rocks

**4.2 The relationship between reflectance spectra and content of lithium**

The absorption depth on 1910 nm of thirty-eight samples at different depth of ZK1101 drill were calculated, and the content of lithium were also acquired using ICP-MS (inductively coupled plasma mass spectrometry) which was conducted with the sample powder at each depth, then the relationship between absorption depth and content of lithium was charted (Fig. 3). It revealed that the content of lithium was few hundred to 2000μg/g in the surrounding rocks, and their absorption depth were less than 0.01; while the content of lithium in the ore-bearing rocks were 5000-18000μg/g, and their absorption depth were 0.02-0.08, which were well above the surrounding rocks. The absorption depth on 1910 nm was positive correlated with the content of lithium, and R2 was 0.75 (Fig.4).

**5 Implications**

The spectral characteristics of lithium deposit in Jiajika were studied, and it provide a new method for lithium prediction. The spectra of surrounding rocks, ore-bearing rocks and ore-barren rocks can be distinguished by the absorption depth on 1910 nm, which can be applied to lithium prediction for hyperspectral remote sensing.
Acknowledgements

This work was supported by the China geological survey project “Survey of lithium deposit in Jiajika area of western Sichuan province, China” (Grant No.DD20160055). I would like to thank Miss Liu Lijun (China University of Geosciences (Beijing)) for assisting in sampling in Jiajika deposit, and Prof. Yan Bokun (China Aero Geophysical Survey and Remote sensing Center for Land and Resources) for the valuable comments and suggestions leading to improvement of the paper.

References


Soil magnetic susceptibility mapping as a vectoring tool for mineral exploration: an example from southern New Zealand

Adam P. Martin
GNS Science

Christian Ohneiser
University of Otago

Rose E. Turnbull
GNS Science

Delia T. Strong
GNS Science

Philip Rieger
GFZ Potsdam

Abstract. Element concentration patterns in soil are a commonly used vectoring tool in mineral exploration as they are both time- and cost-effective to collect and can be useful at district- to prospect-scales. However, complications can arise in interpreting patterns if the soil parent material is distal, or a mix of distal and proximal sources. Proxies can be used to link soil back to its parent material, such as physical properties, isotopic composition or its volumetric composition (e.g. organics, lithics, clays and minerals). In this study, the magnetic mineralogy of soil was tested as a proxy for soil provenance on samples in a 20 000 km² region of southern New Zealand at 323 sites, on both topsoil and subsoil. Samples were measured for volume-specific magnetic susceptibility using a handheld device, and for mass-specific magnetic susceptibility in the laboratory, with results being strongly, positively correlated. Additional hysteresis, isothermal remanence and thermomagnetic measurements were made on a sample subset. The soil provenance using magnetic minerals can be traced back to likely sources in outcrops of igneous rocks within the same catchment, terrane or rock type in southern New Zealand: <100 km but frequently <1 km.

1 Introduction

Understanding the pattern of dispersion related to ore-forming processes is fundamental to mineral exploration (Hawkes and Webb 1962). The footprint from an ore body is typically larger than the ore-body itself, with landscape-surface dispersion of said footprint related to processes of soil formation, sediment movement, weathering and/or hydrothermal pathways (Groves et al. 1998). Proxies in the soil can be used to trace it back to its parent, which in mineral exploration helps vector towards mineralisation. Proxies include pathfinder elements, isotopic composition, physical properties or volumetric composition (minerals, lithics, clays, etc; Cullers et al. 1998). This study focuses on a specific aspect of the latter, the magnetic mineralogy in soil, to test the hypothesis that soil magnetism is both a time- and cost-effective soil provenance tool useful to mineral exploration (Martin et al. 2018). The measurement of magnetic minerals in soil has been undertaken several times in European (e.g. Rachwal et al. 2017; Dearing et al. 1996) and Chinese (e.g. Bian et al. 2014) regional studies.

A study area in southern New Zealand (Fig. 1) was
chosen as a test locality because of a wide range in magnetic susceptibility values from potential bedrock sources in the region. Sample sites with a regional (c. 20,000 km²) coverage at grid sites spaced at eight km intervals were chosen. Topsoil (0–20 cm) and subsoil (50–70 cm) samples were measured for magnetic susceptibility (323 sample sites), and a subset (21 sample sites) of soil magnetic (hysteresis, isothermal remanence and thermomagnetic) measurements were also made.

2 Geological setting and environment

Sites in this study occur above eight major basement terranes of southern New Zealand (Fig. 1). The basement terranes are characterized by rocks of distinctive composition and age relating to the formation and evolution of Gondwana and include a variety of continental-sourced quartzofeldspathic metasedimentary rocks, calcalkaline volcanic rocks, island arc igneous and sedimentary rocks, ultramafic ophiolite rocks and I-, S- and A-type plutonic rocks. In the west of the survey area, plutonic rocks of the Median Batholith (pink lithologies in Fig 1) occur mostly in Fiordland National Park. Igneous mafic to ultrabasic rocks form prominent hills in the west and southwest of the survey area about the Takitimu Mountains and the Longwood Range. In the north of the survey area, the Dun Mountain Ophiolite Belt is made up of ultramafic to mafic lithologies, with rivers draining through these lithologies to the centre and southern parts of the survey area. The Murihiku Terrane in the centre and east of the survey area comprises several volcaniclastic units and tuff units. Together these, and other units in part makeup the Austral Superprovince.

Overlying the Austral Superprovince are the younger rocks of the Zealandia Megasequence (yellow in Fig. 1), which in the study area is comprised mainly of Quaternary aged river gravels, flood plain deposits and alluvial deposits. In the east of the survey area, Cenozoic, alkaline rocks make up volcanoes and lava flows of the Dunedin Volcanic Group, also part of the Zealandia Megasequence.

Five of the 14 major soil orders found in New Zealand occur within the study area. Cambisols and luvisols are particularly common in the study area, with regosols, gleysols and podzols also well represented. Of interest in this study are soils derived from igneous parent material, which include mafic cambisols and allophane soils. The latter contains allophane minerals as well as ferrhydrite and imogolite and typically occur as the weathering products of igneous rocks.

Catchments in the survey area drain southwards, eroding and redepositing sediment over distances of ≤100 km. The climate is cool temperate, with rainfall decreasing eastwards from >4000 mm yr⁻¹ to 250–500 mm yr⁻¹. Of the c. 220,000 people that live in the study area, 73 per cent live within two cities. The rest of the land area is sparsely populated and used for agriculture (beef, sheep, deer and dairy) or exotic forestry.

3 Magnetic measurements

The handheld magnetic susceptibility results range between 1.1 and 424 x 10⁻⁸ S.I. for the topsoil and between 1.2 and 594 x 10⁻⁸ S.I. for the subsoil. The laboratory data results range between 0.5 and 534 x 10⁻⁸ m³ kg⁻¹ for topsoil samples and 0.2 and 640 x 10⁻⁸ m³ kg⁻¹ for subsoil samples. The isothermal remanent magnetization (IRM) analyses resulted in a coercivity of remanence (Hcr) of between 25 and 77 mT and a saturation remanent magnetization (Mrs) of between 0.12 and 131 mAm² kg⁻¹. Hysteresis analyses revealed a coercivity (Hc) of between 2.3 and 19 mT, saturation magnetization (Ms) of between 0.85 and 938 mAm² kg⁻¹ and remanent magnetization (Mr) of between 0.10 and 134 mAm² kg⁻¹. Hysteresis loops are narrow waisted with all samples saturating at low fields.

Figure 2. Topsoil mass-specific magnetic susceptibility (laboratory method) versus topsoil volume-specific magnetic susceptibility (handheld method). The strong correlation (r = 0.91) allowed a linear regression to be calculated as shown on the diagram.

4 Discussion

4.1 Handheld versus laboratory techniques

There is a strong, positive relationship between mass-specific susceptibility measured in the laboratory and volume-specific susceptibility measured by handheld techniques (Fig. 2). A linear regression equation calculated for this data (including outliers; Fig. 2) means the handheld data can be converted into mass-specific values (10⁻⁸ m³ kg⁻¹). This is important for studies where budget, time or laboratory access are issues, such as for exploration personnel, science students or other researchers where magnetic susceptibility is a secondary concern. The associated costs in personnel and laboratory times are an order of magnitude less using a handheld magnetic susceptibility meter. The advantages to the laboratory technique are higher precision. A range
of additional data about remanence, mineralogy, etc. can also be determined in the laboratory, assuming the time and equipment are available. Using a handheld meter in the field is thus acceptable for studies of soil magnetic susceptibility where an appropriate regression can be calculated or studies where high precision is a lower priority.

Figure 3. Subsoil magnetic data. A. A day plot indicating pseudo-single domain (PSD) magnetite is the dominant remanence carrier (Dunlop 2002a,b; Day et al. 1977). Some analyses which approach the PSD-single domain (SD) mixing line may be biased by minor contributions of higher coercivity grains and a single sample from near the Longwood Range plots in the multidomain (MD) field. A biplot of magnetic susceptibility versus Ms and Mrs (Fig. 3B) reveals a close correlation between the two, indicating that magnetic susceptibility for most samples is controlled by changes in mineral concentration rather than changes in mineral type, or in the proportions of ferromagnetic versus para/diamagnetic contributions. Samples with a higher average Hcr value of 61 may indicate a greater quantity of high coercivity grains.

4.2 Nature of magnetic minerals

The Hcr values are consistent with magnetite mineralogy where values can vary depending on grain size and composition (Day et al. 1977). Overall, the median coercivity of 41 mT indicates magnetite is the dominant remanence carrier at anomalous sites. A minor contribution from haematite may be present in some samples with higher Hcr values above 60 mT (Özdemir and Dunlop 2014). A day plot (Fig. 3A) indicates magnetic grains are mostly in the pseudo-single domain (PSD) and single domain (SD) grain size range, with the exception of one sample which falls in the multidomain (MD) field. A biplot of magnetic susceptibility versus Ms and Mrs (Fig. 3B) reveals a close correlation between the two, indicating that magnetic susceptibility for most samples is controlled by changes in mineral concentration rather than changes in mineral type, or in the proportions of ferromagnetic versus para/diamagnetic contributions. Samples with a higher average Hcr value of 61 may indicate a greater quantity of high coercivity grains.

4.3 Source of the magnetic susceptibility minerals in soil

Three different approaches, the difference method, Tukey boxplot method and geoaccumulation index (Igeo) method, were used to identify the background magnetic susceptibility of soil in the survey area. Sites with anomalous magnetic susceptibility could also be identified using this method. The threshold for identifying anomalies is as follows: difference method < Tukey boxplot < Igeo, such that the difference method detects many more anomalies than the Igeo method, as has been found in other studies (e.g. Reimann 2005). Below, areas with anomalously high magnetic susceptibility (i.e. above background) are discussed.

In the west of the survey area, the provenance of magnetic minerals in soil in the catchment is suggested to be from igneous rocks of the Median Batholith, sourced from the upper part of the catchment in Fiordland National Park. Median Batholith rocks are moderately to strongly magnetic with I-type granites, gabbros and peridotites. The provenance of the magnetic soils in these rocks is therefore 1 to 30 km.

In the west and southwest of the survey area there is likely local input from the Takitimu Mountains, and in the southwest part of the survey area, input from the Longwood Suite in the Longwood Range may be the dominant source. The Takitimu Mountains contain likely titanomagnetite-bearing rocks and this study suggests they are an unrecognized source of a high coercivity mineral such as haematite. The basic and ultrabasic rocks of the Longwood Suite that are known to contain titanomagnetite-bearing rock types. The magnetic minerals in these soil samples have travelled ≤20 km.

Sample sites in the centre of the survey area occur along river flood plains above Late Pleistocene river gravels in cambisol or regosol soil types. The main river catchments in this region drain the Dun Mountain Ophiolite Belt and Takitimu Mountains, both of which have high concentrations of magnetic minerals. It has been shown elsewhere that heavy minerals from the ophiolite belt have been eroded and redeposited along these flood plains (Martin et al. 2016) and a similar
exploration is envisioned to explain the magnetic susceptibility anomalies in the central part of the survey area. Namely, magnetite has been eroded and redeposited along the river floodplains, a distance ≤100 km.

Other anomalously high magnetic susceptibility sights sampled above the Murihiku Terrane have formed in magnetic, allophonic soils and cambisol soils. These formed adjacent to tuffaceous beds and volcanioclastic sandstone units derived from a basaltic–andesitic volcanic arc that are known to contain magnetite, haematite and pseudomorphs after haematite. This suggests the provenance of magnetic minerals at these sights is proximal, certainly less than the terrane width (maximum 80 km), but most likely <1 km.

In the east of the survey area, several high magnetic susceptibility results are from mafic melanic soils and mafic cambisol soils formed from igneous protoliths. These occur either directly above or adjacent to Dunedin Volcanic Group rocks that are known to contain titanomagnetite and are relatively magnetic. The provenance of magnetic minerals in these anomalous sites is proximal (<1 km).

5 Discussion and conclusions

The volume-specific magnetic susceptibility (handheld method) and mass-specific magnetic susceptibility (laboratory method) of topsoil and subsoil were measured in a regional study of southern New Zealand. A strong correlation between the volume- and mass-specific methods suggests the faster and more economic handheld method could be justifiably used in future soil studies in New Zealand. A linear regression calculation on the data in this study could be used in the future to convert volume- to mass-specific magnetic susceptibility.

The magnetic mineralogy is dominated by magnetite, but certain areas around the Takitimu Mountains and Longwood Range in the west, and Dunedin Volcanic Group in the east, indicated variable magnetic mineralogy, e.g. a minor contribution of haematite.

The provenance of magnetic mineralogy is generally confined to the rock type, catchment or terrane the sample was taken in. This is a distance ≤100 km and frequently much closer (<1 km). In the west of the survey area, the source of magnetic mineralogy is from Median Batholith rocks from within or near Fiordland National Park, with proximal sources from the Takitimu Mountains or Longwood Range becoming significant, or even dominant, in the southwestern areas of the survey. In the centre of the survey area the dominant source of magnetic minerals is the Dun Mountain Ophiolite Belt or volcanioclastic rocks or tuffs in the Murihiku Terrane. In the east, the Dunedin Volcanic Group rocks are an important source of magnetic minerals in soil.

The study of soil magnetic susceptibility allows a more thorough understanding of soil distribution and is a powerful tool for provenance studies in regions where the magnetic susceptibility of the soil parent material is sufficiently varied. This study suggests that handheld magnetic susceptibility measurements will be sufficiently accurate and precise for field based mineral exploration. Magnetic susceptibility of soil should be used in conjunction with other parameters (chemistry, soil type, colour, etc.) during mineral exploration campaigns, when the source of soil parent material is in question.

Acknowledgements

This work was funded by the Government of New Zealand through a GNS Science strategic development fund. Amy Beaton and Chantelle Hillier assisted with sample collection and processing.

References


Dunlop DJ (2002a) Theory and application of the Day plot (Mrs/Ms versus Hcr/Hc) 1. Theoretical curves and tests using titanomagnetite data Journal of Geophysical Research: Solid Earth 107:EPM 4-1-EPM 4-22

Dunlop DJ (2002b) Theory and application of the Day plot (Mrs/Ms versus Hcr/Hc) 2. Application to data for rocks, sediments, and soils Journal of Geophysical Research: Solid Earth 107:EPM 5-1-EPM 5-15


Martin AP et al. (2016) The regional geochemical baseline soil survey of southern New Zealand: Design and initial interpretation J Geochem Explor 167:70-82


Rachwal M, Kardel K, Magiera T, Bens O (2017) Application of magnetic susceptibility in assessment of heavy metal contamination of Saxonian soil (Germany) caused by industrial dust deposition Geoderma 295:10-21

The new approach for kimberlite pipes exploration based on passive seismic and radiometric methods (the example of the Arkhangelsk province)

Konstantin Danilov, Evgenii Iakovlev, Nikita Afonin
N. Laverov Federal Centre for Integrated Arctic Research RAS (FCIARctic)

Abstract. Kimberlite pipes are objects, which are difficult to explore for due to their shapes and sizes. The effectiveness of traditional exploration methods for kimberlite pipes significantly decreases in complex landscape-geological conditions in remote and covered environments. That is why developing of new exploration methods for kimberlite pipes is crucial. In this paper, we present the results of a study of a new model for exploration for industrial diamond pipe based on joint using several geophysical methods: microseismic sounding, passive seismic interferometry, the H/V method, gamma-spectrometry and emanation survey. The studies were carried out using the Lomonosov kimberlite pipe named after M. Lomonosov of the Arkhangelsk diamondiferous province. The main result of our work focus on the model for kimberlite pipe and near pipe medium and their main structural elements. The model includes the kimberlite-caused fault, obtained by passive seismic methods. Radiometric data shows the kimberlite pipe as local radio-geochemical anomalies of an isometric shape. Thus, we shown that the proposed set of methods can be useful in planning exploration. In addition, the robustness of the results suggests that the applicability of these joint methods during exploration.

1 Introduction

Physical properties of kimberlites and enclosing rocks can vary over a wide range. For example, the Lomonosov pipe is characterized by a difference in rock composition differences of near 30% compared to samples extracted from neighbour pipes (Verzhak et al. 1983). Therefore, using geophysical methods for prospecting and exploration of diamond pipes is difficult (Milashev 1984; Kutinov and Chistova 2004). Because of this reason, the effectiveness of exploration in the territory of the Arkhangelsk diamondiferous province using traditional methods is low. In the early 80s, the effectiveness of the verification of magnetic anomalies was 20%. Today, it is now it is less than 0.5% (Korotkov 2011). Therefore, it is necessary to improve the methods for kimberlite pipes exploration. To that instance, the effectiveness of using passive seismic methods and emanation survey was shown earlier by Kiselev et al. (2018) and Francuzova and Danilov (2018). These methods have not been tested together in the same area. Moreover, these approaches were tested using an example of 1-2 profiles on each pipe (Kiselev et al. 2018). The purpose of this work is to examine the possibility of obtaining a model of a pipe, based on the joint use of passive seismic and radiometric methods.

2 Geology

The Lomonosov kimberlite pipe named is part of the Zolotitskoe ore field of the Arkhangelsk diamondiferous province (Bogatikov et al. 1999). We used this pipe in this study as it is a well studied pipe by various geological (including drilling) and geophysical methods (Verzhak et al. 1987). The pipe was previously studied using microseismic sounding method and emanation survey, which made it possible to estimate the repeatability of the results.

Upper Vendian sediments (sandstones, siltstones) with a thickness of about 920 m are hosting the Lomonosov pipe and Neogene-Quaternary sediments (sand and gravel mix) are overlain the pipe (Eremenko and Nenakhov 2002).

The pipe is 202,198 m² (585×441 m) and has an oval shape. In the vertical section, the pipe is a cone-shaped body slightly narrowing with depth. The pipe is completely devoid of the crater facies and is composed of two main varieties of the kimberlites - tuff breccias and autolithic breccias (Bogatikov et al. 1999).

The age of the pipe estimated by the K-Ar method is about ~ 355 Ma (Eremenko and Nenakhov 2002)

3 Methods
3.1 Passive seismic methods

Passive seismic interferometry with advanced method of stacking (Afonin et al. 2019), H/V method (Nakamura, 1989) and microseismic sounding method (Gorbatikov et al. 2013) were used. The passive seismic interferometry allows evaluating empirical Greens function by cross-correlation of seismic noise and stacking of cross-correlation functions. Method H/V allows the estimation of depth of the kimberlite boundary by analysis of resonance frequencies of seismic noise (Lane et al. 2008; Ibs-von Seht and Wohlenberg 1999). The microseismic sounding method (Gorbatikov et al. 2013) based on spectral analysis of a vertical component of ambient noise and aims to isolate sub-vertical inhomogeneities inside the studied medium. This method have been used to isolate fault fractures, intrusive bodies, magma focuses, igneous pipes (Gorbatikov et al. 2013; Francuzova and Danilov 2018).

3.2 Radiometric methods

Radon activity measurements were carried out along sub latitudinal profiles with an outlet beyond the pipe. The distance between stations was about 100 m and the distance between each measurement was about 50 m. Measurements of the volumetric activity of radon (VAR) in the soil were carried out using an automated radiometer PRA-01M-03, following the methodology (VNIIFTRI 2006). In total, over 200 measurements of VAR over the kimberlite pipe were measured.

Gamma-spectrometry measurements were performed in situ using the high-precision mobile scintillation gamma-spectrometry complex RS-700 (RSI 2016). The measurements were carried out at a height of 0.7 m above the ground in the pedestrian variant using a profile system on a scale of 1:10 000 using the same points as the microseismic measurements.

4 Results and discussion

4.1 Passive seismic interferometry

We used the surface wave part of the empirical Greens function to extract the dispersion curve. Model of the dispersion curve inversion has been selected according to general geological conditions of the studied area. According to the calculated model, the medium presented by three layers with boundaries on depths of about 70 m and 750 m. The shear-wave velocities in the layers are about 400 m/s, 1200 m/s and 1900 m/s, respectively. These boundaries correspond to the boundaries between the Quaternary and Vendian deposits (70 m) and the surface of the crystalline basement (750 m) (Verzhak et al. 1983).

The values obtained in the Vendian sediments are close to the model. Nevertheless, velocities in the crystalline basement are one-third less than typical for the studied region.

4.2 Microseismic sounding and H/V methods

Method H/V allowed revealing boarders on depths of 20m, 50m and 800m (Fig. 2). The shallowest boarder feature disappears above the pipe.

According to microseismic sounding result, the pipe correspond to low-velocity cone-shaped heterogeneity with the relative intensity of microseisms 1.5-2 dB. The anomaly appeared in depths between 100 m and 500 m. The heterogeneity is partially out of the boundary, obtained from previous study results at depths 250-450 m on the west and in depths more than 450 m on the east. This part of heterogeneity could not found in previous geological studies Verzhak et al. 1983)

The east vertical border of the pipe has the strongest contrast with the medium. Probably, the reason for this is more consolidate medium , bordered with the west part of the pipe. According to the shape of heterogeneity and variation of microseisms intensities, the pipe has east and west blocks bordered in point 8 of the profile 3 (Fig. 2). The most contrast fault zone located under point 2 of the profile 8. From the south of the pipe, there is also fault under point 10 (profile 5). These faults located inside the sediment and the bedrock. Points 2 and 3 of the profile 8 and point 10 of the profile 5 located along the one line. Relatively both faults and pipe, the near pipe medium separated to more fractured on the west part and more consolidate on the east part. Therefore, one can assume, that kimberlite-caused fault crossed the points marked above. In the same time, the low-velocity heterogeneities in bedrock may be a feed channel.

4.3 Radon method and gamma spectrometry

The VAR of soil over the pipe varies from <1 to 133 kBq·m⁻³, with average VAR value at ~ 15 kBq·m⁻³ (Fig. 3).
Figure 3. Distribution of VAR in soil gas near the studied pipe. 1 - radon measurement points; 2 - microseisms measurement points; 3 - projection of the pipe contour onto the surface; 4 - water channels; 5 - boundary of the explosion phases; 6 - kimberlite-caused fault.

The standard deviation of the VAR values is 19.7 kBq·m⁻³. Therefore, according to the 3-sigma rule the values exceeding 59.1 kBq·m⁻³ are anomalous for the local studied area. The pipe stands out in contrast to the field of soil radon. Local anomalies are within the contour of the pipe, as well as on its eastern boundary. The increased values of radon well contoured the pipe from the west, east and southeast and correspond to the sub-vertical boundaries of the pipe according to the section in Figure 1 (section along the line 1-1). Probably, these boundaries correspond to the zones of increased fracturing of the enclosing rocks. Outside the pipe, the VAR decrease significantly to less than 20 kBq·m⁻³. Nevertheless, when approaching the channel of Zolotitsa river the radon activity increases slightly, which, probably associated with an increase of the radium content in the near-channel sediments. In addition, a linear zone of increased activity of radon in the soil air is clearly distinguished, crossing the pipe in the direction of the north-east - south-west. Spatially, this zone coincides with a channel of small taiga stream - Tuchkin. The formation of elevated values in this linear zone may be due to an increase in the concentration of radium in the near-channel sediments. In addition, a linear zone of increased radon activity in the soil air is clearly distinguished, crossing the pipe in the direction of the north-east - south-west. Spatially, this zone coincides with a channel of small taiga stream - Tuchkin. The formation of elevated values in this linear zone may be due to an increase in the concentration of radium in the near-channel sediments. In addition, a linear zone of increased radon activity, which has a sub-circus morphology. In the data on uranium, this area was not manifested in any way, which may be due to the increased permeability of the medium because of the presence of faults. In addition, the eastern and northern boundaries of the pipe are poorly distinguished in the uranium data, but the maximum of values the VAR (more than 120 kBq·m⁻³) are observed on these elements of the pipe. Thus, we can conclude that the pipe named after M. Lomonosov is well distinguished in the gamma-spectrometric data, as well as on the activity of radon. By
the activity of radon, some boundaries of the kimberlite pipe are well fixed, which may indicate the presence of permeable zones in the near-pipe space of the kimberlite pipe associated with faults.

4.4 Comparison of the results

The horizontal boundaries inside the medium, obtained by inversion of dispersion curve fully corresponds to results of data processing by the H/V method. In the same time, the boundaries, obtained by H/V method, correspond to microseismic sounding result. The dispersion curve, calculated from surface wave part of an empirical Greens function, allowed to calculate the depths in microseismic sounding and in H/V method. Moreover, the velocity heterogeneity, caused by the pipe body, totally corresponds to the drilling data, that prove our results. The low-velocity character of the bedrock may be caused by fractured zones near the studied pipe. The points with anomaly values of radon volumetric activity, located within pipe along the kimberlite-caused fault. This fault localised by the microseismic sounding method. This fact also proves the results of interpretation.

5 Conclusion

The kimberlite pipe named after M. Lomonosov appeared as the low-velocity anomaly in Vendian deposits. On the ground surface, the pipe looks like the field of relatively high radon, potassium, thorium concentration and total radioactivity. Nevertheless, anomaly values of radon emanation concentrated near vertical borders of the pipe, borders of injection phases and along the kimberlite-caused fault (Fig. 3). Moreover, above the pipe, there is disruption of the overburden boundary. Joint interpretation of results allowed revealing kimberlite-caused fault and, probably, supplying channel. Joint application of described methods allows significantly increasing the effectiveness of pipes exploration because of study not only shallow, but also deeper elements of a structure. In the same time, joint using of the methods allows increasing of provability of obtained results.

Acknowledgements

The presented study was funded by RFBR according to the research project № 19-05-00481 A «Structure and dynamics of the lithosphere of the White Sea» and the research project of state assignment «The evolution of island and continental territories of the European Arctic sector under the influence of natural and anthropogenic factors» (0409-2015-0134, № AAAA-A16-116052710105-1).

References


Delineation of the permissive tract using computational mineral prospectivity modelling

Johanna Torppa, Kalevi Rasilainen
Geological Survey of Finland

Abstract. We test two mineral prospectivity modelling based approaches for delineating regions favorable for the occurrence of specific types of mineral deposits. We adopt the term permissive tract to mean the favorable region, and call the left-over region non-permissive. The idea behind the permissive tract defined using mineral prospectivity modelling is identical to the permissive tract that is generally defined manually in the three-part quantitative assessment for estimating mineral resources. The motive for using mineral prospectivity modelling is the possibility to use more complex data sets than in manual tract delineation. One of the mineral prospectivity modelling approaches we use integrates continuous fuzzy memberships of each evidence data set to generate continuous prospectivity values across the study area. The non-permissive and permissive areas are delineated by setting a suitable prospectivity threshold. The other approach uses clustering to produce a number of regions, each one representing homogenous bedrock properties. Prospectivity of a region is defined using the frequency of known mineral occurrences and deposits within the cluster, and the non-permissive region is defined as the region with zero prospectivity.

1 Introduction

Identifying regions that are geology favorable for mineral occurrences is crucial, for instance, in land-use planning and quantitative mineral resource assessment. To describe such regions, we have adopted the term permissive tract from the three-part quantitative assessment for mineral resource estimation (Singer 1993; Singer and Menzie 2010).

The three-part quantitative assessment is a widely used method for evaluating mineral resources on regional scale. So far, the permissive tract has generally been defined manually by experts, based on geological maps and complimentary information, such as geophysical, geochemical and drill core data. The process of defining the permissive tract can be affected by biased expert opinions, and the decisions or choices made by the expert are sometimes hard to justify and even harder to track after years have passed. Due to the constantly increasing amount and improving quality of data, along with the increased efficiency of computers, the possibility to use computational mineral potential modelling (MPM) methods for defining the permissive tract has become worth considering. MPM is used to integrate information from a number of different data sources to generate prospectivity scores across the study area. Methods for computational MPM were presented already in the 80’s and 90’s (e.g., Agterberg 1989; Agterberg 1990; Bonham-Carter et al. 1990), and they have become a popular tool for evaluating the prospectivity of specific minerals. Due to their usefulness, the development of MPM methods has been rapid in the past few decades (Carranza 2017). Using MPM to target mineral exploration and make quantitative estimates of mineral resources transfers the focus of the expert work from routine data processing towards interpretation of the data and the results. It also makes it possible to efficiently derive information from large and complex data sets.

The United States Geological Survey (USGS) has implemented software to carry out the three-part quantitative assessment. Currently, however, running the entire assessment procedure requires executing a number of different computer programmes, which has been considered to be complicated. A more user-friendly version of the assessment software, based on the existing USGS code, is currently being developed in the European Institute of Innovation and Technology RawMaterials-funded project “Mineral Resource Assessment Platform” (MAP) coordinated by the Geological Survey of Finland (GTK). Besides generating an easy to use interface to the method, additional tools are implemented for documenting the assessment process and reporting the results. Also, an important step forward is an addition of the possibility to define the permissive tract using MPM.

Comparison of permissive tracts delineated manually by experts to tracts generated using computational MPM has been done previously by Raines (1999), who used the weights of evidence MPM, and Raines and Mihalasky (2002), who used the weights of evidence and weighted logistic regression MPM. Both studies suggest that computational MPM provides tracts comparable with manual delineation, assuming that the data set is appropriate. It is also emphasized in Raines (1999) and Raines and Mihalasky (2002) that the expert delineation suffers from generalization of the tracts, possible inclusion of non-permissive areas and inconsistent tract delineation approaches between different expert groups.

In this study, we will test two MPM approaches for defining the permissive tract, and compare the result to the tract defined manually by experts. One of the approaches uses fuzzy logic based MPM, which will also be implemented in the MAP project. Fuzzy logic has been used for mineral prospectivity modelling since An et al. (1991), and provides means to transform knowledge into numerical form. Fuzzy logic has been one of the most popular MPM methods and different
ways to apply, improve the quality and estimate the uncertainty of the results have been presented in a large number of studies (e.g., Cheng and Agterberg 1999; Yousefi et al. 2012; Lisitsin et al. 2014; Torppa et al. 2015; Yousefi and Nykänen 2016). The other MPM approach uses data clustering with self-organizing maps (Kohonen 2001) and k-means, and defines the prospectivity of clusters based on the frequency of known mineral occurrences and deposits in the clusters. This approach was used by Torppa et al. (2019) in delineating the permissive tract for orogenic gold prospectivity modelling of the Central Lapland Greenstone belt. Clustering geoscientific data using SOM has also been used in several studies, such as Fraser et al. (2006), Torppa et al. (2015) and Carneiro et al. (2018).

Prospectivity values produced by different MPM techniques and computed using different data sets are not generally comparable and there is no universal prospectivity threshold value that could be used to distinguish permissive region from non-permissive. Thus, an important part of the method development is to generate guidelines and justification to specify the threshold for defining what is permissive and what is not.

We will apply MPM for generating the permissive tract for volcanic massive sulfide (VMS) deposits in the Pyhäsalmi and Vihanti Groups in Finland. A manual delineation of the permissive tract for Pyhäsalmi and Vihanti VMS deposits has been carried out before (Rasilainen et al. 2014), and the result obtained using the MPM approach will be compared to the one obtained by the manual generation by experts.

In this paper, we describe the proposed MPM approaches and the data, while the results will be presented in the conference.

2 Permissive tract delineation methods

In the context of the three-part quantitative assessment, a permissive tract represents the surface projection of a volume of rock where geology allows the existence of mineral deposits of one or more specific types. The delineation of the permissive tract using conventional methods requires binary thinking, as the study area is directly divided to permissive and non-permissive parts. Mineral prospectivity modelling methods differ from this in the sense that, even if each single data set would be split to permissive and non-permissive classes, the resulting prospectivity map has a range of prospectivity scores, either discrete or continuous, depending on the modelling method. For generating the permissive tract from the prospectivity map, a prospectivity threshold must be defined. The threshold can be set to exclude the regions that are most likely non-permissive, leaving the rest of the region permissive, or it can be set to include the regions that are most likely permissive, leaving the rest of the region non-permissive. The difference between the tracts defined in these two ways depends on the data sets and MPM methods that were used. In any case, the permissive tract defined using the latter approach is a subset of the tract defined by the former approach. By defining a suitable threshold, the tracts defined manually by an expert, and computationally using MPM should be approximately the same. However, the data used in MPM have higher spatial resolution, producing a more detailed permissive tract.

2.1 Expert delineation

In a three-part assessment process, the permissive tracts are generally delineated by experts using available geological information. Delineation mostly relies on the lithological map that is used to manually select the regions that are expected to contain or not to contain the deposit of interest. In addition to the lithological map, also drill core, geochemical and geophysical data are used if applicable, to refine tract boundaries. The criteria for the delineation are expressed in the descriptive deposit model, which contains the characteristic features of the deposit type and its geological environment. As the purpose of the permissive tract is to represent a surface projection of the permissive volume, the geology below the surface is in principle defined as well. However, the workflow usually starts with first defining the 2D surface projection, and then extending this downwards, rather than starting with generating a 3D model and then projecting this to the surface. In the assessments carried out by the GTK, 1 km is usually used as the assessment depth.

2.2 Computational delineation

We use two MPM approaches (fuzzy logic and clustering with training data) to define the prospectivity of the study area, and divide the area to non-permissive and permissive parts, based on the prospectivity scores. A fuzzy logic based approach is used to calculate a continuous prospectivity score, in which case a threshold is needed to be defined for splitting the prospectivity values to permissive and non-permissive. The clustering based approach provides areas with discrete prospectivity values, and the zero prospectivity class is used to represent the non-permissive region and all the other clusters the permissive region.

2.3 Fuzzy logic

The idea of fuzziness is used in the fuzzy logic MPM to define the membership values for each input data set. Instead of making just a binary division of the data to favorable and non-favorable, continuous membership values are defined according to how the values of each data set correspond to or are expected to correspond to the occurrence of a specific mineral. The major advantage of the approach is that the membership values can be defined based on expert knowledge, without using any known mineral occurrences as training data. Memberships, however, can also be defined using training data by finding the function that describes the frequency of known occurrences as a function of the data value (Torppa et al. 2019). In an
optimal case the fuzzy logic prospectivity maps computed from memberships generated by expert and those computed using training data are the same. However, due to restrictions in both the number of known occurrences and expert knowledge, the maps may differ significantly.

We use ArcGIS Fuzzy Overlay functions to combine the fuzzy memberships. One of the overlay functions OR, AND, SUM, PRODUCT and GAMMA is used, depending on does the existence of minerals require a high membership of only one or of all the evidence data sets, or does the prospectivity increase as any of the evidence memberships increases.

A drawback in the membership approach is, that it assumes each data set to be independently correlated to the occurrence of minerals, which does not generally apply.

2.4 Clustering

The main idea of the clustering approach is to divide the study area into regions with internally homogenous geological properties, and define the prospectivity for each region. Clustering is a mathematical procedure that requires no geological modelling or assumptions. The success of clustering in representing the variation in geology depends purely on the choice of the data sets. A single data cluster can be a single solid region in the geospace or, more commonly, it can form several spatially separate regions with similar properties.

The prospectivity of each cluster can be defined either knowledge-based or empirically. In the knowledge-based approach, the expert uses the distribution of data within each cluster to evaluate whether the cluster represents geology favourable for the occurrence of mineral deposits or not. The empirical approach uses the frequency of known mineral deposits and occurrences in the clusters to compute the favourability.

We use the unsupervised clustering methods self-organizing maps (SOM) and k-means to define the clusters, and known mineral deposits and occurrences to define the prospectivity score for each cluster. SOM is applied for generating a large number (of order 10000) of proto-clusters to reduce the size of the data set and to remove outliers. SOM proto-clusters are further clustered with k-means to produce of order 10-20 clusters that represent the variation in geology of the study area.

3 VMS deposits in the study area

GTK has previously assessed the undiscovered resources in VMS deposits in Finland (Rasilainen et al. 2014). For the present study, we selected an area in the central part of Finland, which contains the important Vihanti and Pyhäsalmi VMS areas in Finland (Fig. 1). The study area contains four permissive tracts delineated by GTK experts during the previous assessment. Two of the tracts (Vihanti tract, Pyhäsalmi tract) are delineated for the felsic-type VMS deposits (Mosier et al. 2009), and they contain 11 well-known VMS deposits, five of which have been mined, and 41 occurrences. The other two tracts (Rauhala tract, Upper Svecofennian tract) belong to the bimodal-mafic-type and contain one well-known deposit and 11 occurrences.

4 Data available for VMS permissive tract delineation using MPM

The study area has a good coverage of geochemical and geophysical data. It contains over 7000 diamond drill holes, and large part of it has been actively explored for VMS, gold and nickel deposits since the early 1900s.

Based on the report by Leväniemi and Karell (2013), gravity, magnetic, electromagnetic and possibly radiometric data as well may be useful to indicate the locations of VMS deposits. Magnetic, electromagnetic and radiometric data are extracted from GTK’s low altitude airborne geophysical survey data products. Gravimetric measurements have been carried out across the entire study area by the Finnish Geospatial Research Institute (Kääriäinen and Mäkinen 1997), and supplementary gravity measurements across part of the study area have been carried out by GTK.

Figure 1. Location of the study area in Finland, and the magnetic anomaly map with the manual delineation of VMS deposits.

Geochemical data are available from both till and whole rock samples. Till geochemical data are available from the GTK regional till geochemical survey from the entire study area with approximately 2 km sampling point spacing. The data, thus, provides average concentrations in till with low resolution compared to geophysical data. Whole rock geochemical data of the
Rock Geochemical Database of Finland (Rasilainen et al. 2007) are available from the whole study area. The data are unevenly distributed with approximately 7 km sampling point spacing. Geochemical data from drill cores and outcrop samples are also available. Due to the low spatial density of the samples with whole rock geochemistry, the data will not be used as interpolated concentrations, but as an indicator of existence and non-existence, based on a specified concentration threshold of the elements. The indicator elements for VMS prospectivity modelling include all the main ore metals (Cu, Zn and Pb). In addition, the applicability of several other trace elements, including S, Se, Ag, Au and Fe, will be tested.

Geological map will be used to rule out certain areas. Since VMS deposits are hosted by volcanic-sedimentary sequences, rocks not belonging to such sequences are not permissive. Within the study area, the 1.93–1.91 Ga lower Svecofennian volcanic and sedimentary rocks of the Pyhäsalmi and Vihanti groups, and the 1.88 Ga upper Svecofennian supracrustal rocks define the minimum boundaries of the permissive areas.

References


Carranza EJM (2017) Natural Resources Research publications on geochemical anomaly and mineral potential mapping, and introduction to the special issue of papers in these fields. Natural Resources Research 26:379–410.


Life with Ore Deposits on Earth