15th Biennial SGA Meeting
Glasgow, Scotland
August 27 -30 2019
Life with Ore Deposits on Earth

PROCEEDINGS VOLUME 2
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 publicaannot be reproduced in whole or in part without the permission of The Society for Geology Applied to Mineral Deposits (SGA).

A digital version of these volumes is available from the SGA website at [www.e-sga.org](http://www.e-sga.org)
# TABLE OF CONTENTS

**Volume 2**

**Magmatic sulfide and oxide systems**

<table>
<thead>
<tr>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Towards a stratigraphic framework for the Platreef, Northern Limb,</td>
<td>Danie F Grobler, Albie JAN Brits, Alexandra Crossingham</td>
<td>467</td>
</tr>
<tr>
<td>Bushveld Complex, South Africa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The structure and syn-magmatic tectonic influence on the Flatreef</td>
<td>J.A.N Brits, D.F Grobler, A.J Bumby, A Crossingham</td>
<td>470</td>
</tr>
<tr>
<td>Deposit, Northern Limb, Bushveld Complex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrothermal modification of magmatic sulphide Cu-Ni-PGE deposits in</td>
<td>Katie A. McFall, Iain McDonald, Bianca Kennedy, Dominique Tanner,</td>
<td>474</td>
</tr>
<tr>
<td>the Northern Bushveld Complex, South Africa</td>
<td>R.E. (Jock) Harmer, Brian Tattitch</td>
<td></td>
</tr>
<tr>
<td>Platinum-group mineralization at the Tubane area, northern Molopo</td>
<td>Jacob Kaavera, Akira Imai, Kotaro Yonezu, Thomas Tindell, Koichiro</td>
<td>478</td>
</tr>
<tr>
<td>Farms Complex, southern Botswana</td>
<td>Watanabe, Kenzo Sanematsu</td>
<td></td>
</tr>
<tr>
<td>Spatial variations trace elements in magmatic Ni deposit: evidence</td>
<td>Sebastian Staude, Gregor Markl, Marcus Oelze</td>
<td>482</td>
</tr>
<tr>
<td>for immiscible Te-As-rich melt formation (Kambalda, Western</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Australia)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Platinum Mineralization in Ural-Alaskan Complexes of Koryak</td>
<td>Anton V. Kutyrev, Eugene G. Sidorov</td>
<td>485</td>
</tr>
<tr>
<td>Highlands (Far East Russia)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nova – Bollinger Ni – Cu Sulfide Ore Deposits, Fraser Zone, Western</td>
<td>Valentina Taranovic, Stephen J. Barnes, Steve Beresford, Steven</td>
<td>489</td>
</tr>
<tr>
<td>Australia: Petrology of the Host Intrusions</td>
<td>Rennick</td>
<td></td>
</tr>
<tr>
<td>Sulfide-silicate textures and emplacement mechanisms of the Nova-</td>
<td>Steve Barnes, Valentina Taranovic, John Miller</td>
<td>493</td>
</tr>
<tr>
<td>Bollinger ores, Fraser Zone, Western Australia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Grasset Ultramafic Complex – A new nickel district in the</td>
<td>Michael J. Tucker, Darin Wagner, Michel Houlé</td>
<td>497</td>
</tr>
<tr>
<td>northern Abitibi greenstone belt, Canada</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The enigma of the Ni-Cu-PGE sulphide ores of the Sudbury Igneous</td>
<td>Reid R. Keays, Peter C. Lightfoot</td>
<td>501</td>
</tr>
<tr>
<td>Complex: what was the source of the metals?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Review of the formation of the thick chromitite of the Jacurici Layered Complex (Brazil): new evidences from inclusions in chromite.................................................................505
Juliana C. Marques, Betina M. Friedrich, Gema R. Olivo, Brian Joy, José C. Frantz, Natanael Cezario, Jhenifer Paim

Apatite-hosted melt inclusions from the Panzhihua gabbroic layered intrusion associated with a giant Fe-Ti oxide deposit in SW China..................................................................................................................509
Christina Yan Wang, Kun Wang, Zhong-Yuan Ren

Field and geochemical constraints on the origin of massive magnetitite layers of the Bushveld Complex, South Africa ..........................................................................................................................513
Willem Kruger, Rais Latypov

Geology and ophiolite complex-hosted magmatic Fe-Ni-Cu±Co-Au mineralization in Sebuku Island, Indonesia..........................................................................................................................516
Yoseph C. A. Swamidharma, Andhi Cahyadi, Ade Kadarusman, Ernowo Harjanto, Arifudin Idrus

KEYNOTE: Pathfinder mineral geochemistry for magmatic oxide and sulfide mineralization: insights from trace elements in Fe-oxides determined by laser ablation ICP-MS ...............520
Sarah. A.S. Dare, Mark Grant, Matthew Polivchuk, Erin Bethell

KEYNOTE: Reactivation and enrichment of a Gondwana margin Ni-Cu-PGE-(Te-Au) mineral system during the breakup of Pangea..................................................................................................................................................524
Marco Fiorentini, Steve Denyszyn, Greg Dering, David Holwell, Daryl Blanks, Roland Maas, Marek Locmelis, Crystal Laflamme

Formation and disruption of Cu-Ni-PGE deposits in a giant deep-seated mafic-ultramafic conduit system..................................................................................................................................................528
Rune B. Larsen, Bjørn E. Sørensen, Even Nikolaisen

Ni-Cu-(PGE) fertility of the Zambezi belt rift magmatism: source and temporal controls........532
Ward A. Laura, Holwell A. David, Tapster Simon

Insights into the origin of the Munali magmatic sulfide deposit: Evidence for a hidden Cu orebody?..............................................................................................................................535
Daryl Blanks, David Holwell, Stephen Barnes, Louise Schoneveld

Fluorine and PGE-Au elevated signature of alkaline magmas from the Yilgarn Craton: insights into mantle fertility..............................................................................................................................538
Eunjoo Choi, Marco Fiorentini, Andrea Giuliani, Stephen Foley

Widespread PGE depletion in the Tarim CFBs of NW China and implications for the ore potential in the Tarim LIP .........................................................................................................................542
Yin-Qi Li, Zi-Long Li, Shu-Feng Yang, Han-Lin Chen, Ya-Li Sun

Using Platinum Group Element geochemistry to determine magma fertility of Mount Hagen, Papua-New Guinea..........................................................................................................................546
Monika Misztela, Ian Campbell

Distinct sulphur saturation histories of the Palaeogene Magilligan Sill, Northern Ireland: Implications for Ni-Cu-PGE exploration in the North Atlantic..................................................................................550
Morphological and compositional features of native platinum from the Yaman-Sandra river placer deposit (Altai, Russia) ................................................................. 597
Mikhail Brysin, Irina Tretiakova, Natalia Pozdnyakova, Sergei Shabalin

LA-ICP-MS study of sulfide blebs from a gabbroid intrusion in North-Western Mongolia……. 601
Maria Cherdantseva, Andrey Vishnevskiy, Pedro Jugo

Rathbun Lake revisited: a magmatic-hydrothermal Pd-Pt-Cu occurrence possibly related to the Sudbury impact.................................................................................................................. 605
Alexander Kawohl, Hartwig E. Frimmel, Wesley Whymark, Andrejs Bite

The nature and distribution of magmatic Ni-Cu-PGE sulfide occurrences in the Labrador Trough, Northern Québec .................................................................................................................. 609
W.D. Smith, W.D. Maier, J.Ø. Anderson, I. Bliss

Tracking the origin of the magmatic magnetite-(apatite) deposits of the Coastal Cordillera of the Andes with Sr-Nd isotopes............................................................................................ 613
Fernando Tornos, John M. Hanchar, Rodrigo Munizaga, Francisco Velasco

Reef-type PGE-enrichment in the 2.44 Ga mafic-ultramafic Näräinkävaara layered intrusion, Northern Finland ................................................................................................................. 617
Ville Järvinen, Tapio Halkoaho, Jussi S. Heinonen, Jukka Konnunaho, O. Tapani Rämö

Petrography of the hydrothermally altered ultramafic rocks of the Kemi layered intrusion ..... 621
Fabian M. Botello, Sheng-Hong Yang, Timo Huhtelin, Sari Grönholm

The Maracás vanadiferous district, Bahia-Brazil-geology, mineral resources, descriptive and genetic models..................................................................................................................... 625
Reinaldo Santana Correia de Brito, Rodrigo C. Lordão, Joadson A. Carvalho, Matheus P. Feitosa

Gold from Orogenesis to Alluvial

The structural setting of the Barsele Au deposit, Sweden ......................................................... 627
Tobias E Bauer, Marcello Imaña, Kåre Höglund, Helen Thomas

The structural control on the gold mineralization at the Galat Sufar South deposit (Block 14, NE Sudan) .......................................................................................................................... 631
Julien Perret, Julien Feneyrol, Rémi Bosc, Aurélien Eglinger, Anne-Sylvie André-Mayer, Craig Hartshome, Emmanuel Abanyin

The Invincible deposit: An example of pre-orogenic gold mineralization in the Eastern Goldfields, Western Australia ................................................................. 635
Sarah Jones
Reverse shear, horizontal shortening and lode-gold mineralisation along the Mougooderra Shear Zone, Western Australia ................................................................. 639
Jamie J. Price, Tom G. Blenkinsop, Andrew C. Kerr, Kathryn M. Goodenough, Adrian J. Boyce, Clinton Kuehnapfel

Stratigraphic and structural controls on Carlin-type mineralization in central Yukon (Canada) ................................................................. 643
Nicolas Pinet, Patrick Mercier-Langevin, Denis Lavoie, Benoit Dubé, Patrick Sack, Julia Lane

Structural controls on ore formation at the Zaozigou gold-antimony deposit, West Qinling, China ........................................................................ 647
Duncan C. McIntire, Kunfeng Qiu, Haocheng Yu, Zongyang Gou, Richard J. Goldfarb, Zhaoshan Chang

KEYNOTE: Metabasalts as sources of gold in Archean greenstone belts ......................... 651
Iain Pitcairn, Alexandre Peillod, Clifford Patten, Jean Goutier, Carl Guilmette, Georges Beaudoin

Geochemical paragenesis of pyrite associated with orogenic gold at Curraghinalt, Northern Ireland ........................................................................ 655
James P. Stratford, Sean H. McClenaghan

Gold mineralization in the Mesoproterozoic Karagwe-Ankole belt (Byumba, Rwanda): new insights from petrography and trace element mapping ........................................ 659
Sander Wouters, Philippe Muchez, Stijn Dewaele, Pim Kaskes, Philippe Claeys

The source of Au in Paleoproterozoic orogenic gold deposits: insight from the Central Lapland Greenstone Belt, Finland ........................................................................ 663
Patten C.G.C., Kolb J., Molnár F., Pitcairn I.K.

The paragenesis of veining and Au mineralisation at the Barsele Au deposit, Sweden ........ 667
Evelina Rann, Iain Pitcairn, Marcello Imaña, Kåre Höglund

Polyphased gold mineralization at the Yaou deposit, French Guiana ............................. 671
Vincent Combes, Aurélien Eglinger, Anne-Sylvie André-Mayer, Yoram Teitler, Christophe Scheffer, Arnaud Heuret, Pierre Gibert, Didier Béziat

Geochemical signature of native gold from various Au-bearing deposits – implications for mineral exploration .......................................................... 675
Haiming Liu, Georges Beaudoin, Sheida Makvandi, Simon Jackson

Trace element signature of pyrite from Bagassi gold deposit, western Burkina Faso .......... 679
Hilaire S. Dakouré, Aurélien Eglinger, Anne-Sylvie André-Mayer, Naba Seta, Wilfried A.B.Toé, Luc Siebenaller

Synthesis of gold compositional data from petrography and detrital gold particles to characterize complex lode gold mineralisation .............................................. 683
Carl P. Spence-Jones, Rob J. Chapman, David A. Banks, Graham W. McLeod

Quantification of gold grains morphology in alluvial sediments, Moulin River, Appalachian Province, Québec, Canada ........................ 687
François-Xavier Masson, Georges Beaudoin and Denis Laurendeau
Detrital gold, heavy minerals and sediment geochemistry elucidate auriferous mineralization in southeast Ireland ................................................................. 691
Moles, Norman R., Chapman, Robert J.

Placer gold provenance, a site study comparing placer and lode gold chemistry and inclusions Black Mountain, Alaska........................................................................ 695
Erin E Marsh, Robert J Chapman, David T Adams, Jakub Skrzynecki

Naturally occurring Au nanoparticles associated with high-grade mineralization at the world-class Callie deposit, Northern Territory, Australia ........................................................................ 699
Laura Petrella, Nicolas Thébaud, Denis Fougerouse, Katy Evans, Zakaria Quadir, Crystal LaFlamme, Sandra Occhipinti, Stephen Turner

Geochronological and multi-isotopic evidence for the genesis of the post-magmatic and deeply-sourced Daliuhang orogenic gold deposit, Jiaodong, China ........................................... 703
Kai Feng, Hongrui Fan, David I. Groves

Mineralization, Alteration and Age of the host at the Barsele orogenic gold deposit, Northern Sweden ................................................................................................................ 707
Helen V. Thomas, Marcello Imaña, Kåre Höglund, Christopher Mark, Thomas Riegler, Claire Florence Ansberque, Tobias Bauer, Glenn Bark

Tracking an Archean orogenic gold deposit evolution through multiple sulfur isotopes ....... 711
Dennis Sugiono, Nicolas Thébaud, Marco L.Fiorentini, Laure Martin, Crystal K. LaFlamme, Jamie Rogers, Giovanna Lorusso

A refined view of the 'Mesoarchaean gold event' ........................................................................ 715
Nicolas J. Saintilan, David Selby, Joshua Hughes, Denis M. Schlatter, Jochen Kolb, Adrian Boyce

Tracing the S source reservoir of the Tropicana gold camp, Western Australia .................... 719
Nicolas Thébaud, Steffen Hagemann, Laure Martin, Stefano Caruso, Stanislav Ulrich, Douglas Allan

The Saattopora orogenic Au-Cu deposit, Central Lapland Greenstone belt, Finland: fluid sources and timing of hydrothermal processes ........................................................................ 723
Ferenc Molnár, Yann Lahaye, Hugh O’Brien, Matti Kurhila, Helena Hulkki, Attila Demény, Nathanâel Kirsch, Antonin Richard

Evolving the genetic model for the Cononish gold deposit, Scotland: from prospect to mine. 727
Calum Lyell, Adrian J. Boyce, Darren F. Mark, William McCarthy, Christopher J.S. Sangster, Peter Flindell, Maurits van den Berg

KEYNOTE: Concepts and Revised Models for Phanerozoic Orogenic Gold Deposits ............ 731
Mortensen, J.K., Craw, D., MacKenzie, D., Allan, M., Chapman, R.J.

Welsh and Spanish orogenic gold – a comparative study ......................................................... 733
Cunningham J.K., Gómez-Fernández, F., González Menéndez, L., and Beard, A.D.

Orogenic Gold Deposits in the Variscan Belt in Northwestern Iberia ..................................... 736
MacKenzie, D., Craw, D., Mortensen, J.K.
Topology as a tool to characterize gold stockworks .......................................................... 739
François Turlin, Michel Jébrak, Stéphane De Souza, Jordi Turcotte

KEYNOTE - SEG Invited Speaker: Linking fluid flow to gold mineralisation in the Senoufo greenstone belt, northern Côte d’Ivoire .............................................................. 743
Lynnette Greyling, Johann Diener, Chris Harris, Tshepiso Bopape, Joe Holliday

Ore-bearing fluids of the Blagodatnoye gold deposit (Yenisei ridge, Russia): fluid inclusions data ............................................................................................................................................ 745
Elena O. Shaparenko, Taras A. Bul’bak, Margarita O. Khomenko, Maria A. Ryabukha, Anatoly M. Sazonov

Exceptionally Au-rich Mid-Crustal Fluids from the Kola Super Deep Borehole .................. 748
Prokofiev Vsevolod Yu., Banks David A., Lobanov Konstantin V., Selektor Sofiya L., Milichko Valentin A., Akinfiev Nikolay N., Borovikov Andrey A., Lüders Volker, Chicherov Mikhail V.

New constraints on fluid composition of the Neoarchaean Black Reef, South Africa .......... 752
Hunadi K. Maselela, Glen T. Nwaila, Grant M. Bybee, Raymond J. Durrheim, Jeremie Lehmann

Fluid inclusion analysis and isotopic investigation of two structurally constrained gold mineralization in the Fairview mining complex, Barberton, South Africa............................... 756
Christina M. Comuso, Bjorn P. von der Heyden, Matthew Severs, Chris Harris

Shearing and fluid evolution of Porto Nacional Orogenic Gold District, Transbrasiliano-Kandi Shear System, Brazil ......................................................................................................... 760
Maria Jose Mesquita, Jefferson Picanço, Iain Samson, Leo Hartman, Marcia Boscato Gomes

A unique (?) telescoped orogenic system: Insights from the Fosterville gold deposit ............ 764
C. R. Voisey, A. G. Tomkins, Y. Xing

Gold metallotects and mineralization styles of northwestern Abitibi greenstone belt, Canada ............................................................................................................................................ 768
Sébastien Castonguay, Benoît Dubé, and Patrick Mercier-Langevin

Au- and U-bearing conglomerates in the Bababudan Group, Dharwar Craton, India......... 772
Hartwig E. Frimmel, Venkatraman S. Hegde, Wyatt E.L. Minter, Chris Harris

The geological characteristics of metasedimentary rock-hosted orogenic gold deposit in Awak Mas area, Indonesia ........................................................................................................ 776
Ernowo Harjanto, Franz Michael Meyer, Arifudin Idrus

Gold in Irish coal: Palaeo-concentration from metalliferous groundwaters ......................... 780
Liam A. Bullock, John Parnell, Joseph G.T. Armstrong, Sam Spinks, Erico M. M. Flores, Paola A. Mello, Filipe S. Rondan, Marcia F. Mesko

Gold growth under low temperature conditions: a case study from the Amani Placer Gold Deposit, Tanzania ........................................................................................................................................ 784
Stephan C. Dunn, Bjorn P. von der Heyden, Abraham Rozendaal, Rikard Taljaard

Formation mechanisms of quartz veins in orogenic gold deposits: Insights from Grass Valley, California, USA ............................................................................................................. 788
Ryan D Taylor, Thomas Monecke, T. James Reynolds
Freixo de Numão Au-W deposit, Northern Portugal: ore features and mineralization controls
Sara Leal, Alexandre Lima, Fernando Noronha

Role of pre-ore barren quartz veins in orogenic-gold mineralization: A case study from
Huangjindong deposit, Jiangnan Orogen, China
Liang Zhang, David I. Groves, Li-Qiang Yang, Si-Chen Sun, Jiu-Yi Wang, Rong-Hua Li, Roberto F. Weinberg, Sheng-Gang Wu, Lei Gao, Lan-Ling Yuan

The Mustajärvi gold occurrence - telluride-hosted orogenic gold in the Central Lapland
Greenstone Belt, Finland
Matthias Mueller, Petri Peltonen

High Resolution 3D X-ray Computed Tomography: Application for the Study of Gold-Bearing
Arsenopyrite
Evgeny Naumov, Konstantin Kovalev, Yuri Kalinin, Galina Palyanova, Viacheslav Voitenko

Constraining the source of the alluvial gold from the Whiteadder River drainage, SE Scotland
Abdulkadir A.M., Cunningham J.K., Beard, A.D., Smith, A.S.

Normalisation of pathfinder element in soil data to aid orogenic gold exploration with an example
from southern New Zealand
Adam P. Martin, Michael F. Gazley, Rose E. Turnbull, Grace Frontin-Rollet, Delia T. Strong

The giant Muruntau deposit (Uzbekistan) – Au-Bi-Te-W type of orogenic gold deposits hosted
by black shales
Rustam Koneev, Reimar Seltmann, Alla Dolgopolova, Mamat Karabaev

Impurities in pyrite from the gold deposits of Central Aldan ore area (Sakha-Yakutia, Russia):
study using LA ICP-MS
Elena V Belogub, Konstantin A Novoselov, Dmitriy A Artem’ev, Olga N Filimonova

Mineralogical and geochemical characteristics of the Sekisovka gold deposit (East Kazakhstan)
Marina Mizernaya, Anastassiya Miroshnikova, Arkady Mizerny, Evgeniy Naumov, Alla
Dolgopolova, Reimar Seltmann

Gold as a powerful proxy to trace gold and unravelling gold systems, an insight into French
Guiana (France)
Anthony Pochon, Anne-Marie Desaulty, Laurent Bailly, Philippe Lach, Jérémie Melletton,
Isabelle Duhamel - Achin

Characterization of gold grains from Bigorne deposit: search indicators to hypogene
mineralization. Preliminary studies
Sara Leal, Alexandre Lima, Fernando Noronha

Pb-Zn-Sb-Ni-Au mineralization from the Kizhnica area, central Kosovo: new data on the
listwaenite type mineralization
Sławomir Mederski, Jaroslav Pršek, Katarzyna Hincyngier
The gold Zun-Kholbinskoe deposit (Russia, Republic of Buryatia): ore mineralogy, geochemistry, geochronology ................................................................. 838
Anikina E., Aristov V., Chugaev A., Borisovsky S., Travin A.

The source of Au and S of the orogenic gold deposits in the Llamas de Cabrera district (Iberian Variscan Massif) ................................................................. 842
Fernando Gómez-Fernández, John K. Cunningham, Pablo Caldevilla, Antonio Herrero-Hernández, Andrew D. Beard

Understanding of the genesis of an orogenic gold deposit in the Central Cordillera of Colombia: constraints on gold grade variation ........................................ 846
Daniel G. Sandoval M., Juan C. Molano M., Diego Peñaloza

Geological and Structural Evolution of the Madenköy Gold Occurrence in Bolkar Mountains (Niğde-Turkey): Preliminary Results ........................................ 850
Duygu İşbil, Hayrettin Koral, Nurullah Hanlıçi, Hasan Emre

Structural controls of orogenic gold in Northern Ireland: Implications to orogenic gold genetic models ................................................................................. 853
James I. Shaw, Taija M. Torvela, Robert J. Chapman, Mark R. Cooper, Steven P. Hollis, Cian O’Meara

Recent developments on the origin of gold mineralization in East Kazakhstan ..................... 857
Marina Mizemaya, Asel Akylbaeva, Joyashish Thakurta, Evangelia Murgia

Bismuth and antimony mineralization in deposits of the Zarmitan gold ore zone (Uzbekistan) 860
Anna Krivosheeva, Rustam Koneev, Oybek Tursunkulov

Gold chalcogenides natural occurrence in Maletoyvayam (Kamchatka, Russia) - an experimental approach ................................................................. 863
Marek Tuhý, Anna Vymazalová, Nadhezda D. Tolstykh, Jakub Plášil, František Laufek

Synthetic study of the sources and origin of the gold deposit in the western Hoggar prospect (South of Algeria) ................................................................. 866
Ismahane Chaouche, Mohamed Talbi

---

**Supergenes, gems and non-metallic ores**

---

**KEYNOTE**: Single and Multiple Weathering-Erosion Cycles in Supergene Ore Genesis ...... 870
Paulo M. Vasconcelos

Mineralogy and chemistry of Ni-phyllosilicates in the Wingellina Ni-Co laterite deposit (Western Australia): alteration processes of mafic to ultramafic lithologies ................................................................. 873
Francesco Putzolu, Maria Boni, Nicola Mondillo, Jens Najorka, Giuseppina Balassone, Piergiulio Cappelletti, Fabio S. Graziano, Licia Santoro
New data on the Francevillian manganese ore from Bignomi plateau, Gabon

Alexis Ndongo, Norbert Ondo Zue Abaga, Benjamin Musavu Mousavou, Simplice M. Ndongo Ondo, Kalle Kirsimae

Characterisation of the nonsulphide zinc ore at Huoshaoyun, Northwestern China, and its genetic aspects

Wenbin Jia, Fengyue Sun, Guangsheng Yan

Mineralogy and geochemistry of black beach sands along the coastline of Milos and SW Kimolos Islands, Greece

Marianthi Anastasatou, Michael Stamatakis, Aristomenis Karageorgis

Characterization and origin of the industrial minerals and rocks of NE Kimolos Island, Aegean Sea, Greece

Michael Stamatakis, Marianthi Anastasatou, George Tselepis, George Kotsis

KEYNOTE: Constraints on gem opal formation: a case study of Ethiopian opals

Boris Chauviré, Benjamin Rondeau

The origin of sapphires in alluvial and marine placers from the Loire River, France

Gaston Giuliani, Anthony E. Fallick and Adrian J. Boyce

Geology of the La Pava emerald mine, Colombia


Using weathering and alteration minerals to constrain water table movement and supergene enrichment of Central Andean porphyry copper deposits

J.M. Shaw, F.J. Cooper, A.J. Boyce, K.A. Farley, L. Evenstar

Multiple fluid infiltration in the supergene Fe-deposit at Petronell (Germany) - chronology of events by goethite and todorokite U-Pb dating

István Dunkl, Hilmar von Eynatten, Keno Lünsdorf

The potential use of multi- aliquot goethite (U-Th)/4He geochronology for understanding late Cenozoic climate change across Eurasia

David Currie, Fin Stuart, Luigia di Nicola, John Faithful, Serdar Keskin

Mineralogical and geochemical characteristics of alkaline phosphate ore from a supergene zone in the Catalão Region, Brazil

Sebastian Maak, Andreas Kamradt, Gregor Borg

Rare Earth Element contents of Kızıldağ and Kemiklitepe bauxite deposits, Central Tauride, Turkey: Implications for REE potential in bauxites

Bihter Hepvidinli, Nurullah Hanilçi

Hydration of volcanic glass and genesis of perlite deposits based on oxygen and hydrogen isotope data

Peter Koděra, Peter Varga, Peter Uhlik, Rastislav Milovsky, Jaroslav Lexa, Milan Kohút, Anthony E. Fallick
Study of stable isotopes as a proxy for emerald exploration in the Western Emerald Belt, Colombia ……………………………………………………………………………………………………….. 927
Gabriel F. Nino Vasquez, Sheng-Rong Song

Photoluminescence analysis to determine the origin of emeralds from the Eastern and Western belts in Colombia ……………………………………………………………………………………………………….. 931
Towards a stratigraphic framework for the Platreef, northern limb, Bushveld complex, South Africa

Danie F Grobler, Albie JAN Brits, Alexandra Crossingham
Ivanplats (Pty) Ltd, An Ivanhoe Mines Company, Mokopane, South Africa

Abstract. Current high Pd metal prices and the search for large Ni deposits has increased the importance of the Platreef mineralised zone in the Northern Limb of the Bushveld Complex significantly. Poor understanding of the Platreef geology remains a complex problem for many exploration companies. The Ivanplats exploration team have shown that understanding lateral lithological facies variations in the Upper Critical Zone may be the most important aspect in unravelling the stratigraphy of the Platreef on the Northern Limb of the Bushveld Complex. Detailed examination of the eastern and western limb stratigraphy and observed lateral variations led to the recognition of key stratigraphic lithological indicators within the Platreef rock sequence on the Ivanplats properties. Grobler et al. (2019) have demonstrated a new stratigraphic interpretation for the Turfspruit area comparable to the Critical Zone of the BIC. The Platreef is shown to contain recognisable Upper Critical Zone stratigraphic units in addition to the Merensky Reef. Here we discuss the application of the new proposed stratigraphy in a regional sense to the Northern Limb.

1 Introduction

A regional stratigraphic subdivision for the Platreef has always remained problematic. Exploration companies have mostly followed their own project-bound interpretations and correlation between projects was mostly very complex or untenable.

Historically, the Platreef was defined as contact-style mineralization found at the base of a mafic-ultramafic intrusion (McDonald and Holwell 2011). Direct correlations with the Merensky Reef failed due to attempts to correlate the entire thick package of hundreds of metres of variably mineralized Platreef rock with the aforementioned narrow reef. Arguments listed included the following:

- Low Pt/Pd ratios (1:1 - calculated across entire Platreef compared to a 1.7:1 Merensky ratio);
- huge thickness (100 – 400 m) compared to Merensky Reef (~1 m);
- Few PGM sulfides;
- Only erratic chromitite occurrences compared to the stratiform chromitites recognised in the Critical Zone elsewhere;
- No magmatic cyclicity – (Platreef pyroxenite dominant) compared to well-developed cyclicity of the Critical Zone;
- Irregular complex sedimentary footwall zone compared to predominant quartzitic footwall of main Bushveld Complex.

The recent recognition of normal Upper Critical Zone (UCZ) stratigraphy on Turfspruit through the study of > 720 km of drill core allowed for a detailed examination of the magmatic stratigraphy (Grobler et al. 2019; Yudovskaya et al. 2017). For the first time, a direct correlation with the UCZ of the western and eastern Bushveld was possible. Several key papers have previously been published on the main Bushveld Complex, in an attempt to explain the stratigraphic relations in the upper part of the Critical Zone. Davey (1992) illustrated the lithological and thickness variations through the Bastard – Merensky and UG2 reefs in the Marikana area of the western Bushveld, while Lea (1996) did the same for the north-eastern Bushveld. Understanding these variations were key in unravelling the complex stratigraphy of the Platreef on Turfspruit. Although magma-sediment interaction processes disrupted the normal magmatic stratigraphy, areas do exist where mostly pristine magmatic cyclical units are still recognisable. This is especially true for the down-dip deeper portions of Turfspruit. Understanding the stratigraphic relationships within these areas allowed for extrapolation up-dip into more complex typical Platreef areas.

Several MSc and PhD studies related to the Laurentian-Limpopo university collaboration funded by Ivanhoe Mines over the past five years have contributed significantly to our understanding of the local geology. Of much importance is the Strontium isotope study completed by Mayer (2018). The results show a significant \( ^{87}\text{Sr}/^{86}\text{Sr} \) ratio shift through the mineralized section of the upper Platreef which matches the isotopic shift previously documented through the Merensky and Bastard Cyclic Units in the eastern and western limbs of the Bushveld Complex. The studies all focussed on establishing a detailed ore deposit model for the Turfspruit Platreef. Completed MSc projects through Cardiff University and papers published by University of the Witwatersrand academic staff were important during the process of unravelling the stratigraphic framework. (Yudovskaya et al. 2017) correlated the Merensky-style mineralisation within the Turfspruit Thick Reef Facies directly with the Merensky Reef elsewhere in the Bushveld Complex. The combination of the scientific studies and the stratigraphic framework established by Ivanplats exploration geologists allows us now to attempt a detailed regional stratigraphic correlation for the Platreef across the entire northern limb.

2 Platreef stratigraphy

Extensive exploration drilling by Ivanplats established a new stratigraphy for the layered complex on Turfspruit (Grobler et al. 2019). Focussing on the Platreef mineralised package, several key stratigraphic units were recognised below the Main Zone contact that can be
directly correlated with the Critical Zone of the main Bushveld Complex. These include the Bastard, Merensky and UG2 cyclic units for which equivalents were proposed for the latter two, in the southern segment of the northern limb by Maier et al (2008). Furthermore, studies by Yudovskaya et al. (2013, 2017) on Turfspruit have contributed significantly in recognizing important stratigraphic units lower down in the Platreef stratigraphy. This includes recognition of mafic-ultramafic units of the Lower Zone stoping into host rock Transvaal sediments.

### 3 Lithological and thickness variations

It is evident from a literature study on the thickness variation of the MCU and the BCU across the Bushveld Complex that these cyclic units are significantly developed across large areas. What is not readily evident from the literature is the thickness variation of individual lithologies within the specific cyclic units. Lateral facies variation has been described across the Bushveld (Davey 1992; Lea 1996; Viljoen 1999). These need to be taken in consideration during stratigraphic correlations. Rock types are seen to grade from pyroxenite through norite cyclical units into anorthosite at the same stratigraphic level. Figure 1 is a schematic illustration depicting the lateral lithological and thickness variations observed in the project area.

Thickness variations of individual lithological units are evident within the BCU and the upper part of the MCU on the project area (Fig. 1). Table 1 illustrates the variation in maximum thickness across the Bushveld for the MCU and BCU intervals, respectively, and corresponding thickness variation for the comparative equivalents on Turfspruit 241KR. The average thickness for the mineralized Merensky Reef at a 2 g/t cut-off is 25.23 m for the study area (Table 2).

### 4 Conclusions

Recognition of UCZ stratigraphic units within the Northern Limb allows for a direct correlation with the rest of the Bushveld Complex. These observations show that the stratigraphy of the layered complex remained generally consistent across the entire intrusion. Although remarkably similar across the different geographic areas, there are significant lateral lithological variations on a detailed scale within the larger stratigraphic units. Understanding the complexity of these variations forms the key to unravelling the stratigraphy of the layered sequence observed within the Northern Limb (Fig. 2).

The broad zone of erratically mineralised “Platreef” found at the base of the northern limb includes a large part of the Critical Zone and Lower Zone stratigraphy (Grobler et al. 2019) (Fig. 3). In particular, it explains the failure of previous attempts of direct correlation with the Merensky Reef. It is of utmost importance to note that only the high-grade upper part of the Platreef should be correlated with the Merensky and Bastard reefs.

### Table 1. Thickness variations of the MCU and BCU across the Bushveld Complex compared to Turfspruit (from Grobler et al. 2019).

<table>
<thead>
<tr>
<th>Mine Area</th>
<th>MCU (m)</th>
<th>BCU (m)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amandelbult Section</td>
<td>16</td>
<td>32</td>
<td>Viljoen et al (1986)</td>
</tr>
<tr>
<td>Rustenburg Section</td>
<td>10</td>
<td>100</td>
<td>Viljoen and Hieber (1986)</td>
</tr>
<tr>
<td>Northam Mine</td>
<td>23</td>
<td>61</td>
<td>Vining and Cowell (1999)</td>
</tr>
<tr>
<td>Impala Platinum Mine</td>
<td>11</td>
<td>110</td>
<td>Juo-Do Toll (1986)</td>
</tr>
<tr>
<td>Union Sections</td>
<td>32</td>
<td>35</td>
<td>Viljoen et al (1986b)</td>
</tr>
<tr>
<td>Atok Platinum Mine</td>
<td>27</td>
<td>55</td>
<td>Loosen and Hieber (1999)</td>
</tr>
<tr>
<td>North-eastern Bushveld</td>
<td>18</td>
<td>59</td>
<td>Lea (1996)</td>
</tr>
<tr>
<td>Turfspruit 241KR</td>
<td>25</td>
<td>32</td>
<td>Av. thickness this study (439 holes)</td>
</tr>
<tr>
<td>Average excl Turfspruit</td>
<td>20</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Average incl Turfspruit</td>
<td>20</td>
<td>61</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Thickness variations of the UCZ stratigraphic units recognised on Turfspruit.

<table>
<thead>
<tr>
<th></th>
<th>MAN</th>
<th>BCU</th>
<th>MDU</th>
<th>MCU</th>
<th>MLU</th>
<th>M1U</th>
<th>M1L</th>
<th>M1U+M1L</th>
<th>BCU 2g cut-off</th>
<th>MCU 2g cut-off</th>
</tr>
</thead>
<tbody>
<tr>
<td># of Holes</td>
<td>285</td>
<td>312</td>
<td>478</td>
<td>425</td>
<td>244</td>
<td>439</td>
<td>366</td>
<td>303</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>29.09</td>
<td>140.71</td>
<td>119.77</td>
<td>70.76</td>
<td>66.24</td>
<td>99.15</td>
<td>18.18</td>
<td>87.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Min</td>
<td>0.03</td>
<td>0.39</td>
<td>0.32</td>
<td>0.15</td>
<td>1.11</td>
<td>0.33</td>
<td>2.06</td>
<td>2.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>4.32</td>
<td>29.84</td>
<td>32.10</td>
<td>15.28</td>
<td>20.02</td>
<td>25.23</td>
<td>4.47</td>
<td>22.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>2.09</td>
<td>25.39</td>
<td>22.35</td>
<td>13.10</td>
<td>17.54</td>
<td>22.25</td>
<td>3.51</td>
<td>19.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std Dev</td>
<td>5.25</td>
<td>23.46</td>
<td>26.67</td>
<td>13.34</td>
<td>13.65</td>
<td>15.81</td>
<td>2.29</td>
<td>14.89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Vertical section through the Flatreef displaying lateral facies variations (Cr-stringers shown as black stippled lines).

Figure 2. Preliminary stratigraphic interpretation for the Platreef of the northern limb (modified after Mayer 2018). For explanation of abbreviations refer to Mayer 2018.
Figure 3. Simplified stratigraphic correlation of the northern limb Platreef with the main Bushveld Complex (after Grobler et al. 2019).

References

Davey SR (1992) Lateral variations within the upper Critical Zone of the Bushveld Complex on the farm Rooikoppies 297JQ, Marikana, South Africa. SAJG, 95(3/4):141-149.


The structure and syn-magmatic tectonic influence on the Flatreef Deposit, Northern Limb, Bushveld Complex

J.A.N Brits1, D.F Grobler1, A.J Bumby2, A Crossingham1
1Ivanplats (Pty) Ltd., an Ivanhoe Mines Company, Mokopane, South Africa
2Department of Geology, University of Pretoria, Pretoria, South Africa

Abstract. The Flatreef deposit is part of the Upper Critical Zone stratigraphy of the Rustenburg Layered Suite (RLS) of the Northern Limb (NL). Recently discovered by Ivanplats and described by Grobler et al. (2019), the Flatreef was the focus of a definitive feasibility study executed by Ivanplats (Pty) Ltd. on its Platreef Project. From this study it became evident that structural elements and the timing thereof played a significant part in the formation of the phenomenon which became known as the Flatreef deposit. The Flatreef deposit is a distinct magmatic sequence of cyclical units which stratigraphically correlate with the Upper Critical Zone of the Bushveld Complex. Remarkable features of the Flatreef deposit includes the preservation of magmatic layering of extraordinary width and associated poly-metallic mineralisation. Multiple tectonic events contributed to the formation of the Flatreef structure. Ductile tectonic events on both a regional and a project scale influenced the orientation and shape of the sedimentary rocks prior to intrusion of the RLS and controlled processes during emplacement of magma. Semi-brittle tectonism at various stages during late to post-emplacement is evident as brittle overprints on shear zones and faults.

1 Regional tectonic setting of the Northern Limb

Emplacement of the Northern Limb has been influenced by two principal transpressional events which caused strain along the Thabazimbi-Murchison Lineament (TML) in the south and displacement along the Palala Shear Zone (PSZ) in the north. According to Nex, (2005) this has led to the formation of two main open fold expressions within the Transvaal sediments. The dominant folding event was caused by NE-SW sinistral transpression resulting in low amplitude open folding. Subsequent NW-SW trans-pressive inversion refolded the earlier NW fold axis resulting in a basin and dome fold interference pattern (Friese, 2012).

The layered magmatic rocks of the RLS forming the Northern Limb has been intruded into the moderately undulating sediments of the Transvaal Supergroup. The transgressive nature of the lower contact of the RLS up-dip and along strike towards the north is well documented (Kinnaird, et.al., 2005). Intrusion and the space required for emplacement into a closed system within clastic and chemical sedimentary strata was facilitated by means of melting and assimilation of the siliceous clastic sediments. Northward the magmatic rocks of the northern limb transgress through the lower clastic sediments of the Magaliesberg and Timeball Hill Groups into the dolomite-limestone, quartzite and shale interbedded strata of the Chuniespoort Group found along the eastern boundary of the Turfspruit farm. Further north the RLS transgresses through the Penge and Malmani Formations up to the north of the Sandsloot (Angloplats) farm where ultramafic and mafic rocks are in contact with gneissic and granitic basement floor rocks (Fig. 1).

Structurally, the Northern Limb is separated from the rest of the Bushveld Complex by the Thabazimbi-Murchison Lineament (TML). The TML is a pre-Bushveld, major, compressional tectonic boundary (suture zone) that transects the Kaapvaal Craton (Friese, 2003, 2004). The most prominent fault group influencing the RLS of the Northern Limb consists of NE-SW striking dextral block faults of which the Ysterberg-Planknek and Zebediela Faults are the most prominent southern structures. The Zebediela Fault forms part of a southward dipping, anastomosing fault zone which off-sets the Northern Limb from the Eastern Limb by left-lateral, normal displacement. The Zoetfontein-Melinda Fault (ZMF), found along the northern boundary of the known Kaapvaal Craton, is part of the Palala Shear Zone (PSZ). The ZMF, as the eastward expression of the PSZ, displays similar kinematics to the southern faults. The PSZ forms the boundary between the southern marginal zone and central zone of the Limpopo Belt.
2 Structural influence on the Flatreef

The Flatreef is the down-dip extension of the Platreef, forming a laterally continuous, sub-horizontal sequence of PGE mineralized magmatic cyclical units of interlayered chromitite-pyroxenite-norite-anorthosite, several tens to locally >100 m in thickness, found along the base of the Main zone of the Northern Limb. Detailed structural modelling has defined a number of fault blocks related to six fault and shear structures transecting the study area (Fig. 2). In addition, recent mine development has shown the existence of low angle thrust duplex structures and confirmed the structural control on early and later granite sill and dyke intrusion into the Critical Zone and Main Zone found along this section of the Northern Limb.

2.1 Stratigraphy

The identification and subsequent introduction of Critical Zone stratigraphy to the upper part of the Platreef (Grobler, et.al., 2019) has been instrumental in building the detailed structural model for the Flatreef and surrounding areas. Stratigraphic units of the Bastard and Merensky Cyclic Units (BCU and MCU) and their respective mineralized pyroxenite units namely the Bastard Reef (BAR) and Merensky Reef (T2U or M1u) enabled the identification of features related to magma response to tectonic influences. The characteristic thickening of the pyroxenite units of the Flatreef can in part be attributed to fault induced dilation within the magma chamber and subsequent infill during consolidation (Fig. 3). Further evidence of syn-magmatic structural influence is found within the upper portions of the BCU where the cyclical nature of the noritic units has been disrupted in response to magma reacting to strain which caused anorthositic fluid to accumulate preferentially in thrust induced dilation zones (Fig. 4). Later syn-magmatic extensional re-activation can also be noted.
2.2 Mineralization

The combination of the grade block model in Leapfrog with the geological model has shown the occurrence of footwall mineralization which could possibility be attributed to structural control on mineralization within the footwall units to the MCU (which includes the T2U (M1U) and T2L (M1L)) of the Flatreef section (Fig. 5), (Grobler et al. 2019) Preliminary findings show that occasional mineralization occurs within the footwall blocks and within close proximity, to the modelled major shear zone structures. Mineralization occurs as weakly constrained, lens shaped layer parallel zones with their long axes oriented parallel to the structures. Strike lengths can be up to 400m length. In addition, there appears to be some degree of control on footwall mineralization by the Nkwe Shear and the low angle structures (LAF40 and LAF50) and that the structural influence on footwall mineralization can be attributed to late syn-tectonic strain which caused re-activation of the major ductile structures (to various degrees). This is based on the observation that there is significant but variable brittle overprint and extensional features associated with the primarily ductile shears. This may also be the reason for the apparent control on footwall mineralization which is not that obvious within the Merensky Cyclic Unit. The latter indicates a time constraint due to diminished re-activation of the shear structures later on during emplacement/consolidation of the Upper Critical Zone and Main/Upper Zones.

2.3 Alteration

The relationship between calc-silicate xenoliths within the footwall strata and the proximity of these to olivine bearing rock is well established, but there appears to be an additional control on the distribution of the sediment derived fluids which can be observed as localised occurrence of olivine-bearing (Mg-rich magmatic units) in relation to the low angle structures within the footwall to the MCU. In some instances it appears that shale hornfels xenoliths may have acted as obstructions to the normal upward migration/percolation of the fluids (Fig. 6). This leads to the unusual distribution and/or absence of olivine-bearing rocks within areas interpreted as the up-dip or low-pressure, lee-ward side of these shale hornfels xenoliths (Fig. 6(a)). The presence of harzburgite within the lower portion of the MCU, known as the T2L, within an area where the footwall consists of normal cyclical norite sequence (Fig. 6(b)) can be explained by the lateral and up-dip migration of calcic fluid controlled by the low angle structure (in this instance LAF50) which acted as a conduit or suture zone for diagonal upward movement of fluids with concurrent lateral migration accommodated along the principal magmatic contact, namely the basal contact of the MCU pyroxenite.
3 Conclusions

Progressive tectonic strain on the Flatreef block caused an end product that can be attributed to a combination of tectonic events. Sinistral fault block rotation contributed to strata thickening. This oblique dip-slip rotation was accommodated by layer parallel to sub-parallel thrusting and flexural slip thrusting due to flexure and drag folding. Late- to post intrusive trans-tensional and extensional tectonism is evident as brittle normal and oblique dip-slip re-activation of existing fault and thrust structures. Extension related intrusions include the partial healing of shear and thrust zones by granitic fluids and structurally controlled low-temperature alteration fluid overprint. Dolerite dykes are preferentially intruded into fracture zones formed by re-activation of original ENE to ESE trending regional block faults such as the Ysterberg-Planknek fault (Friese, 2012).

Recent discoveries from the underground development of the Ivanplats Platreef Mine have confirmed the interpretations made from high density data and 3D modelling. Kinematic characteristics of the Nkwe shear zone have been described and the reverse sense of movement, oblique sinistral strike-slip component and multiple re-activation events identified. Additionally, steep shear zones and later brittle reactivation have been studied. These explain the difficulty in modelling some of the junction zones where lower order structures will be more persistent. Low angle faults or thrusts are confirmed to be part of a duplex system, similar to what has been reported at Sandsloot (Friese, 2012) and Booyensdal (Couto and Theron, 2014). Later transtensional re-activation and granitic fluid intrusion into the preferred low angle faults have been confirmed. The orientation of a steeply-dipping granite dyke swarm has been confirmed and also the existence of multiple granitic pulses. Intrusion was structurally controlled and the timing of granite intrusion is now constrained to correspond to the consolidation of the Main Zone magma. In addition, low angle granite sills intruded preferentially along low angle fault planes, which are part of the thrust duplex system. These sills transgress the stratigraphic boundaries of the Critical and Main zones, the fluids thought to be originating from floor rock and sedimentary xenolith melts.

Underground exposure of the noritic cyclical units of the Bastard Cyclical Unit (Grobler et al. 2019) shows evidence of a syn-magmatic response to tectonic strain. On a larger scale, the reaction to strain induced on variably viscous, crystallizing magma explains the thickness variations noted within the geological model across structural features, thus confirming the influence of growth faults and layer sub-parallel thrusting during consolidation of the Critical Zone strata.

The structural control on late moderately high to low temperature alteration fluids has been confirmed. The most intense alteration being related to shear zones and thrusts where the host rock experienced syn-magmatic semi-ductile to ductile shear strain.

References

Grobler, D.F., Brits, J.A.N., Maier, W.D., Crossingham, A., (2019) Litho- and chemostratigraphy of the Flatreef PGE deposit, northern Bushveld Complex, accepted January 2018 for publication in Mineralium Deposita. The references are in 8pt Arial with a hanging indent (Reference List Style) See instructions for authors and the specimen abstract for formatting requirements.


Hydrothermal modification of magmatic sulphide Cu-Ni-PGE deposits in the Northern Bushveld Complex, South Africa

Katie A. McFall, Iain McDonald & Bianca Kennedy
School of Earth & Ocean Sciences, Cardiff University, Cardiff, UK

Dominique Tanner
School of Earth & Ocean Sciences, University of Wollongong, Australia.

R.E. (Jock) Harmer
Department of Geology, Rhodes University, P.O. Box 94, South Africa

Brian Tattitch
University of Bristol, Tyndall Ave, Bristol, U.K.

Abstract. Unlike the rest of the Bushveld Complex, the Northern Limb contains Cu-Ni-PGE deposits hosted not only in the ultramafic Lower and Critical Zones of the Rustenburg Layered Suite, but also in the leucocratic rocks of the Main Zone. The Aurora Ni-Cu-PGE deposit is hosted in Main Zone gabbronorites and shows evidence of hydrothermal modification. The base metal sulphides (BMS) have low PGE concentrations, with PGE grade controlled by platinum group minerals (PGM). 75 area% of PGM are hosted in hydrothermal alteration minerals, with 52% spatially removed from BMS. Aurora also contains intercumulus olivine, formed by replacement of orthopyroxene through reaction with a volatile phase. Vapour and brine fluid inclusions were identified in primary magmatic silicates, showing volatiles were present while the system was still at least partially molten. Brine inclusions were also identified in primary magmatic silicates in the Platreef, and in the mineralised Troctolite Unit. These deposits contain intercumulus olivine, as does the Waterberg PTM project to the north of Aurora. Assimilation of dolomite from the Lower Transvaal supergroup is proposed to have released volatiles which remobilised PGE, modifying magmatic sulphide deposits across the Northern Limb. The presence of intercumulus olivine is suggested to indicate the presence of volatiles.

1 Introduction

The Northern Limb of the Bushveld Complex, South Africa is one of the most important Ni-Cu-PGE provinces in the world. Not only does it contain the Platreef – one of the largest platinum-group element (PGE) deposits, with one of the lowest extraction costs in the world – but it also hosts several additional PGE deposits (Fig. 1) hosted in the higher parts of the stratigraphy that have no known equivalent in the rest of the Bushveld Complex (Maier and Barnes 2010; Holwell et al. 2013; Kinnaird et al. 2017; McDonald et al. 2017; Huthmann et al. 2018; McCreesh et al. 2018; McFall et al. 2019). In these the mineralisation is present as PGE-rich base metal sulphides (BMS) and platinum group minerals (PGM) hosted in gabbronorites.

Figure 1. Map of the Northern Limb with deposits discussed highlighted (adapted from McFall et al. 2019).
Unlike the rest of the Bushveld Complex, the RLS in the Northern Limb intrudes highly reactive country rocks; most notably the Malmani dolomites of the Lower Transvaal Supergroup (Van der Merwe 1976, 2008). Calc-silicate xenoliths are common in many Northern Limb deposits, showing assimilation of dolomite during deposit formation (e.g. Harris and Chaumba 2001; Maier et al. 2008; McDonald et al. 2017). This assimilation releases volatiles, and the deposits in the Northern Limb commonly contain hydrothermal alteration minerals and textures (e.g. Holwell et al. 2013, 2017; Smith et al. 2014; McFall et al. 2019).

2 The Aurora Cu-Ni-PGE deposit

The Aurora deposit is a Ni-Cu-PGE-Au prospect to the north of the Northern Limb (Fig 1). It has a JORC-compliant inferred resource of 125 Mt of sulphide ore at 1.34 g/t Pt + Pd + Au, 0.08% Cu and 0.05% Ni (Venmyn-Rand 2010).

The host cumulates are interpreted to represent the Upper Main Zone and intrude the dolomites of the lower Transvaal Supergroup. Stratigraphically the prospect consists of peridotites and melagabbronorites (Unit 1) below gabbronorites and leucogabbronorites (Unit 2), and pigeonite gabbronorites (Unit 3). Unit 1 is intruded by coarse grained gabbronorite veins. The deposit contains pervasive, predominately talc-carbonate, hydrothermal alteration minerals, and xenoliths of calc-silicate. The highest whole rock Pd + Pt concentrations (up to 6.8 ppm, McDonald et al. 2017) are in Unit 2, and in the gabbronorite veins.

2.1 Base metal sulphide mineralisation

Table 1. Average trace element concentrations (in ppm) of sulphides from LA-ICP-MS analysis, divided by host unit. Pn = pentlandite, Cp = chalcopyrite and Py = pyrite (McFall et al. 2019).

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit 2 Pn</th>
<th>Veins Pn</th>
<th>Unit 2 Cp</th>
<th>Veins Cp</th>
<th>Unit 2 Py</th>
<th>Veins Py</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>13</td>
<td>7</td>
<td>31</td>
<td>9</td>
<td>45</td>
<td>4</td>
</tr>
<tr>
<td>Pd</td>
<td>30</td>
<td>10.4</td>
<td>1.7</td>
<td>1.3</td>
<td>0.9</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Pt</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.1</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Ru, Rh, Os, Ir</td>
<td>&lt;0.6</td>
<td>&lt;0.5</td>
<td>&lt;0.6</td>
<td>&lt;0.2</td>
<td>&lt;0.6</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Au</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Ag</td>
<td>1.3</td>
<td>1.3</td>
<td>23.7</td>
<td>22.5</td>
<td>4.1</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Bi</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.6</td>
<td>0.9</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Te</td>
<td>1.7</td>
<td>3.3</td>
<td>1.3</td>
<td>5.3</td>
<td>1.6</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Se</td>
<td>179</td>
<td>213</td>
<td>232</td>
<td>256</td>
<td>206</td>
<td>126</td>
</tr>
<tr>
<td>As</td>
<td>0.9</td>
<td>1.6</td>
<td>1.1</td>
<td>&lt;0.5</td>
<td>21.6</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>

Unit 2 and the gabbronorite veins are the only units to contain abundant base metal sulphides (BMS). Unit 2 contains pyrrhotite–pentlandite–chalcopyrite assemblages, with pentlandite exsolving from pyrrhotite. These are present as small (1-5 mm) rounded inclusions within primary silicates. Unit 2 also contains chalcopyrite–pyrite assemblages. These are angular, hosted in alteration minerals, and are interpreted to be a secondary, hydrothermal phase. The gabbronorite veins contain up to 50 modal % interstitial pyrrhotite–pentlandite–chalcopyrite±pyrite assemblages with granular pentlandite and primary pyrite (McFall et al. 2019).

LA-ICP-MS of sulphides shows the BMS in Aurora have lower PGE concentrations than other Bushveld magmatic sulphides. Pentlandites from Aurora contain an average of 23 ppm Pd (Table 1), compared to >100 ppm in the Platreef and Merensky Reef (Holwell and McDonald 2007; Osbahr et al. 2013; McFall et al. 2019).

2.2 Platinum-group minerals

SEM-EDS analysis of 26 sections characterised 995 platinum-group minerals (PGM) and precious metal-bearing minerals (PMM), with a total area of 27850 μm² and an average size of 28.2 μm² (McFall et al. 2019). Of the PGM and PMM identified in Aurora 85% (by area) are Pd-Te-Bi minerals (merenskyite with minor kotulskite), with 6% Pd-Te minerals (sopcheite with minor borovskite), 4% electrum and 3% Ag-Te minerals (hessite), along with minor Pd-Bi, Pd-As, Pt-Te-Bi, Pt-As and Pt-S minerals that collectively comprise 2% of total area. Only 25% of the PGM and PMM in Aurora are BMS hosted (Fig. 2A), with the rest hosted in silicates. Of the total PGM and PMM area 22% are hosted in alteration-silicates (quartz, chloride or actinolite) in an alteration halo around sulphides (Fig. 2C). Unusually, 52% of the PGM and PMM are spatially removed from BMS, instead hosted in alteration silicates and within cracks in primary silicates away from any BMS (Fig. 2D; McFall et al. 2019).

There is a systematic difference in the composition of merenskysites based on host mineral. BMS hosted merenskysites are more Bi-rich (mean 9.2 wt.% Bi), while those hosted in hydrothermal alteration minerals contain less Bi (mean 6.1 wt.% Bi). This compositional difference is also seen in other deposits – comparing merenskyite composition data from deposits globally, including hydrothermal deposit types such as porphyry Cu deposits, merenskysites which are hosted in hydrothermal
2.3 Evidence for hydrothermal modification

The low PGE content of the BMS in Aurora, coupled with the majority of PGM being associated with hydrothermal alteration minerals, suggests that hydrothermal fluids played an important role in metal remobilisation in this deposit. The difference in composition of merenskyites and their host minerals suggests that these PGM were reprecipitated by a hydrothermal fluid, rather than just transported away from the sulphides. The PGM present in the alteration halo immediately around BMS (Fig. 2C) are suggested to be the result of low temperature (<250°C) hydrothermal alteration resulting in volume loss of sulphides, stranding PGM in the alteration halo (c.f. Holwell et al. 2017). The PGM which are spatially removed from the BMS (Fig. 2D) are suggested to have been transported away by high temperature (>250°C) hydrothermal fluids earlier in the deposit genesis (McFall et al. 2019).

SEM-EDS mapping has shown the gabbronorites in Aurora to contain reverse zoned cumulus plagioclase. There is also a layer of olivine gabbronorite in Aurora, where the olivine is intercumulus, mantling cumulus plagioclase (Fig. 3A). It has been shown that reverse zonation of plagioclase and late, intercumulus olivine in layered ultramafic intrusions can be a result of reactions between a gabbronorite composition melt and an exsolved volatile phase (McCallum and Boudreau 1992; Boudreau 1999).

Fluid inclusions (Fig. 3B) are also present within the Aurora deposit, both in secondary quartz and in primary magmatic silicates (McFall et al. 2018). These consist of vapour, brine and salt-melt inclusions. Preliminary data shows the inclusions in cumulus plagioclase and intercumulus orthopyroxene have high temperatures (>800°C). This provides strong evidence for a volatile phase having been present while the system was at least partially molten.

The brine inclusions have very high salinities (>60 wt.% NaCl equivalent). Experimental work has shown that highly saline hydrothermal fluids are capable of carrying Pd (and Au, Ag, Cu and Fe, Xiong and Wood 2000), and so these volatiles, proposed to have been released during assimilation of Malmani dolomite and associated evaporites, may have transported metals.

3 Hydrothermal modification in other Northern Limb deposits

Aurora is not the only deposit in the Northern Limb to contain evidence of hydrothermal modification. The Platreef also contains late, intercumulus olivine (Fig. 3C), and a preliminary survey has shown primary magmatic silicates from the Platreef to contain brine and vapour inclusions, similar to those observed in Aurora (Fig. 3D). The Platreef also contains large rafts and xenoliths of dolomite (Armitage et al. 2002), which may be the source of these volatiles.

The Troctolite Unit, a mineralised layer of troctolite within the Main Zone, also contains intercumulus olivine. Brine inclusions have been identified in primary magmatic silicates, including olivine, in the mineralised sections of the Troctolite Unit (Kennedy et al. 2018).

The Waterberg PTM project, to the north of Aurora, also contains late, intercumulus olivine, however it is not thought to have assimilated dolomites (Kinnaird et al. 2017), meaning any volatiles present would likely be magmatic. Further work will be carried out to identify if fluid inclusions are present here also.

4 Effect of volatiles on PGE mineralisation

The presence of volatiles during the formation of orthomagmatic sulphide deposits has important implications both for deposit formation mechanisms and for grade control and processing methodology. High temperature, high salinity volatiles can transport PGE (Boudreau and McCallum 1992; Xiong and Wood 2000), along with other precious and base metals including Cu, Au, Ag and Fe. The Aurora deposit shows clear evidence of PGE remobilisation away from BMS during its formation, both through the reduction of sulphide volume during late, low temperature alteration, and potentially through high temperature volatiles remobilising metals while the system is still at least partially molten. These volatiles may have been released due to the assimilation of dolomite country rocks, and it is striking that many of the deposits in the Northern Limb which contain calc-silicate xenoliths also contain fluid inclusions in magmatic silicates, late intercumulus olivine and other evidence of hydrothermal modification. Further work will be done on fluid inclusions from these deposits in order to establish temperature and composition.

Fluid inclusions have also been identified in quartz and olivine around the J-M Reef deposit in the layered ultramafic Stillwater Complex, Montana, USA (Hanley et al. 2008), and in postcumulus quartz within the Merensky Reef (Bailhaus and Stumpf 1986; Schiffries 1990; Zhitova et al. 2016). The inclusions in these other magmatic sulphide deposits are brine and vapour inclusions, similar to those observed in the Northern Limb, with homogenisation temperatures >650°C. This
suggests that the presence of volatiles during magmatic sulphide Cu-Ni-PGE deposit formation in layered ultramafic intrusions may be a relatively common occurrence.

Acknowledgements

We thank the management of Pan Palladium, especially Jackie Van Schalkwyk, for access to samples and Eric Rooyt for facilitating further sampling of unit 1 veins in borehole LAP-04. This work was funded by a NERC SoS Consortium grant NE/M010848/1 “TeaSe: tellurium and selenium cycling and supply” awarded to Cardiff University.

References


Marquis E (2015) Petrogenesis of the Harzburgitic to Troctolitic Units in the Turfspruit Cyclic Unit, Northern Bushveld Complex, South Africa. Cardiff University


McFall KA, McDonald I, Tanner D (2018) Evidence for hydrothermal modification in the Aurora Cu-Ni-PGE prospect, Northern Bushveld Complex, South Africa. In: 13th International Platinum Symposium, pp 144–145


Platinum-group mineralization at the Tubane area, northern Molopo Farms Complex, southern Botswana

Jacob Kaavera
Kyushu University and Botswana International University of Science and Technology

Akira Imai, Kotaro Yonezu, Thomas Tindell, Koichiro Watanabe
Kyushu University

Kenzo Sanematsu
Geological Surveys of Japan

Abstract. Low-grade platinum-group mineralization has previously been reported in the cumulate rocks of the Molopo Farms Complex, but the nature and distribution of mineralization is poorly understood. This study documents the occurrence of platinum-group elements (PGE) at the northern lobe of the complex from a borehole intersection. PGE are confined to sulfide bearing feldspathic pyroxenite units with up to 0.47 ppm 2PGE+Au, up to 0.3 wt. % Ni and up to 0.12 wt. % Cu. Platinum-group minerals (PGM) are located towards the grain margins of magmatic sulfides and found as discrete grains within altered silicates. The PGM assemblages are dominated by froodite (PdBi2), michenerite (PdBiTe), sperrylite (PtAs2), and moncheite (PtTe2). Locally the orthopyroxenite occurs as enclaves within harzburgites. This suggest that the harzburgitic magma was at some point in contact with previously formed, partially crystallized orthopyroxenite cumulates that got disrupted and assimilated into them. Variations in NiO content of olivine from the poikilitic harzburgite and orthopyroxenite suggest that the magmas were in equilibrium with sulfide melt either prior to or during crystallization. Silicate-melt sulfide-melt immiscibility, likely occurred when the magma was contaminated with Archaean basement rocks and pyrite bearing dolomitic siltstone of the Transvaal Supergroup.

1 Introduction

The Molopo Farms Complex was discovered during the early 1960s through recognition of ultramafic rocks in wells at Keng pan (Boocock, in Carney et al. 1994; Fig. 1). Following its discovery, exploration activities including drilling campaigns, regional aeromagnetic and gravity surveys facilitating the delineation of the Complex as well as correlation of lithologies to those of the Bushveld Complex (Carney et al. 1994). Between 1980 and 1984, a technical cooperation project was established between the Government of Botswana and the British Geological Survey that resulted in the first comprehensive documentation of the Molopo Farms Complex including a geological map (Gould et al. 1987). An intensive prospecting program was carried out by Gold Field Botswana (Pty) Ltd to follow up on the mineralization reported by Gould et al. (1987). This project initially focused on three prospecting blocks; Bray, Keng and Tubane Blocks. Prospecting in the last two blocks terminated and concentrated in the Bray area (Reichhardt 1994; Fig. 1). Molopo Botswana Pty Ltd followed up on the Tubane section where up to 1g/t PGE was reported (Gould et al. 1987). In particular, their target was finding mineralization analogous to Volspruit type (northern Bushveld) within the ultramafic rocks of the Tubane section (McGeorge 1992). Two gap boreholes, TB3 and TB11, were drilled across strike to investigate for continuity of the mineralized horizon. This study provides the first detailed documentation on the occurrence of PGE from drill core TB11 (Fig. 1) focusing on the description of rock units and mineralogy of silicates, with the aim of establishing if they represent previously unrecognized mineralization style within the complex.

2 Geologic setting

The Molopo Farms Complex layered intrusion is situated towards the western margin of the Archaean Kaapvaal craton straddling the border into some parts of South Africa (Gould et al. 1987; Von Gruenewaldt et al. 1989; Fig. 1). The complex intrudes Proterozoic sandstones, siltstones, carbonates, andesitic lavas of the Transvaal Supergroup. The complex is unconformably overlain by the Red Bed sequence belonging to the Waterberg Group and the Tertiary to Recent Kalahari beds. Based on the composition of the marginal facies of the Molopo Farms Complex a cogenetic relationship to the Bushveld Complex is suggested (Kaavera et al. 2018). The ages of Molopo Farms Complex samples 2054 ± 5 Ma (207Pb/206Pb ID-TIMS baddeleyite) from a gabroic sample and 2056 ± 10 Ma (U-Pb zircon) from highly altered and metamorphosed quartzite in direct contact with the Molopo Farms Complex (Beukes et al. 2019) are indistinguishable from the ca. 2.05 Ga age of the Bushveld Complex (Scoates and Friedman 2008). With a thickness of approximately 3km, the Molopo Farms Complex layered intrusion is an elliptical, saucer shaped and elongated in a NE-SW direction, covering an area of about 13,000km² (Reichhardt 1994). The complex is composed of three main units; Lower Ultramafic Sequence, Layered Mafic Sequence and Minor Intrusive Suite (Gould et al. 1987). The former comprises cyclic differentiates of dunites, poikilitic harzburgite, granular harzburgite enveloped by feldspathic pyroxenite and
norite. The Layered Mafic Sequence comprises of feldspathic pyroxenites while the Minor Intrusive Suite consists of a number of basic to intermediate sills (Gould et al. 1987; Von Gruenewaldt et al. 1989; Reichhardt 1994; Prendergast 2012).

3 Analytical techniques

Mineralized samples are distinguished by the presence of visible base metal sulfides. These were sampled along with apparently barren samples from below and above them, and samples representing specific rock types. Samples were cut into representative sizes for thin and polished sections and one half was crushed into a tungsten bowl and milled for geochemical analysis. Geochemical compositions including major oxides and minor trace elements were analyzed at the Department of Earth Resources Engineering, Kyushu University by RIX3100 XRF using pressed pellets. Precision and accuracy were based on replicate analysis of the JA-3 standard supplied by the Geological Survey of Japan. Polished slabs were searched for PGM using the SU 3500 scanning electron microscope attached with EDX analyzer in Kyushu University and at the Geological Survey of Japan using Quanta 250FEG SEM and mineral liberation analyzer (MLA). Mineral chemical composition were determined using a JEOL JXA-8530F electron probe microanalyzer.

4 Results and discussion

4.1 Lithological and mineralogical relations

The occurrences of the different lithologies observed in borehole TB11 are shown in Fig 2. The dolomitic siltstone belonging to the Transvaal Supergroup underlies the magmatic stratigraphy (Fig. 2a). It is fine-grained and composed of poorly sorted quartz grains with embayed grain boundaries found within a carbonate matrix. Accessory pyrite is conspicuous throughout the unit. The next unit is a marginal norite that preserves a fine grained, altered chilled margin roughly a few centimeters in thickness, in contact with the dolomitic siltstone country rock (Fig. 2b). Above the marginal norite is the feldspathic pyroxenite that is host to the PGE mineralization (Fig. 2c). Two occurrences of the feldspathic pyroxenite unit were observed; the first one towards the boarder of the intrusion directly above the marginal norite and the second in the middle of the stratigraphy sandwiched by harzburgite units. The first pyroxenite is overlain by a harzburgite that contains enclaves of an orthopyroxenite within it (Fig. 2d). The petrography of the enclaves exhibit elongated orthopyroxene grains indicating internal chilling. This suggests that the harzburgite magma was in contact with earlier formed, partially crystallized orthopyroxenite cumulates that became disrupted and assimilated. This supports Walker et al. (2010) who hypothesized that the intrusion was emplaced as polyphase and discontinuous lopolithic sheet intrusions. The position of borehole TB11 is within the feeder zones of the Complex as postulated by Walker et al. (2010). Therefore, we suggest that the enclaves resulted from assimilation of earlier crystallized orthopyroxenite cumulates as new harzburgite magma was re-injected in the feeder zone. Above the second feldspathic pyroxenite is a poikilitic harzburgite with orthopyroxenite inliers (Fig. 2e).

4.2 Mineral chemistry

Chemical composition of minerals in selected samples including the enclaves, poikilitic harzburgite and the orthopyroxenite were determined. The chemical composition of the PGE bearing feldspathic pyroxenite is currently unavailable. The composition of orthopyroxenes, plagioclase and clinopyroxene from the enclaves are; Mg# = ((Mg/(Mg+Fe²⁺)) atomic) 0.87-0.88; En (enstatite component mole fraction) = 0.84-0.85; An
(anorthite component mole fraction) = 44-48; and clinopyroxene Mg# = 0.74-0.95 and En = 0.48-0.54. In the orthopyroxenite associated with the top most poikilitic harzburgite, orthopyroxene Mg# = 0.84-0.87; En = 0.82-0.85 (slightly more variable than the enclaves); An = 0.48-0.59; and clinopyroxene Mg# = 0.89-0.95 and En = 0.49-0.50. The olivine composition of this unit is marked by high forsterite Fo contents of 0.81-0.84 mol. % and variable NiO contents of 0.10-0.46 wt. % (Fig. 3). The variable NiO contents likely suggests equilibration of the magmas with sulfide melts during or prior to crystallization (e.g. Andersen et al. 2017).

The poikilitic harzburgite records the highest Mg# of orthopyroxene (0.90-0.92) and En = 0.89-0.91. The Mg# of this unit is the highest reported for the Molopo Farms Complex and is within the range of the orthopyroxene composition reported from the eastern Bushveld Complex (Wilson 2012). In the poikilitic harzburgite clinopyroxene Mg# = 0.9-0.97 and En = 0.5-0.52, with Fo of olivine = 0.87-0.88 and variable NiO contents in olivine of 0.27-0.48 wt. % (Fig. 3). The variable NiO in olivine suggest equilibration of the magmas with a sulfide melt.

### 4.3 PGE and sulfide mineralization

PGE mineralization is confined to a sulfide-bearing felspathic pyroxenite unit with up to 0.47 ppm 2PGE+Au, 0.3 wt. % Ni and up to 0.12 wt. % Cu. The sulfides are generally disseminated but the felspathic pyroxenite towards the boarder of the intrusion may carry larger centimeter-sized sulfide droplets.

![Figure 2. Lithologies of Molopo Farms Complex at Tubane section from borehole TB11. (a) Dolomitic siltstone constituting the country rock (b) Marginal norite containing fine grained chilled margin, (c) Felspathic pyroxenite containing centimeter sized sulfides droplets (d) Harzburgite with felspathic pyroxenite enclaves (e) Poikilitic harzburgite from the top most stratigraphic level, locally with orthopyroxenite inliers.](image)

![Figure 3. Variations in NiO content wt. % in Olivine and forsterite contents (mol. %) of olivine in the poikilitic harzburgite and orthopyroxenite, Molopo Farms Complex intrusion Compositional fields for Lower zone (LZ), Critical zone (CZ) and Upper zone (UZ) of Bushveld Complex included for comparison.](image)

The sulfides are associated with plagioclase and quartz interstitial to the cumulus subhedral and elongated orthopyroxene. PGM are rarely enclosed within sulfide minerals but mostly towards their grain margins and within altered silicates (Fig. 4). Platinum-bearing PGM are sperrylite (PtAs₂) and moncheite (PtTe₂) both found within altered silicates (Fig. 4a). Froodite (PdTe₂), michenerite (PdBiTe) are found within pyrrhotite, along the grain margin of sulfides or at the interface between pyrrhotite and pentlandite (Fig. 4b, c, e). In one example, moncheite is found within a pyrrhotite grain (Fig. 4d). Similar occurrences were described in the Grasvally Norite–Pyroxenite–Anorthosite (GNPA) and Platreef (e.g. Smith et al. 2011; Hutchinson and Kinnaird 2005). Although more prevalent in the bottom felspathic pyroxenite unit, the assemblages of the PGM are the same in both units suggesting a common origin.

### 5 Implications for Ni-Cu (PGE) mineralization

This study documents the typical orthomagmatic assemblage of sulfides associated with PGE mineralization. As discussed above the occurrence of enclaves of orthopyroxenite within the harzburgite suggest disturbance of previously crystallized cumulates as new magma was reinjected in the feeder zones. Although no mineral chemistry data were available from the PGE-bearing felspathic pyroxenite, compositional data from the poikilitic harzburgite and orthopyroxenite bear significant implications. The variable NiO contents from both units suggest that the magmas equilibrated with the sulfide melt prior to, or during crystallization, as explained in Andersen et al. (2017). The position of borehole TB11 is within the zone delineated as the feeder
zones to the Molopo Farms Complex (Walker et al. 2010; zone E in their Fig. 6). Therefore, it seems to be reasonable to suggest that the large centimeter sized fractionated sulfides droplets represent unfractionated sulfide liquid retained as droplets in the host feldspathic pyroxenite. Such droplets did not have time to reach the base of the chamber or feeder zone by gravitational settling. Such a model has previously been suggested for the disseminated ores of Aquablanca Ni-Cu-(PGE) deposit in Spain (Ortega et al. 2004; Pina et al. 2008) and for the Alexo komatite sulfide deposit, Canada (Barnes and Naldrett, in Pina et al. 2010).

Sulfide saturation might have occurred due to interaction of the magma with the pyrite bearing dolomitic siltstone resulting in segregation and gravitational settling of sulfide melt, perhaps in the feeder zones. The possibility of such mineralization in feeder zones of the Molopo Farms Complex is not new. Walker et al. (2010) recommended future exploration to focus on the feeder zones in search for the Voisey’s Bay, Noril’sk and Jinchuan style mineralization but represents an exciting exploration frontier.

Acknowledgements

Botswana Geoscience Institution is thanked for allowing access to the core shed facilities.

References


Magmatic Sulfide and Oxide Systems
Spatial variations trace elements in magmatic Ni deposit: evidence for immiscible Te-As-rich melt formation (Kambalda, Western Australia)

Sebastian Staude, Gregor Markl
Department of Geosciences, University of Tübingen, Germany

Marcus Oelze
GFZ, Inorganic and Isotope Geochemistry, Germany

Abstract. Fractional crystallisation of magmatic sulphide melts is responsible for a wide variety of economic sulphide deposits, comprising the largest Ni, Cu and platinum group element (PGE) enrichments on Earth; however, systematic studies over the whole orebody are rare, as many orebodies are too large to be completely accessible in a short time for sampling or their original geometry obscured by younger overprint. The Moran sulphide komatiite-hosted deposit (Kambalda, Western Australia) was systematically sampled for whole rock and mineral chemistry (pyrrhotite, pentlandite, and chalcopyrite) along, across, and vertically through the whole massive sulphide body to identify any variations in PGEs and accompanying elements.

Whole rock Ir, Os, Ru, and Rh show higher concentrations in samples from the margin of the deposit (which is typically a 5-25m, wide pinchout, where the sulphides are bound by older basalt from beneath and above due to lateral thermomechanical erosion by the sulphide melt), whereas Pt, Pd, Au, Cu, Te, and As are enriched in the centre. Modelled fractionation reproduces the observations indicating that the orebody crystallised from its margins towards the centre. Whole rock Co does not vary which is in line with published partition coefficients. The Co-content of pentlandite, however, strongly decreases from the margin to the centre together with a strong increase in Te+As. This can be explained by the formation of another Co-bearing phase, cobaltite, which is intergrown with PGE-bearing arsenides and tellurides. This indicates that an immiscible Te-As-PGE-rich melt formed from highly fractionated sulphide melt in the centre of the orebody prior to sulphide (MSS) crystallisation. Thus, systematic sampling of the whole orebody shows that (1) the sulphide melt pool crystallised from its margin to the centre and (2) fractionates during crystallisation to form an additional immiscible As-Te-rich melt in the centre.

1 Introduction

Magmatic Fe-Ni sulphide melts carry traces of Cu, Co, platinum group elements (PGE), as well as Te, As, Bi, and Sb (TABS) in varying amounts. Upon cooling and fractionation of the melt, Fe-rich mono-sulphide solid solution (MSS) crystallises first followed by Ni-rich high-pentlandite, leaving Cu, PGE and TABS in the melt (Kitakaze et al. 2016). Elements that remain in the sulphide melt form Cu-rich intermediate solid solution (ISS) with the TABS crystallising last (Liu and Brenan 2015). MSS and high-pentlandite recrystallise to pyrrhotite and pentlandite upon cooling, respectively, whereas ISS forms chalcopyrite. From natural samples (Sudbury, Noril’sk-Talnakh) of highly fractionated melts it is suggested that the TABS form the last solidifying melt (Dare et al. 2014, Duran et al. 2017).

Investigated samples from natural occurrences are from Cu- and PGE-rich and highly fractionated deposits and none have investigated a complete deposit from its margin to its centre. The Moran massive sulphide deposit (Kambalda, Western Australia) is a deposit with low Cu- and PGE-contents and was systematically sampled along, across, and vertically through the sulphides to investigate variations in main and trace element chemistry by whole rock analysis and electron microprobe and LA-ICP-MS analysis. The deposit is situated in an embayment of the footwall basalt and completely surrounded by a 5-25m wide pinchout, where the sulphides are bound by older basalt from beneath and above due to thermomechanical erosion (Staude et al. 2016).

2 Trace element variations of Moran (Kambalda) massive sulphides

All whole rock PGE data display some variations over the orebody and are in line with published partition coefficients (Barnes and Ripley 2016 and references therein). The same is visible with TABS elements, where Te (Figure 1) and As are most abundant compared to Bi and Sb. A strong increase of TABS is visible from the margin to the centre.

The whole rock Co content is constant over the entire orebody, which is in line with published partition coefficients around 1 (Barnes and Ripley 2016). Cobalt (and Te) is mostly hosted by pentlandite. Contrary to the whole rock data, Co in pentlandite exhibit some drastic variations over the orebody (Figure 2), and decreases from the margin to the centre. This decrease is concomitant to the Te increase (Figures 1, 2).

3 Discussion of the trace element variations.
Trace element data over the Moran orebody are in line with fractional crystallisation based on experiments (Kitakaze et al. 2016) and published partition coefficients between sulphide melt and ISS (Barnes and Ripley 2016). Thus, the data show that the orebody cooled and crystallised from the margin towards the centre.

The Te increase for example (Figure 1) can be explained by fractional crystallisation. From 80% to 90% crystallisation of the sulphide melt the Te concentration in the remaining melt doubles. Cobalt however, behaves differently from fractional crystallisation trends. The partition coefficient of Co is around 1, and therefore the whole rock Co content on the other hand does not decrease indicating that another Co-bearing phase forms. The only other Co-bearing mineral in the orebody is cobaltite (CoAsS), which occurs together with sperrylite (PtAs2) and various tellurides.

If cobaltite, which is usually intergrown with tellurides, form in the centre of the orebody prior to MSS and pentlandite formation, it could suggest that an immiscible (Te-and As-dominated) TABS melt formed from the highly fractionated sulphide melt. Once the TABS melt...
formed at >90% crystallisation, Co partitions into the TABS melt and is therefore not available for high-pentlandite. The idea of an immiscible TABS melt is supported by the textures. Sperrylite crystallised first, followed by cobaltite and lastly the tellurides. This was also observed in experiments (Helmy et al. 2007).

4 Summary

The whole rock data reflect fractional crystallisation of the sulphide melt pool. Due to the geometry of the sulphide melt pool (i.e., colder basalt beneath and above in the pinchout (Figures 1 and 2)), it will crystallise from the pinchout (margin) towards the centre. Thus, early crystallised MSS is found in the pinchout, the most fractionated sulphides in the centre.

A strong decrease in pentlandite-hosted Co (at constant whole rock Co) together with a strong increase in Te and As suggests that another Co-bearing phase formed (cobaltite) prior to MSS or high-pentlandite crystallisation. The formation of immiscible Te- and As-rich melt from a highly fractionated sulphide melt can explain the observed variations in Co.

Acknowledgements

We are grateful to Independence Group for samples, partially funding the whole rock analysis, and for the allowance to publish. The research was funded by the German Research Foundation (grant number: 407352165) to S. Staude.

References


Liu Y, Brenan B (2015) Partitioning of platinum-group elements (PGE) and chalcogens (Se, Te, As, Sb, Bi) between monosulphide-solid solution (MSS), intermediate solid solution (ISS) and sulphide liquid at controlled fO2-fS2 conditions. Geochim Cosmochim Acta 159:139-161.

Platinum mineralization in Ural-Alaskan complexes of Koryak Highlands (far east Russia)

Anton V. Kutyrev and Eugene G. Sidorov
Institute of Volcanology and Seismology, Petropavlovsk-Kamchatsky, Russia

Abstract. Ural-Alaskan type complexes are the source of unique platinum placers. The Galmoenan complex and related placers were the subjects of numerous studies, however, many other complexes remain under investigated. Four massifs investigated in this work (Epilchik, Matysken, Itchayvayamsky, and Prizhimny) host three different assemblages or mineralization styles. The isoferroplatinum assemblage, which originates from the chromitite lodes in dunites, is the most abundant and may be found in every placer. Native platinum assemblages primarily occur in mineralized zones in clinopyroxenites. This type plays a significant role at Itchayvayamsky and Prizhimny and occurs as a minor component at the Epilchik. A third assemblage formed by Au, Hg, Pd, and Pt minerals is associated with bornite-chalcopyrite mineralized zones in gabbro units of the Itchayvayamsky massif and its satellites. Platinum mineralization may be divided into several stages. At the first stage formed isoferroplatinum, native osmium, and laurite. The second stage is related to the first part of the hydrothermal history of complexes and is represented by isoferroplatinum intergrown with pentlandite and pyrrhotite. The latest stages formed Pt-Fe alloys, including rare compounds such as Fe$_3$Pt and a wide range of sulfides, arsenides and other minerals.

1 Introduction

Ural-Alaskan complexes were the ultimate source for platinum first used by humans. Native Americans at the Pre-Columbian era knew the metal processing technologies for platinum (Scott & Bray 1980), and the most probable source of the first platinum taken to Europe from South America were the placers related to Ural-Alaskan complexes in Colombia (Tisti et al. 1994) and Venezuela (Murray 1972). In Russia, platinum mining started at the beginning of the 19th century in the Ural Mountains (Stepanov et al. 2017). 150 years later, a group of geologists suggested that ultramafics of Koryak Highlands in Kamchatka, which were previously linked to an ophiolite association, better match the Ural-Alaskan type (Kutyev et al. 1991). This brilliant insight led to the discovery of Galmoenan placers, which produced more than 60 metric tones (19.93 Moz) of platinum during 1994-2012. However, among Galmoenan, in the Koryak-Kamchatka region, there are still tens of complexes which are the potential source for yet undiscovered placers. In this work, we present new data on the mineralization in Ural-Alaskan complexes of the northernmost, and the most hard-to-achieve part of the Koryak Highlands.

2 Geological setting and structure of Ural-Alaskan complexes

2.1 Geological background

Koryak-Kamchatka platinum belt is parallel to the border between the Kamchatka Peninsula and the Pacific Ocean and stretches over about 1300 km (Fig. 1). The host rock for the complexes are the late-Cretaceous formations, which, generally consist of basalts, volcanic-sedimentary rocks, and jaspers.

Figure 1. Location of Koryak-Kamchatka Platinum Belt. (1) – land area, (2) – Cretaceous volcanic and sedimentary formations of Achayvayam-Valaginskaya zone which holds Ural-Alaskan complexes. After Batanova et al. 2005.

2.2 Geological structure of complexes

Classical Ural-Alaskan complexes display the following features: (a) they occur at the ocean-continent margin and are usually parallel to the ophiolite belts, (b) – they display a zonal structure with ultramafic rocks (mainly dunites) in the central part of the massifs, (c) – rocks containing orthopyroxene are absent or almost absent (Talylor 1967; Batanova et al. 2005), (d) – most PGMs in dunites occur in a form of Pt-Fe alloys intergrowths with chromian spinel and sulfides are minor or almost absent (Malitch and Thallhammer 2002; Palamarchuk et al. 2017).

All these features are inherent to studied complexes.
Matysken and Epilchik massifs are of the zonal structure with dunite core grading to the wehrlite-clinopyroxenite rim. At the same time, Itchayvayamsky complex is of clinopyroxenite-gabro composition with narrow zones of dunite at the central part. Prizhimny massif is also composed of clinopyroxenite and gabbo, however, dunites are absent at the present day surface (Kutyrev et al. 2018). In combination with the present geophysical data, the differences in the complexes structure are considered to result from their different erosion levels.

3 Platinum mineralization

3.1 Morphology of nuggets

Platinum-group minerals (PGM) were studied in 2 lode and 5 placer deposits. In lode deposits, PGMs were found in podiform chromitites which occur at the central dunite part of the complexes, and much more seldom in wehrlite units. The most abundant mineral is isoferroplatinum PtFe which forms intergrowths with chromite (Fig. 2).

![BSE images of the isoferroplatinum grains gravitationally extracted from crushed chromitites of the Matysken Ural-Alaskan complex.](image)

Placer platinum usually occurs as grains which vary in size vary from 0.1 to 1.5 mm. As it was mentioned for lodes, the main mineral phase is isoferroplatinum or native platinum. The latter dominates in placers, related to the Itchayvayamsky and Prizhimny massifs. The second most abundant mineral is native osmium, which occurs as inclusions in Pt-Fe minerals and only seldom forms individual nuggets.

3.2 Three major PGM assemblages

The composition of the most abundant group platinum minerals – Pt-Fe alloys – is sensitive to the geological structure of source complex as it was shown on the base of Galmoenan complex (Tolstykh et al. 2004). Deeply eroded Matysken and Epilchik complexes are the sources for isoferroplatinum close to stoichiometry or with a slight PGE deficit, while the low-eroded Itchayvayamsky and Prizhimny produced a large amount of native platinum (Tab. 1, Fig. 3). Another difference is the abundance of secondary alloys, mainly – tetraferroplatinum (PtFe) and tulameenite in the deeply-eroded, at the same time, the total lack of these minerals in the low-eroded complexes (Tab. 1, Fig. 3). These data allow discriminating two mineral assemblages: isoferroplatinum and native platinum.

**Table 1. Abundances of major PGM and some other minerals in the studied complexes (1 – Matysken, 2 – Elichik, 3 – Itchayvayamsky, 4 – Prizhimny). “*” – mineral is absent, “*+” – mineral was met once or twice, “+++” – mineral is usual for this object, “+++” – mineral is abundant or dominates in the studied assemblage. Base metal sulfides are mentioned only if they form intergrowths with PGM or have platinum group elements in their composition. Data Prizhimny and Itchayvayamsky complexes taken from (Kutyrev et al. 2018, Sidorov et al. 2019).**

<table>
<thead>
<tr>
<th>Mineral/object</th>
<th>Lodes</th>
<th>Matysken River</th>
<th>Lodes</th>
<th>Steggyavam River</th>
<th>Itchayvayam River</th>
<th>Kamianyaya River</th>
<th>Prizhimny Creek</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoferroplatinum PtFe</td>
<td>+++</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Native platinum Pt</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Native osmium Os</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Native iridium Ir</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Tetraferroplatinum PtFe</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Tulameenite PtFeCu</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Nickelferroplatinum PtFeNi</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>FePt</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>CuPt</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ni3FePt</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Native iron Fe</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Au-Hg-Pd</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Cooperite PtS</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Vysotskite (Pt,Pd)S</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Laurite RuS2</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Erlichmanite OsS2</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Rh sulfides</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Cuprideidite CuIr2S4</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Cuprorhodsite CuRhS4</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Malanite CuPtS4</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Sperrilite PtAs2</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Irasite IrAsS</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Hollingwhortite RhAsS</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Platarsite PtAsS</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Osarsite OsAsS</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>(Fe,Rh)As</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Keithcommite Pd30Te7</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>PtTe2</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>(Ir,Br)(Te,Sb)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ir oxide</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Awaruite Ni3Fe</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Pentlandite (Fe,Ni)S8</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Pyrrhotite Fe7S8</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Bornite CuFeS4</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Another feature which correlates with geological structure of the complexes is related to the abundance of Pd-rich minerals. Some of these minerals form inclusions in platinum of the Prizhimny Creek placer, however, their most intriguing occurrence in placers is related to the Itchayvayamsky massif, where they form an unnamed Au-Hg-Pd alloy which is intergrown with vysotskite.
cooperite, malanite, and native gold (Tab. 1). The source of this association is the bornite-chalcopyrite mineralized zones at the gabbro units of the Itchayvayamsky massif and its satellites (Sidorov et al. 2019).

Figure 3. Composition of Pt-Fe alloys: (1) lodes of the Matysken massif and related placers, (2) – lodes of the Epilchik massif and related placers, (3) – placers related to the Itchayvayamsky massif, (4) – Prizhimny Creek placer.

The best polygon for understanding the role of these assemblages is the Itchayvayamsky complex. It is surrounded by two major rivers: Itchayvayam and Kamenistaya, each of which bears different platinum group minerals. In Itchayvayam river, one may find all of three mentioned assemblages, while Kamenistaya river holds only isoferroplatinum assemblage (Sidorov et al. 2019). This can be explained by the higher maturity of the Itchayvayam River which eroded many larger quantities of clinopyroxenite and wehrlite which probably bear low-grade native-platinum mineralization, as it was shown for Galmoenan massif (Mochalov & Bortnikov 2008).

3.3 Stages of the mineralization

Study of the platiniferous chromitites together with placer platinum allows to reveal the following mineralization stages which are characterized by the following sequence of mineral formation:

**Stage 1** Native osmium – native iridium – laurite RuS2/erlichmanite OsS2 – isoferroplatinum/native platinum – chromite. The main phase is isoferroplatinum which cements the chromite crystals. However, they both are not euhedral what can be interpreted as a result of their co-crystallization (Fig. 4a).

The first stage is typical for both isoferroplatinum and native platinum assemblage. The second stage was tracked down only in platiniferous dunites. It consists of the second generation of isoferroplatinum and sulfides, which require low sulfur fugacity and/or high temperature:

**Stage 2** Isoferroplatinum – pentlandite – pyrrhotite (Fig. 4b).

The third stage should be divided into two types. The first one relates to the latter serpentinization. It is represented by secondary PGE and base metal alloys and belongs to the isoferroplatinum assemblage:

**Stage 3a** Tetraferroplatinum PtFe / tulameenite PtFeCu / nickelferroplatinum PtFeNi – unnamed compounds Fe3Pt, Cu3Pt, native iron, awaruite (Ni3Fe) – hexaferrum (Fe,Os) – unnamed Fe-Rh-Ir and Os-Pt-Ir-Fe compounds (Fig. 4c, d).

These minerals usually form rims after the minerals of stages 1 and 2. This stage is interesting because it shows the mobility of refractory platinum group elements such as Os and Ir during the late hydrothermal processes.

The second type belongs to the native platinum assemblage and its origin remains unclear, because of the poor data on such mineralization in lodes. It is represented by two main sulfides which take place of all minerals mentioned at the stage 3a:

**Stage 3b** Cooperite PtS – malanite CuPt$_2$S$_4$.

The last stage is collective for a wide group of secondary minerals, including sulfides, tellurides, arsenides, mercurides etc.

**Stage 4** Sperrylite PrAs$_2$ – irarsite IrAs$_2$ – osarsite OsAs$_2$ – holingworthite RhAs$_2$ – As-bearing erlichmanite Os(S,As)$_2$ – cuprorhodsite CuRhsS$_4$ – keithconnite Pd$_5$Te$_{20}$ – etc.

This stage may have different sources of energy which are the objects of further discussions. Some of these minerals may have formed during the latest stages of the serpentinization, another – as a result of interaction with later intrusions which may not be present on the contemporary daylight surface.
4 Concluding remarks

Ural-Alaskan complexes should be observed as a multi-tiered system with different mineralization style inherent to every tier. Comparison with other, better-studied Ural-Alaskan complexes, like Galmoenan (Tolstykh et al. 2002) or the complexes of Ural-Mountains (Palamarchuk et al. 2017) show that the isoferroplatinum assemblage probably is the only one among those mentioned which may form economic deposits. However, the native-platinum assemblage, which is hard-to-detect in lodes due to the poor platinum grade of this type, may form an additional impact in the resources of gold placers nearby to the Ural-Alaskan massifs.

The differences in the stages of mineralization between shallow and deeply eroded massifs show that in the first case postmagmatic redistribution of PGE occurred under reducing conditions (illustrated by the presence of such minerals as tetraferroplatinum, Fe₃Pt Pt-bearing native iron etc.) while in the second case it occurred at high sulfur fugacity which led to a massive formation of cooperite and malanite. Several models may be used to explain this difference. First one is that the high sulfur fugacity conditions occurred due to the influence of hydrothermal system related to the latter felsic intrusions. This is supported by high distribution of sulfidization at the host rocks of Prizhimny massif. The second model proposes that the high sulfur fugacity is a typical feature of postmagmatic processes of the Ural-Alaskan complexes upper tiers. In our view, this idea is close to the truth, because the predominance of sulfides in later PGM association is a key feature of several complexes, which among ones described in this work include Pustaya river placer at Kamchatka (Tolstykh et al. 2000).

Acknowledgments

We are grateful for all geologists who took part in the field works of the 2016-2017 year, especially – to Daria Bukhanova, Alexander Sorokin and Roman Novakov. We are also thankful to the CEO of KAMP ltd. Dmitry Korobov. This work was financially supported by RFBR project no. 18-35-00126.

References

Sidorov EG, Kutyrev AZh, Zhitova ES, Chubarov VM, Khanin DE Origin of platinum group mineral assemblages from placers in rivers draining from the Ural-Alaskan type Itchayvayamsky ultramafics, Far East Russia. Can Min 57, 1-14
Stepanov SY, Malitch KN, Kozlov AV, Badanina IY & Antonov AV (2017) Platinum group element mineralization of the Svetly Bor and Veresovy Bor clinopyroxenite–dunite massifs, Middle Urals, Russia. Geology of Ore Deposits 59(3):244–255
Abstract. The Nova – Bollinger Ni-Cu – sulfide ore deposits, in Western Australia, are the most significant Ni – sulfide discovery in Australia over the past decade. The host rocks are mafic- ultramafic cumulates subdivided into two intrusions: Upper and Lower. The Upper Intrusion is bowl-shaped and modally layered with alternating peridotite and norite mesocumulate layers; the Lower is a much thinner semi-conformable chonolith comprising unlayered mafic to ultramafic orthocumulates. A distinctive rock-type containing both orthopyroxene and olivine as cumulus phases is a characteristic of the Lower Intrusion. The intrusions differ in olivine and spinel chemistry, and in the volume of sulfides. Sector zoning in Cr content of pyroxenes is observed in the Lower Intrusion, and in the lower marginal zone of the Upper, and is attributed to crystallisation under supercooled conditions. Symplectite orthopyroxene-spinel-amphibole coronas at olivine-plagioclase contacts are attributed to near-solidus peritectic reaction between olivine, plagioclase and liquid during high pressure emplacement (>6 Kb), consistent with high Al contents in igneous pyroxenes. These rocks represent cumulates from a similar parental magma, derived via multiple magma pulses, variably fractionated and undergoing sulfide saturation prior to emplacement into the deep crust at pressures of 6-10 Kb during the peak of regional metamorphism.

1 Introduction

The Nova – Bollinger Ni – sulfide ore deposits are hosted in a suite of cumulate mafic and ultramafic intrusive rocks of the Mesoproterozoic Fraser Zone, located about 160km east-northeast of Norseman, Western Australia. The Fraser Zone is the innermost of the three geographical, structural and fault-bound zones produced during ca. 1345–1260 Ma Albany – Fraser Orogen representing reworking of Archean Yilgarn Craton with contemporaneous magmatism (Spaggiari et al. 2009, Smithies et al. 2013, Maier et al. 2016). The Nova – Bollinger intrusive suite occurs within a prominent fold interference feature called an “eye” structure (Parker et al. 2017). The regional metamorphic grade is granulite, with peak conditions up to 850C at 7-9 Kb (Clark et al. 2014).

The mineralization is dominantly hosted by the lower of a pair of stacked intrusions: an Upper Intrusion, a thick, layered ultramafic-mafic body with a dominantly mafic lower zone, and the Lower Intrusion, a thin and predominately mafic/ultramafic chonolith hosting the bulk of the mineralization (Fig. 1) in the form of the Nova and Bollinger orebodies. These are two distinct ore deposits with a combined resource estimate of 13.1Mt at about 2% Ni, 0.8% Cu and 0.1% Co (Independence Group, 2019).

This contribution addresses the geochemistry, internal structure, mineralogy and petrogenesis of the two intrusions, and accompanies Barnes et al. (this volume) on the nature of the sulfide mineralisation.
vary in thickness from about 20cm to 100m, show complicated interdigitation with mafic layers (Fig. 1) and comprise predominantly poikilitic textured heteradcumulate lherzolites. These rocks are primarily composed of medium to coarse-grained olivines with occasional fine-grained olivine clumps, chromian Mg-Fe-Al spinel inclusions in olivines, and both orthopyroxene and clinoxyroxene oikocrysts zoned from Cr-rich cores to Cr-poor rims.

A lower heterogeneous marginal zone up to 100m thick contains predominantly orthocumulate norite, olivine orthopyroxenite and feldspathic lherzolite, and hosts the disseminated CS sulfide resource. Orthopyroxenites have resorbed olivine inclusions in coarse interlocking orthopyroxene oikocrysts comprising ~90% of the rock. Varic-texured rocks (with heterogeneous grain size on a cm scale) are present in this zone. Unevenly distributed patches of various sized clusters of pyroxene, spinel, plagioclase and carbonate are evident in this unit but not elsewhere in the Upper Intrusion.

### 2.2 Lower Intrusion

The lower Intrusion has a maximum thickness of about 100m thick, 300-500m wide and at least 1500m long, significantly thinner than the Upper Intrusion, having a characteristic flattened tube (chonolith) morphology with broadly lenticular cross section. Lithologies are predominantly orthocumulates, ranging from a broadly lenticular cross section. Lithologies are predominantly orthocumulates, ranging from a felDSPathic lherzolite to poikilitic melagabbro, with generally coarse to medium-grained pyroxene and fine-grained olivine clumps. A distinctive lithology in the Lower Intrusion is a poikilitic olivine-orthopyroxene orthocumulate with intercumulus plagioclase, poikilitic clinopyroxene, locally branching olivine grains and pronounced sector zoning of Cr in the pyroxenes. Orthopyroxene – spinel – hornblende symplectites are extensively developed at olivine-plagioclase contacts as reaction coronas. Less abundant lithologies include olivine clinopyroxenites with globular disseminated sulfides, and mixed lithologies with irregular clumps of orthopyroxenite within melagabbro. The Lower Intrusion is host to disseminated and net-textured sulfide mineralization of variable thickness. Massive sulfide lenses and veins are extensively developed below this intrusion forming the bulk of the Nova and Bollinger orebodies (Barnes et al. this volume).

### 3 Petrology and Geochemistry

#### 3.1 Whole-rock geochemistry

Geochemistry of all the intrusive lithologies in the system is consistent with cumulates with variable trapped liquid content forming from related but variably evolved magmas. Two dominant mineral accumulation trends have been observed: one corresponding to the predominant accumulation of olivine in both the Upper and Lower Intrusions and the other for the accumulation of orthopyroxene + plagioclase with or without olivine for the Lower Intrusion and for the lower marginal zone of the Upper Intrusion. A proportion (>50%) of rocks in both Upper and Lower Intrusions have MgO contents greater than 20% and fall on olivine control lines (Fig. 2), representing mixtures of cumulus olivine and parental liquid. Trends of MgO vs FeO for these rocks can be used to estimate the MgO and FeO contents of the liquid end member, by extrapolating through the data from the average olivine end member to the liquid having Mg/Fe ratio in equilibrium with that olivine. The Upper Intrusion trend indicates an average cumulus olivine of Fo85 ± 1 and a parent liquid of 8 ± 1% MgO, while the Lower Intrusion trend indicates Fo83 ± 1 and 7 ± 1% MgO.

Higher abundances of trace elements in the Lower Intrusion are consistent with greater amounts of trapped intercumulus liquid, but the relative proportions of mildly to strongly incompatible elements (REE, Nb, Th, Zr, Ti) vary very little between the Lower and Upper Intrusions, or within either intrusion.

Trends of V vs Ti are distinct between the two intrusions; a vanadiferous chromian Mg-Al spinel appears to have been a cumulus phase in the Lower Intrusion, consistent with the inferred high pressure of emplacement. This conclusion from geochemical trends is borne out by the presence of spinel as chadacrysts within orthopyroxene oikocrysts and inclusions in olivines in Lower Intrusion cumulates.

#### 3.2 Mineral zoning and symplectites

Sector, reverse and oscillatory zoning in Cr content has been identified in the cumulus and poikilitic pyroxenes from the Lower Intrusion and the lower marginal zone of the Upper Intrusion (Fig. 2). These types of patterns, especially the presence of different types in close proximity, is a hallmark of several other ore-bearing small intrusions worldwide including Ntaka Hill (Tanzania), Huangshanxi (CAOB, Northwestern China), Aguablanca (Spain) and Eagle (USA Mid-continent) (e.g. Barnes et al 2016; Mao et al 2019). Sector zoning is significant as an indicator of crystallisation under supercooled conditions.

Symplectites are intergrowth of two or more minerals
on a microscopic scale. This texture typically forms via
the reactive breakdown of assemblages of two or more
phases during changes in pressure and/or temperature.
Though symplectites can form as a consequence of
metamorphism, they can also form in igneous rocks via
magmatic olivine-plagioclase reaction at high pressure,
or by oxidation-reaction with Fe-rich residual melts at low
pressure (e.g. Holness et al, 2011). Complex
assemblages of symplectite textures have been observed
at Nova-Bollinger suite, in all lithologies, including silicate
– silicate, silicate – sulfide, and rarely silicate – oxide
mineral intergrowths. Green spinel – orthopyroxene –
hornblende (Fig. 3A, B), developed as coronas at original
olivine-plagioclase contacts or olivine – sulfide (pyrrhotite
or chalcopyrite most common) (Fig. 3C, D) are the typical
assemblages at Nova.

Figure 3. Symplectite textures in the Nova-Bollinger intrusions: A. Meta-norite/gabbro-norite with remnant Opx and a few large fresh Ol
grains; abundant symplectites, spindle twinning, bent exsolution
patterns in pyroxene, annealed grain boundaries, and fresh Ol with
Opx coronas. B. Opx - green spinel –hornblende symplectites on a
microscopic scale in the same sample. C. Lherzolite with
disseminated sulfides: Fresh Ol/Px pyroxene coronas around Ol and
sulfides; D. Lherzolite with disseminated sulfides (same as C.):
Primary, undifferentiated sulfide assemblage (Po-Pn-Ccp + Mag),
Ccp-rich veinlets/patches vs. Po-Pn (spinel + Mag) domains;
veinlets of sulfides (Ccp and Pn) forming symplectites. Ol – olivine,
Opx – orthopyroxene, Plag – plagioclase, Sulf – sulfide, Pn –
pentlandite, Po – pyrrhotite, Ccp – chalcopyrite, Sp – spinel, Symp -
symplectite.

3.3 Mineral chemistry

Olivine Fo content ranges from 84 to 78 with Ni content
for the highest Fo of 1800ppm for the Upper Intrusion,
and from 82 to 67 with Ni content of 1400ppm for the
Lower Intrusion. These compositions are slightly more
magnesian than the average cumulus olivine
compositions estimated above from whole-rock FeO-
MgO trends; this is due to reaction of cumulus olivine with
trapped intercumulus liquid. The Upper Intrusion shows a
normal Ni-depletion trend (i.e. positively correlated Ni and
Fo) whereas the Lower Intrusion shows evidence for
sulfide equilibration with olivine during trapped liquid
crystallisation, giving rise to a weak negative Fo-Ni
correlation. Vanadium in olivine is very low, indicating
redox conditions around the QFM buffer or above.

Orthopyroxenes have high Al2O3 contents, typically
2.5-3.5% in plagioclase-poor rocks and ranging as high
as 5%, indicative of crystallisation at pressures of at least
5 Kb based on experimental data (see review by
Cawthorn, 2017).

4 Discussion

The Upper Intrusion itself is interpreted as the result of
multiple pulses of variably fractionated magma of
common parentage, to account for the alternation of
peridotite and norite mesocumulate layers with similar
incompatible trace element ratios. The Lower Intrusion
appears to be a distinct unit, much thinner and lacking
distinct internal variations, though with more extensive
accumulation of orthopyroxene together with olivine. The
lower marginal zone of the Upper Intrusion overlaps with
the Lower Intrusion in several aspects of its whole rock
and mineral chemistry. Abundant sector zoning in the
pyroxenes in the Lower Intrusion is indicative of growth of
these pyroxenes under mildly supercooled conditions.
Addition of silica during assimilation of country rocks is a
likely explanation for the abundance of cumulus
orthopyroxene.

The cumulate rocks of both intrusions preserve
primary igneous cumulus textures with only minor
evidence of post-solidification deformation.

Parent magmas to the intrusions were typical tholeiitic
basalts in composition, with ~6-8% MgO, having major
and trace element characteristics similar to typical island
arc and back-arc basalts. Trace element patterns
between Lower and the Upper Intrusion are essentially identical and do not provide unequivocal evidence of crustal contamination.

The origin of the symplectite coronas developed between olivine and plagioclase is a significant question given that they are found in a granulite facies metamorphic terrane. Either they were related to late stage mineral reactions during final solidification of trapped liquid at high pressure, where olivine and plagioclase are not stable together, or to metamorphism of initially low-pressure cumulus assemblages. However, the presence of cumulus low-Cr Mg-Al spinel coupled with high-Al pyroxenes strongly indicates high pressure crystallization, consistent with the independent evidence (Barnes et al. this volume) that sulfides were forming an infiltration-melting front into the underlying gneisses, implying emplacement into granulite facies country rocks already close to the onset of partial melting. The symplectites therefore probably record near-solidus late magmatic reaction, a consequence of the expanded stability field of low-Cr spinel at high pressures.

Olivine chemistry data is consistent with multiple magma pulses, variably fractionated and experiencing sulfide saturation at different stages of their evolution history with a significant postcumulus sulfide liquid equilibration trend evident for the Lower Intrusion.

The Nova – Bollinger mafic-ultramafic suite was formed from multiple pulses of magmas derived by varying degrees of fractionation of a common parental magma. The intrusions were emplaced into the deep crust contemporaneously with the regional metamorphic peak.

Acknowledgements

We thank IGO NL for financial support, access to drill core and underground workings and permission to present data, and IGO geologists and staff for helping organize Nova mine site visits and assistance in various phases of the project. The image in Fig. 2 was collected on the XFM Beamline of the Australian Synchrotron, Clayton, Victoria, operated by ANSTO.

References


Barnes SJ, Taranovic V, Miller JM, Beresford SW (2019) Sulfide-silicate textures and emplacement mechanisms of the Nova-Bollinger ores, Fraser Province, Western Australia SGA. SGA, Glasgow


Spaggiari CV, et al. (2009) Interpreted bedrock geology of the south Yilgarn and central Albany–Fraser Orogen, Western Australia, Geological Survey of Western Australia, Record 2009/10:p. 84.
Sulfide-silicate textures and emplacement mechanisms of the Nova-Bollinger Ni-Cu ores, Fraser Zone, Australia

Steve Barnes, Valentina Taranovic, John Miller* CSIRO Mineral Resources, Perth, Australia. *present address UWA-CET, Perth

Steve Beresford, Steve Rennick
Independence Group NL, Perth, Australia

Abstract. The Nova-Bollinger Ni-Cu ores show a remarkable assemblage of textures indicative of emplacement into hot, soft country rocks at a large-scale melting-infiltration front. This produced features ranging from hard-walled extensional vein arrays to complex infiltrations of disseminated sulfide within chaotically folded paragneiss. Sulfide infiltration was accompanied by partial melting of the country rock producing felsic melts of the paragneiss. Coarse grained pentlandite – chalcopyrite – pyrrhotite “loop textures” are characteristic of all ore types, down to the scale of the infiltrating sulfides within the gneisses, and are regarded to be diagnostically magmatic textures generated by sulfide liquid fractionation and growth of high-T pentlandite by peritectic reaction between fractionated sulfide melt and early crystallised MSS. The highly distinctive features of the Nova-Bollinger ores are a consequence of emplacement in the mid to lower crust under peak granulite facies conditions at extremely low cooling rates. Under these unusual conditions the timescales for deformation matched those for cooling and solidification, allowing the country rocks to undergo deformation during ore emplacement.

1 Introduction

Sulfide-silicate textures in magmatic ore deposits can contain a wealth of information about ore genesis, but in many cases are overprinted by tectonic deformation. The Proterozoic (~1300 Ma) ores of the Nova-Bollinger deposit (Parker et al. 2017) display a spectacular array of textures which can almost entirely be attributed to magmatic processes. However, the strongly deformed nature and lower granulite metamorphic grade (Clark et al. 2014) of the country rocks, coupled with the presence of a large proportion of the sulfide-rich ores within the country rock immediately adjacent to the host intrusions, give the immediate impression that the ores have been subjected to tectonic remobilization. In this contribution, we critically assess the extent to which this is supported by field observations. We make extensive use of decimetre-scale microbeam XRF mapping of a range of ore types, in the light of recent findings by Barnes et al. (2017a,b; 2018a,b) on the tendency of magmatic sulfides to develop melting-infiltration fronts at interfaces with less-refractory country rocks, and to migrate through partially solidified crystal mushes.

2 Geological setting of the Nova-Bollinger Orebodies

The Nova-Bollinger ores are associated with a small chonolith-style intrusion developed immediately beneath a much larger subhorizontal layered intrusion, described in the accompanying abstract (Taranovic et al. 2019). They are emplaced into a tightly folded sequence of granulite facies gneisses, comprising a mixture of intermediate to felsic garnetiferous meta-sediments and mafic granulite gneisses with minor marble layers. Ni-Cu sulfide ores are found in a wide variety of textural types, both within the host intrusion, and within country rocks to a distance of approximately ~20 m from the basal contact. The intrusion hosted ores are dominated by net-textured (matrix) ores with subordinate globular disseminated ores (Barnes et al. 2017b), the latter mainly found in Bollinger, as discordant massive sulfide veins and (uncommonly) as massive segregations along the basal contact. Exo-contact ores are found as a spectacular variety of sulfide-matrix ore breccias, as heavily disseminated sulfide within the country rock foliation, and as close-spaced vein arrays, with mutual gradation between all these types.

3 Sulfide-rich ores at Nova

Detailed studies on Nova ores were mainly focused on the “panhandle” area in the upper (western) portion of the orebody (Taranovic et al. 2019, this volume). Sulfide-rich mineralisation extends to distances of at least 50 metres from the host intrusion, as well as within the intrusion itself. The bulk of the ore falls on a spectrum between two completely gradational types: sulfides within mainly sharp-walled extensional vein arrays within the footwall gneisses, containing abundant inclusions of the immediate wall rock as well as rare inclusions of host intrusion; and “infiltrating sulfides” that range from soft-walled irregular veins within paragneiss to heavy disseminations of sulfide permeating at grain-scale within the gneisses that form the vein walls (Fig. 1). In many cases sulfides selectively infiltrate particular layers. The gneisses within the infiltrating sulfide zone typically show chaotic rootless folds and appear to have been folded during emplacement of the sulfides. The sulfide-rich veins within the infiltrating sulfide zones commonly contain...
bodies of coarse felsic material interpreted as leucosomes formed by partial melting of the immediately adjacent gneisses. These felsic bodies typically occupy the margins of the sulfide veins and have mineralogy varying widely from coarse grained tonalite with minor garnet to almost pure garnetites with interstitial quartz.

The sulfides themselves show spectacular coarse-grained “loop textures” (Fig. 2) where both pentlandite and chalcopyrite form semi-continuous rims to large (~1 cm) single pyrrhotite grains, interpreted as original monosulfide solid solution (MSS). Such textures have hitherto been regarded as the result of MSS exsolution, but this interpretation cannot explain the close association of pentlandite and chalcopyrite in the “loops” or the characteristic (relatively) high Pd content of the pentlandite. Recent work (Mansur et al. 2019) has solved this problem by interpreting coarse grain-boundary (as opposed to flame exsolution) pentlandite as the result of peritectic reaction between residual sulfide liquid and early-formed solid MSS. On this interpretation, loop texture is diagnostically magmatic. The widespread presence of loop textures in the Nova-Bollinger ores, in almost all settings from massive sulfide pools, veins, tension gashes and permeations into gneiss (e.g. Fig. 1) is therefore further strong evidence for high-P, high-T emplacement into granulite country at or just post the main metamorphism and deformation. Conditions were such that the country rock was able to fail either by folding or by semi-brittle fracturing depending on local lithology and strain rate.

4 Globular and matrix ores at Bollinger

The Bollinger orebody contains a similar assemblage of disseminated, matrix, infiltrating massive and vein-hosted massive ore to Nova, but differs in that infiltrating sulfide is less abundant (probably due to the more mafic and hence more refractory nature of the immediate footwall) and matrix ores show characteristically layered leopard-textures defined by cm-scale sulfide-poor olivine clinopyroxene clusters within typical olivine-sulfide matrix ore (Fig. 3). The clinopyroxene typically forms single or clustered oikocrysts with a shape-preferred orientation imparting a planar magmatic fabric to the rock (Fig 3a). This is a variant of poikilitic leopard-textured ore (Barnes et al. 2017b) formed by percolation of sulfide liquid through a partially consolidated orthocumulate with early-formed oikocrysts. Some of these clinopyroxene clusters or clots have autolithic or xenolithic cores.

Globular ores also define a weak magmatic fabric, and in some cases (Fig. 3b) consist of loop-textured sulfide globules rimmed by clots of Cr-poor clinopyroxene, intermixed at cm scale with patches of fine-grained olivine-sulfide matrix ore.

5 Interpretation and Conclusions

Mesoscopic and outcrop-scale features of the massive and semi-massive ores at Nova indicate emplacement in an extensive infiltration-melting front, under conditions where the country rocks were at or above their solidus temperatures within the thermal aureole of the intrusions.

Figure 1. Phase map based on Tornado x-ray element map of cut slab showing permeation of sulfide into disaggregating garnet granulite, typical of sulfide infiltration zone in Nova orebody.

Infiltration of sulfide served to carry heat effectively into the country rock gneisses, facilitating melting and infiltration of sulfide into the less refractory (garnet-bearing) layers. Partial melting produced felsic leucosomes that segregated by counter-flow into the sulfide-bearing veins. In some cases these leucosomes may have been crystallising as they flowed, leaving behind “cumulates” of quartz, garnet and/or feldspar as vein linings and selvages (Fig. 4). Where country rocks were more mafic and hence less refractory, as in the footwall of Bollinger, partial melting was less extensive and sulfides tended to form sharp-walled vein arrays.
Coarse grained Pn-Ccp-Po loop textures are ubiquitous within the massive ores, regardless of microscale setting, to the extent of being developed within narrow veins and broken fold-hinges. These textures are now regarded as diagnostically magmatic. This implies that sulfide vein emplacement took place under conditions where country rock deformation was either ductile or semi-brittle, despite the high temperatures of emplacement within the sulfide liquid melting range, consistent with estimates of 830-860°C for peak metamorphic temperatures in the metapelitic rocks of the region (Glasson et al. 2019). It is possible that much of the characteristic local deformation of the country rocks was a response to the emplacement of a large body of dense cumulate rocks and sulfide liquid, under conditions of very slow cooling.

Coupled with the clear evidence for high-P crystallisation of the host intrusions (cumulus Mg-Al spinel, symplectic coronas forming from trapped liquid reaction – Taranovic et al. this volume) these observations attest to deep emplacement of the Nova-Bollinger ores at mid to lower crustal depths during the peak of regional metamorphism. Aside from some local post-emplacement shearing, the Nova-Bollinger ores and host rocks retain primary magmatic features and have not been extensively deformed post magmatic emplacement.

Acknowledgements

We are grateful to IGO Ltd for funding this research, providing access to underground working and drill core and giving permission to publish these results. We acknowledge the contributions of IGO mine geological staff, particularly Sebastien Staude, Kyle Hodges and Paul Hetherington.
Figure 4. Model for garnet rinds and leucosomes associated with sulfide infiltration-vein-melting front beneath the Nova Lower Intrusion. Stage 1 – sulfide dykes and veins inject hot gneiss close to its solidus T. Stage 2 – partial melting of gneiss close to sulfide vein (time scale months-years) – garnet rinds form where maximum extraction of melt has happened at vein walls. Partial melt (leucosome) escapes along sulfide vein walls, sulfide infiltrates into foliation where degree of melting is highest.

References


Abstract. The Abitibi greenstone belt within the Superior Craton in Canada is the world’s largest greenstone belt. Historically, however, it has not demonstrated the same prospectivity for economically significant komatiite-associated Ni-Cu-(PGE) deposits as the greenstone belts in the Yilgarn Craton of Australia. The recent discovery of the Grasset Nickel Deposit, one of the largest komatiite-associated Ni-Cu-(PGE) deposits in the Abitibi, located within the heavily overburden covered northern portion of the belt, indicates that potential for additional discoveries of this type remains. While the mineral potential and the exact nature of the komatiitic host stratigraphy around the Grasset deposit has yet to be fully characterized, this discovery and more recent exploration activity in the area highlight the potential for definition of a new nickel district in the northern part of the Abitibi greenstone belt.

1 Introduction

Komatiite-associated sulphide deposits represent an important source of nickel, copper, and platinum group elements (PGE) globally. While komatiites are known to be present in Archean greenstone belts worldwide, komatiite-associated Ni-Cu-(PGE) deposits are much more restricted (Arndt et al. 2008). Economic deposits of Archean age cluster in the Eastern Goldfields Superterrane of the Yilgarn Craton of Western Australia, as well as in the greenstone belts of Zimbabwe and Finland, with few large deposits located outside of these districts. The Abitibi greenstone belt that extends through Ontario and Quebec within the Superior Craton (Canada) is the largest known greenstone belt worldwide yet hosts relatively few deposits of this type and none that rival the larger deposits of Eastern Goldfields. The Grasset nickel deposit, a recently discovered komatiite-associated Ni-Cu-(PGE) deposit is, however, a sizeable sulphide deposit in a previously unrecognized ultramafic intrusive/extrusive complex well removed from other known deposits of this type in the Abitibi. This contribution presents the first descriptions of this new deposit and its host sequence.

2 Geological setting

The Grasset Ultramafic Complex consists of a NW-SE trending komatiitic succession that extends over more than 8 km. The complex is underlain by mafic volcanic and gabbroic rocks and overlain by a thick (~1 km) package of clastic sedimentary rocks with sporadic intervals of oxide-facies iron formation. The complex is composed predominantly of komatiitic lava flows and subvolcanic sills intercalated with coherent and lesser tuffaceous felsic volcanic rocks. Graphitic argillaceous sedimentary rocks typically occur as small lenses (<5 m thick). Structurally, the entire succession is generally a homoclinal sequence younging to the SW that is truncated to the south by the SLDZ. South of this regional east-west trending deformation corridor is an extensive package of Timiskaming-style sedimentary rocks. These rocks are metamorphosed to greenschist facies where primary textures are often well-preserved and the term ‘meta’ is omitted in this contribution for simplicity.
4 Grasset Ultramafic Complex

The GUC is completely overburden covered with overburden depths ranging from 50 to over 80 metres. It is interpreted to extend for a minimum of 8.5 km of strike length based on the total magnetic signature and drilling intersections along this trend. To the northwest the magnetic signature is weaker but the area remains untested for several kilometers. The GUC is composed of several individual ultramafic flows/bodies. Individual flows/sills can extend for up to 2 km, with widths as large as 500 m. The ultramafic rocks of the GUC are typically composed of homogenous olivine ortho-mesocumulates with subordinate spinifex-textured and flow-top breccias. Komatiitic units with the latter textures indicate that at least part of the GUC is characterized by an extrusive mode of emplacement.

4.1 Grasset area

In the Grasset area, at the southern end of the complex, the Grasset nickel deposit occurs within an undifferentiated olivine ortho- to mesocumulate sill which is approximately 300 m wide at its thickest and which extends for ~1000 m in length (Figure 1). This unit is texturally homogenous mesocumulate with little obvious textural variation. Unfortunately, margins of the unit are moderate to strongly sheared relative to surrounding rocks preventing an accurate determination of the mode of emplacement (intrusive versus extrusive) but its slightly cross-cutting relationship to local stratigraphy is suggestive of a sill like morphology. The host ultramafic is also locally cut by late (syn- to post-regional deformation) quartz-feldspar porphyry and lamprophyric dykes. The footwall rocks are composed mainly of basalt and lesser rhyolite tuff and flow units with both locally interbedded with graphitic argillaceous sediments, whereas the hangingwall rocks are predominantly felsic tuffs interbedded locally with sediments. Thinner ultramafic units, potentially of volcanic derivation occur within the hangingwall succession above the host unit. All ultramafic rocks in the Grasset area are pervasively altered to various degrees to serpentine, although this assemblage changes to talc-magnesite in proximity to contacts, faults, and late lamprophyre dykes.

4.2 Fenelon area

In the Fenelon area, located ~7 km to the northwest of the Grasset deposit, diamond drilling in late 2018 discovered a new, and as yet unnamed, occurrence of Ni-Cu-PGE mineralization. This new discovery is hosted at the base of a ~200 m thick sequence of komatiitic flows (Figure 2). The host sequence is comprised of at least five stacked komatiite flow units overlain and locally interbedded with a thick felsic volcanic sequence (Figure 2). Individual komatiite flows consist of a variably brecciated flow top, which attains thicknesses of up to 5

![Figure 1. Geological map of the Grasset area. Grasset deposits are indicated by red (H3) and yellow (H1) polygons. Geologic succession has a SW younging direction.](image-url)
m, locally grading into a spinifex textured zone. The basal portion of each flow sequence is dominated by a thicker, uniform textured cumulate layer. The volcanic sequences sit atop a basement of dominantly tholeiitic basalt flows and subvolcanic sills with locally intercalated fine-grained sedimentary units. The komatitic flow sequence is overlain by thick (~200 m) homogenous olivine orthomesocumulate that appears to cut the host felsic volcanic stratigraphy. Ultramafic rocks are pervasively altered to serpentine.

5 Nickel Mineralization

Exploration by Balmoral Resources Ltd. in 2012 led to the initial discovery of what would, following additional discoveries in 2014, become the Grasset Nickel Deposit. Renewed exploration in 2018 led to the new discoveries in the Fenelon area which remain unnamed. Drill testing between the two areas has also identified numerous occurrences of Ni-Cu-(PGE) bearing sulphide mineralization at various stratigraphic levels throughout the GUC.

5.1 Grasset

The Grasset deposit is comprised of two distinct mineralized zones – Horizon 1 and Horizon 3. The vast majority of the higher grade mineralization within the deposit is located in the Horizon 3 zone, which is located in the upper portion of the host undifferentiated ultramafic unit, proximal (~50 m) to the hangingwall contact. The Horizon 3 zone is dominantly comprised of disseminated to weakly net-textured sulphide mineralization with rare massive sulphide intervals intersected to date. Sulphide mineralization is predominantly pyrrhotite>>pentlandite>chalcopyrite with lesser pyrite locally. The Horizon 1 zone is present at the lower footwall contact of the host unit. This mineralized zone exhibits a similar mineral assemblage to Horizon 3. Horizon 1 locally features textures indicative of sulphide segregation and settling with narrow massive sulphide intervals common at the actual footwall contact.

The Horizon 3 zone of the Grasset deposit may be interpreted as a “Type 2” komatite-associated Ni-Cu-(PGE) deposit due to its stratigraphic position within host ultramafic unit, the sill type morphology, generally disseminated sulphide mineralization, and the lack of clear evidence for sulphide settling textures. However, the overall sulphide content and the grades of the mineralization are quite high for traditional “Type 2” mineralization. It is possible that Horizon 3 mineralization could be an internal “Type 1” deposit, occurring at the base of an indistinct subunit within the thick olivine

![Figure 2](image_url). Geologic map of the Fenelon area. Newly discovered mineralized horizon indicated by red outlines. Geologic succession has a SW younging direction.
cumulate body.

At present, the Grasset deposit hosts an indicated resource of 3.5 million tonnes @ 1.56 wt. % Ni, 0.17 wt. % Cu, 0.03 wt. % Co, 0.34 g/t Pt and 0.84 g/t Pd (Richard and Turcotte, 2016). Nickel grades within the Grasset deposit are variable, ranging from 0.35 to 18.95 wt. % Ni with the average within net textured mineralization being 1-3 wt. % nickel. Massive sulphide zones in Horizon 3 are rare but can locally produce in excess of 18 wt. % nickel. Calculated nickel tenors through the deposit range from 8-10 wt% however, locally remobilized zones can demonstrate values as high as 15 wt%.

5.2 Fenelon

The recently discovered nickel sulphide mineralization in the Fenelon area occurs in distinct volcanic facies of the komatiitic succession, unlike the nearby Grasset Deposit. Sulphide mineralization is present at or near the lower contact of the basal unit of this komatiitic succession. Sulphide zones appear to exhibit typical sulphide segregation and settling textures, with disseminated zones at the top grading into net-textured zones below and further grading into massive sulphide lenses at the base of the unit. Given the stratigraphic location of these discoveries and the style of mineralization, the discoveries are interpreted to be “Type 1” komatiite-associated Ni-Cu-(PGE) mineralization. Massive sulphide zones observed to date range from 50 - 150 cm in thickness. The sulphide mineral assemblage is also typical of magmatic sulphide, being composed of pyrrhotite>>pentlandite >chalcopyrite.

Given its very recent discovery there is no resource calculation for the zone. Drill intercepts from the massive sulphide mineralization reach a high of 4.14 wt. % Ni, 0.26 wt. % Cu, 0.18 wt. % Co, 1.9 g/t Pt and 0.81 g/t Pd over 0.65 m within a broader 7.58 meter thick mineralized intercept grading 1.05 wt. % Ni, 0.31 wt. % Cu, 0.05 wt. % Co, 0.20 g/t Pt and 0.48 g/t Pd.

6 Concluding Remarks

The GUC represent an extensive subvolcanic-volcanic komatiitic succession that hosts one of the largest komatiite-associated Ni-Cu-(PGE) deposit discovered so far in the AGB. Preliminary results indicate that several styles of mineralization occur in this succession. Nickel sulphide mineralization is hosted, dominantly all cases, within massive olivine mesocumulate units either at the base of intrusive and extrusive members of the sequence or within broader, undifferentiated intrusive members.

The discovery of the Grasset deposit highlights the potential for the discovery of significant nickel deposits in the AGB, outside the traditionally recognized prospective nickel-bearing assemblages such as the Kidd-Munro and Tisdale assemblages, in particular within the extensive overburden covered northern segment of the belt. New discoveries in the GUC, within Deloro-correlative assemblages potentially yield new opportunities for additional discoveries in other parts of the AGB. This discovery reinforces the fact that regardless of their age or geochemical type, almost all komatiitic rocks in the AGB are prospective to host Ni-Cu-(PGE) mineralization with the most critical factor being the right physical volcanology as pointed out by Sproule et al. (2005), Houlé and Lesher (2011), and Houlé et al. (2017). Whether portions of the AGB possess similar nickel endowments to those of the Eastern Goldfields remains to be proven, the potential emergence of a new nickel district related to the GUC certainly improves the perceived prospectivity for komatiite-associated Ni-Cu-(PGE) mineralization elsewhere in the Abitibi greenstone belt.

Acknowledgements

The author thanks the Balmoral technical team, with special thanks to Ken Kuiper for his assistance in figure preparation. Thanks to Sarah Jackson-Brown for her assistance with editing and formatting.

References

The enigma of the Ni-Cu-PGE sulphide ores of the Sudbury Igneous Complex: what was the source of the metals?

Reid R. Keays  
School of Earth, Atmosphere and Environment, Monash University, Australia

Peter C. Lightfoot  
Lightfoot Geoscience, Sudbury, Canada

Abstract. Geochemical studies combined with U-Pb zircon age dating on the newly discovered Frood Intrusion and on the Sudbury Gabbro demonstrate that they are members of the 2.45 Ga Matachewan Large Igneous Province (LIP) and the ~2.2 Ga Nipissing Diabase LIP, respectively. The Frood Intrusion has very similar extended spidergrams patterns and geochemistry to other members of the Matchewan LIP including the East Bull Lake and River Valley intrusions. The similarities in geochemistry between Sudbury Gabbro and the Nipissing Diabase demonstrate that the former is a more MgO-rich variant of the latter. Our 2421 ± 3 Ma age of the Frood Intrusion is within error of ages for other EBL intrusions while our 2203 ± 11 Ma and 2168 ± 11 Ma ages for two of the Sudbury Gabbro sills are within error of published ages for the Nipissing Diabase. Mass balance considerations provide strong support for the concept that the metals in the Sudbury Ni-Cu-PGE sulphide deposits were sourced from protoress associated with mafic intrusions in the country rocks that were incorporated into the melt sheet that was formed by the impact of the meteorite that formed the SIC.

Keywords: Sudbury Ni-Cu-PGE sulphides, metal source

1 Introduction

There is an overwhelming consensus that the Sudbury Igneous Complex (SIC) and its Ni-Cu-PGE sulphide ores are the products of a meteorite impact at 1.85 Ga and that the 3 km thick melt sheet produced by that impact was entirely of crustal origin (Lightfoot, 2016). However, the source of the ore-forming metals within the SIC remains problematic because significant Ni-Cu-PGE sulphide deposits are normally only produced by mantle-derived mafic magmas. In addition, Sudbury is the only example of economic Ni-Cu-PGE sulphide mineralisation that is associated with the products of a meteorite impact.

The Ni and Cu contents of the felsic country rocks which make up ~80% of the rocks in the Sudbury area are provided by the analyses of the Sudbury Breccia reported by O’Callaghan et al. (2016). The Sudbury Breccia is a pseudotachylite produced by the shock waves generated by meteorite impact; O’Callaghan et al. (2016) argued that their analyses of Sudbury Breccia were representative of the rocks in which the breccias were developed. The Sudbury Breccias occurring in the felsic country rocks have median Ni and Cu contents of only 18.1 and 20 ppm, respectively.

Most of the mafic rocks in the Sudbury region belong to one of two Large Igneous Provinces (LIPs). The 2.45 Ga Matachewan includes the Matachewan and Hearst Dyke Swarms, the East Bull Lake intrusive (EBLI) suite, and bimodal volcanics and felsic plutons that occur in the footwall of the SIC. The 2.2 Ga Nipissing Diabases are comagmatic with the Senneterre Dyke Swarm and represent the remnants of an eroded continental flood basalt province.

A major aim of this project was to see if the newly discovered Frood Intrusion was a member of the EBL intrusive suite and if the Sudbury Gabbro was a member of the Nipissing Diabase LIP. These are important questions because the Frood Intrusion is directly associated with Ni-Cu-PGE sulphide mineralization in the large Frood and Stobie mines and one of the Sudbury Gabbro sills is directly associated with mineralization in the Totten Mine which is located in the Worthington Offset Dyke.

Figure 1. Geological map of the Sudbury region showing the outcrops of the East Bull Lake intrusive suite and the Nipissing Diabase (modified after Holwell et al. (2014)).

The salient question for the origin of the Sudbury Ni-Cu-PGE sulphide ores is whether there is a sufficient amount of metal in the unmineralized mafic rocks or if a significant proportion of metals was sourced from pre-existing LIP-related magmatic sulphide deposits similar to those that occur in the mafic sills of both the Matchewan and Nipissing Diabase LIPs.
2 Geological relationships in the Sudbury Region

The Sudbury Ni-Cu-PGE sulfide deposits are closely associated with the SIC which consists of the Main Mass overlain by the Onaping Formation and underlain by the Sublayer which is a fragment-rich unit that occurs in “embayment” structure at the base of the SIC. From the top down, the Main Mass comprises the Granophyre, Transition Zone Quartz Gabbro, and the Norite. Approximately 60% of the Ni-Cu-PGE sulfide resource is associated with the Sublayer and 40% is hosted by the Offset Dykes which are directly related to the SIC and occur in its country rocks. The composition of the chilled margins of the Offset Dykes is believed to represent the composition of the impact melt sheet that formed the SIC and its Ni-Cu-PGE sulphide deposits (Lightfoot et al. 1997).

The SIC straddles the boundary between the Archaean granitoid rocks of the Superior Province and the Paleoproterozoic (Huronian) mafic and felsic metavolcanic rocks and metasedimentary rocks of the Southern Province of the Canadian Precambrian Shield (Fig. 1). The Huronian rocks are cut by granite plutons (cf Fig. 2) and intruded by mafic intrusive rocks (the Nipissing Gabbro, Sudbury Gabbro), and early Proterozoic intrusions of the East Bull Lake suite of intrusions.

Figure 2. Geological map of the Frood Intrusion (modified from Lightfoot, 2016) showing locations of samples analysed in this study.

The Frood Intrusion is broken up into several discontinuous bodies of metagabbro and amphibolite that are enveloped in Sudbury Breccia (Fig. 2). The Frood Intrusion is a coarse grained to very coarse grained amphibolite some of which contains felsic megacrysts are up to 8 cm across. Discontinuous segments of the amphibolite comprise the footwall and hanging-wall of the Frood Deposit, and this rock type occurs as inclusions in the semi-massive sulfides at Frood and Stobie. The Frood Intrusion typically occurs within an envelope of Sudbury Breccia which commonly contains inclusions of amphibolite from the Frood Intrusion (Fig. 2), which provides un-equivocal evidence that the intrusion pre-dated the impact event at 1.85Ga.

A number of the mafic intrusive bodies within both the Matchewan and Nipissing Diabase LIPs host significant amounts of Cu-Ni-PGE sulphide mineralisation. For example, the River Valley Intrusion, which is a part of the EBL suite of intrusions, has a resource of 91 million tonnes averaging 0.02 % Ni, 0.08 % Cu, 0.22 g/t Pt, 0.58 g/t Pd and 0.04 g/t Au (Holwell et al. 2014) and the Shakespeare Intrusion, one of the Nipissing Diabase intrusions, has a resource of 11.3 tonnes grading 0.33 % Ni, 0.35 % Cu, 0.33 g/t Pt, 0.37 g/t Pd and 0.19 g/t Au (Sproule et al. 2007).

3 Methods

Samples collected from the Frood Intrusion and also from the Totten and the Nairn Sudbury Gabbro sills were crushed using soft steel plates and ground in soft steel ring mills. Whole rock major element oxides were determined by wavelength dispersive X-ray Fluorescence on glass disks while the trace elements were determined by inductively-coupled plasma mass spectrometry on fused beads. Samples collected from the same sites for U-Pb geochronology were first crushed and the zircons in them concentrated using the Wilfley Table and heavy liquid. The heavy minerals so obtained were prepared as a grain mounts in polished thin sections. The zircons in the thin sections were identified and located using an SEM; the SEM was also used to collect cathode luminescence images of the zircon grains. The zircon analyses were performed with an Agilent 7700x ICP-MS coupled to an ASI RESOlution Excimer laser. Zircon standard 91500 was used for calibration and drift and downhole fractionation correction. The spot sizes for most of the zircons were 18 microns; however, for a few of the smaller zircons, a 12 micron spot size was used. We also re-evaluated geochemical data for diabase inclusions in the Sublayer at the Whistle mine that Lightfoot et al. (1997) had suggested might have been derived from one of the Matchewan dykes.

For comparative purposes we use analytical data for the Nipissing Diabase from Lightfoot and Naldrett (1989), Lightfoot et al (1993), Sproule et al. (2007), and Jobin-Bevans (2004). The data for the East Bull Lake Suite of rocks comes from the East Bull Lake Intrusion (Peck et al. 1995), the River Valley intrusion (Holwell et al. 2014), and the Agnew intrusion (Vogel et al. 1998).

4 Results

Our geochemical data as well as scattergrams and extended spidergram plots prepared from these data show that there are considerable similarities in the composition of the Frood Intrusion of that of the other EBL intrusive suite. This also the case with the Sudbury Gabbro and the Nipissing Diabase intrusions.

The Sudbury Gabbro in the Totten, Nairn and Makada intrusions, as well as inclusions of Sudbury Gabbro that occur in the Worthington Offset Dyke, is generally considerably more mafic than the Nipissing Diabase (Fig. 3). Some of the Nipissing Diabases that
occur in the Sudbury area are also more mafic than the regional Nipissing Diabases and these tend to contain some magmatic sulphides giving them elevated Ni contents (Fig. 3). The elevated Ni contents of some of the Sudbury Gabbro inclusions in the Worthington Offset Dyke may be due to infiltration of sulphides from the Quartz Diorite host rocks. For those samples in which there is no sulphide Ni, there is a continuum in Ni and MgO values from the Nipissing Diabase to the Sudbury Gabbro. Continua in composition between the Sudbury Gabbro and the Nipissing Diabase are shown on other scattergrams such as Ce vs Pb plots. There are also continua in composition between the Frood Intrusion and other members of the EBL intrusive suite.

![Figure 3. Scattergram of Ni vs MgO for both regional and Sudbury area Nipissing Diabases, the mineralized Shakespeare Nipissing Diabase intrusion, and Sudbury Gabbros from the Nairn, Totten, Makada sills and as inclusions in the Worthington Offset Dyke.](image)

The Frood Intrusion has a similar pattern to those of other members of the EBL intrusive suite including the East Bull Lake, River Valley, and Agnew intrusions on an extended spidergram (Fig. 4). In addition, diabase inclusions in the Sublayer at Whistle mine have a similar extended spidergram pattern to other members of the EBL intrusive suite; this provides a strong argument that the precursors to these inclusions was a Matchewan dyke, as suggested by Lightfoot et al. (1997). The Sudbury Gabbro has a similar pattern to that of the Nipissing Diabase on spidergrams constructed for these rocks.

The Frood Intrusion has a discordant U-Pb zircon age of 2421 ± 32 Ma (Fig. 5). This is within error of the 2441 ± 3 Ma of the Falconbridge Township intrusion reported by Prevec and Baadsgaard (2005); the latter, which is a member of the EBL intrusive suite, occurs in the immediate footwall of the SIC (Fig. 1). The Nairn Sudbury Gabbro intrusion has a U-Pb zircon age of 2203 ± 11 Ma which is within error of the 2209 ± 3.5 Ma age of the Triangle Mountain Nipissing Diabase sill reported by Noble and Lightfoot (1992); the U-Pb zircon 2168 ± 11 Ma age of the Totten Sudbury Gabbro sill is slightly younger than of the Nairn intrusion.

5 Discussion

Both the geochemistry and the age of the Frood Intrusion confirm that it is a member of the Matchewan LIP and the EBL suite of intrusions. Similarly, the geochemistry and the age of the Sudbury Gabbro confirm that it is a more mafic member of the Nipissing Diabase suite of intrusions.

The demonstration that the Frood Intrusion is a member of the EBL suite of LIP intrusions and that the Sudbury Gabbro sills are mafic members of the Nipissing Diabase LIP has important implications for both the petrogenesis of the SIC melt sheet and the Ni-Cu-PGE ores associated with it. Extrapolation of the known occurrences of both the EBL intrusive suite and the Nipissing Diabase LIP indicates that pre-existing members of these suites would have been incorporated into the impact melt sheet (cf Fig. 1).

Keays and Lightfoot (1994) demonstrated that there is very significant Ni, Cu and PGE depletion in the sulphide-poor Main Mass rocks and that these rocks contain appreciably less of these metals than those in the parental impact melt sheet. By modelling the distribution of Ni and Cu in the Norites, they were able to demonstrate that the metals in the contact ores segregated out of from the magmas that formed the Main Mass rocks.

Golightly (1994) estimated that the relative proportions of felsic and mafic rocks incorporated into the melt sheet was 80:20. This means that the contribution of Ni and Cu (and other metals) in the mafic rocks to the melt sheet (and the ore deposits) was only 20% of the Ni and Cu (etc.) contents of the rocks. Figure 6 compares the contribution that the Nipissing Diabase and EBLI rocks would have made to the melt sheet with the composition of the parental melt SIC melt sheet given by the average composition of the chilled margins of the Quartz Diorite Offset dykes as reported by Lightfoot et al. (1997). What is obvious is that none of these rocks have sufficient amounts of Ni and Cu in them to account for the Ni and Cu in the parental melt sheet.

![Figure 4. Extended spidergram plot for average analyses of samples of the diabase inclusions from the Sublayer at Whistle mine, as well as from samples from the Dury Township, Agnew, River Valley, East Bull Lake, and Falconbridge Township intrusions normalized against the average composition of the Frood Intrusion.](image)

Holwell et al. (2014) suggested that the Cu-PGE-rich sulphides in the River Valley intrusion had been formed at depth and transported by the magma the formed the
River Valley intrusion to their current sites. They also suggested that it is possible that only a small fraction of the sulfides formed at depth were transported to their current sites in the intrusions and that the remainder of the sulfides remained at depth somewhere along the magma conduit system. If this had also been the case for the EBL intrusion suite and the Nipissing Diabases that had been incorporated into the melt sheet, then considerably more ore metals than those currently associated with their preserved mineralized cousins may have contributed to the melt sheet.

Acknowledgements

Vale is thanked for supporting this work. Abaz Alimanovic, Barry Kohn, Alan Greig, and Graham Hutchinson are thanking for assisting with preparation of the mineral concentrates and analysis on the SEM and LA-ICP-MS at the University of Melbourne.

References


Abstract. The Jacurici Mafic-ultramafic Complex, NE of the São Francisco Craton, hosts a thick massive chromitite and is considered as a single Paleoproterozoic N-S elongated layered body disrupted into many segments by later deformation. Here we discuss the processes that could explain the formation of the thick chromitite. The parental magma is very primitive based on olivine (up to Fo93) and orthopyroxene (up to En94) compositions, and has been considered as originated from a high degree of mantle extraction with subsequent crustal contamination, based on Nd-Os isotopes. Chromites host abundant inclusions, including hydrous silicates, negative-crystal shaped carbonates, base metals sulfides and laurite, indicating an H2O-rich and S-rich country wall-rocks. The crustal contamination has caused erosion and assimilation of metasedimentary rocks – up to 40 m thick) (Marques and Ferreira Filho 2003) (Fig. 2). Isotopic and petrography studies suggested that a large volume of magma flowed through a conduit-like chamber causing erosion and assimilation of metasedimentary country wall-rocks. The crustal contamination has introduced CO2 and H2O, increasing fO2 and favoring chromite crystallization. We proposed a model where chromite started crystallizing in situ and were then overlaid by semi-consolidated chromite slurry that slumped from the margins of the conduit forming a thick chromitite.

1 Introduction

The origin of massive chromitites in layered intrusions has been investigated for decades. Nevertheless, the mechanisms to account for its formation remain debated considering the difficulties to explain the minimum presence of silicates and the volume of magma needed to concentrate large amounts of Cr₂O₃. The classic in situ crystallization models considering shift from cotectic olivine-chromite crystallization to chromite-only formation triggered by different processes, such as crustal contamination (e.g. Irvine et al. 1975, Rollinson 1997), mixing of magmas (e.g. Irvine et al. 1977, Naldrett et al. 2012) or change in pressure (e.g. Lipin 1993), have been challenged. Alternative mechanisms, in particular remobilization of chromite crystals, were proposed to explain the massive chromitites (e.g. Eales 2000, Spandler et al. 2005, Maier et al. 2013, 2018).

The thin (300 m thick) layered mafic-ultramafic intrusion of the Jacurici Complex hosts a thick (5-8 m thick) massive chromitite, explored by FERBASA, and consists of an outstanding site to study chromitite formation. Here, new results from detailed studies of chromite inclusions provide further evidences for the model previously proposed by Marques et al. (2017).

2 Geotectonic and geological setting

The Jacurici Complex, located in the São Francisco Craton, Northeastern Brazil, hosts the largest Brazilian chromite deposit. The Complex is a Paleoproterozoic (2.1 to 2.08 Ga, Oliveira et al. 2004, Silveira et al. 2015) mafic-ultramafic layered intrusion composed by several bodies arranged in a N-S 70 km long belt. The mineralized segments are interpreted as fragments tectonically disrupted (Fig. 1).

The mineralized layered intrusion is composed by a lower ultramafic unit (dunite with minor harzburgite and lherzolite - up to 180 m thick), followed by the thick massive chromitite (5-8 m thick) and an upper ultramafic unit (harzburgite and pyroxenite – up to 60 m thick) covered by a relatively thin mafic zone (gabbro-noritic rocks – up to 40 m thick) (Marques and Ferreira Filho 2003, Marques et al. 2017). The parental magma is considered to be very primitive, originated from high degree of mantle extraction, based on olivine (Fo up to 94) and orthopyroxene (En up to 94) composition (Marques and Ferreira Filho 2003) (Fig. 2). Isotopic and petrography studies suggested that a large volume of magma flowed through the magmatic chamber that acted as a dynamic conduit favoring the formation of chromitite due to crustal contamination (Marques et al. 2003). Marbles were suggested as the possible assimilated material (Ferreira Filho and Araújo 2009).

Marques et al. (2003) proposed that crustal contamination occurred during the formation of the thick chromitite layer based on the decline in εNd and an increase in Yb with more radiogenic signatures located in the horizons immediately above the MCL (Fig. 2). The radiogenic signatures are also coincident with an increase in magmatic amphibole content. The presence of hydrous silicate phases as inclusions in chromite from chromitite led Marques et al. (2017) to suggest the magma was hydrated at the timing of chromitite formation with fluids playing an important role in either chromite crystallization and/or accumulation. A combined model to explain the thick chromitite layer was proposed where semi-consolidated chromite slurry slumped through the conduit after crystallizing in its margins (Marques et al. 2017).
3 The thick chromitite layer

3.1 General features

The chromitite layer is 5 to 8 m thick and extends along strike for several kilometers segmented locally by normal faults. The contacts with the ultramafic rocks are commonly obliterated by later faults. When preserved, they are sharp and planar, locally gradational in the base. The chromitite is a massive fine-grained cumulate with more than 90 vol.% of euhedral to subhedral chromite varying in size from 0.1 to 0.8 mm (Fig. 3).

Near the base of the layer, occurs a chain-textured chromitite interval which comprises 60–80 vol.% of small chromite grains with slightly undulating contact with the massive layer (Marques et al. 2017). Silicates are rare and variably serpentinized. Orthopyroxene and minor amphibole are preserved and commonly form large poikilitic grains (up to 1.5 cm). Diopside occurs locally, only in the chain-textured chromitite intervals. An important feature is the presence of dozens of tiny inclusions in chromite showing variable compositions, sizes and forms (Marques et al. 2017).

3.2 Mineral inclusions in chromite

Chromite-hosted inclusions are abundant along the entire thick massive chromitite being more frequent in the semi-massive interval. Inclusion-bearing chromite occurs side-by-side with inclusion-free grains (Fig. 3A). Most inclusions are 5-20μm across and occur as isolated grains randomly distributed within the chromite. These inclusions show different distribution patterns such as orientation parallel to the crystallographic axes of chromite (Fig. 3A), internal coronas (Fig. 3B) or concentration in the core of the host crystal (Fig. 3B).

Figure 1. Geological setting of the Jacurici Complex and simplified geological maps from Monte Alegre, Medrado and Ipueira segments (modified from Marques et al. 2017).

Figure 2. Cryptic variation in olivine and orthopyroxene compositions and interpreted petrologic evolution showing evidences [$^{146}$Nd (whole rock), amphibole mode and $^{195}$Os (chromite separates)] for possible crustal contamination at the timing of chromitite formation (modified from Marques et al. 2017).

Figure 3. Mineral inclusions in chromite of Ipueira (A) and Monte Alegre (B-D) segments. A: Inclusions oriented along crystallographic axes and in contact to an inclusion-free crystal. B: Internal ring of inclusions (red dashed square) and inclusions close to the core (white dashed square). C: Subhedral prismatic phlogopite and clinopyroxene inclusions, orthopyroxene rounded inclusion and pseudohexagonal sulfide inclusion (chalcopyrite + pentlandite + Ni-sulfide). D: Negative-crystal shaped magnesite inclusion. Chr: chromite; Cpx: clinopyroxene; Phl: phlogopite; Sf: sulfide; Opx: orthopyroxene; Mgs: magnesite.

In the Monte Alegre segment, central part of the Jacurici Complex, the inclusions were characterized in detail using a JEOL JXA-8230 Electron Microprobe equipped with a set of wavelength dispersive spectrometers at Queen’s University (Friedrich 2019). At Monte Alegre, inclusions comprise silicates (enstatite, phlogopite, magnesiohombende, diopside and olivine), carbonates (mainly dolomite and magnesite), sulfides (pentlandite, millerite, heazlewoodite, pyrrhotite, pyrite and chalcopyrite), oxide (rutile) and, eventually, other
phases such as barite, apatite, monazite and scheelite (Fig. 3C,D). Silicate inclusions are commonly monomineralic and sub- to euhedral, and crystallized prior to, or coeval with, chromite. Carbonate inclusions are irregular or negative-crystal shaped (Fig. 3D) suggesting entrapment as melt droplets. Sulfides are commonly polymineralic, irregular or hexagonal-shaped (Fig. 3C), indicating entrapment as sulfide melt and as monosulfide solid solution.

In order to evaluate possible lateral variation, other segments are under investigation. In the Ipueira segment (current being mined), preliminary results using a JEOL 6610-LV scanning electron microscope equipped with an energy dispersive spectrometer at Universidade Federal do Rio Grande do Sul show the inclusions are dominated by orthopyroxene, amphibole and clinopyroxene. Carbonates also occur, but magnesite instead of dolomite is more common. Sulphide inclusions are less abundant.

3.3 PGM inclusions in chromite

PGM inclusions were found in six chromitite samples from the massive layer (Monte Alegre area) using scanning electron microscope (SEM) and microprobe at Queen’s University. Small grains were found in all samples and vary from 0.5µm² to up to 10µm² in size with most grains averaging between 1 to 2 µm². PGM inclusions occur isolated or associated with silicates, sulfides and/or carbonates, less frequent in the borders of chromite grains.

The most common PGM is laurite [Ru(Os,Ir)S₂] followed by irarsite [(Ir,Ru,Rh,Pt)AsS]. They occur either as isolated inclusions or associated to other minerals inside chromite grains. The composite PGM inclusions are spatially associated with Ni-sulfides (pentlandite and/or millerite) (Fig. 4A,B). Ir-rich sulfides, possibly cooperite, and Pt-Ir alloy occur as isolated inclusions.

PGM inclusions also occur in close relationship with chalcopyrite, pyrrhotite, magnesite, dolomite and phlogopite (Fig. 4C). In this context, the PGM are more variable and include, besides laurite and irarsite, sulfides, tellurides and alloys generally enriched in PPGE (Pt, Pd, Rh). Figure 4D shows an interesting feature where irarsite occurs associated to millerite, pyrrhotite, chalcopyrite and to a partially preserved negative-crystal shape magnesite.

Lager composite PGM grains (up to 10 µm²) are rare and occur at the borders of chromite; laurite and irarsite are the most common minerals, followed by PPGE-enriched sulfides, tellurides and alloys.

4 Discussion

The striking thickness of the massive chromitite layer from the Jacurici Complex is not easy to reconcile with the current chromitite formation models. Previous studies showed that the massive chromitite marks an important change in the magmatic evolution (Marques and Ferreira Filho 2003) and a conduit-like intrusion was suggested. Based on isotopic results, crustal contamination was considered as a trigger to chromite crystallization (Marques et al. 2003). Later, Ferreira Filho and Araújo (2009) suggested assimilation of marble country rocks. The role of fluids has also been highlighted by Marques et al. (2017) both as a possible trigger to start chromite sole crystallization and as a player assisting the accumulation process through slumping of semi-consolidated slurry of chromite from conduit-walls. However, chromite crystallization and the proportional huge accumulation observed in the Jacurici Complex remain debated.

The presence of primary inclusions of hydrous silicates (Marques et al. 2017, Friedrich 2019) and carbonates (Friedrich 2019) in chromite supports the contamination with addition of water (Marques et al. 2003) and assimilation of carbonate rocks (Ferreira Filho and Araújo 2009). The presence of diopside at the basal part could be further evidence considering experimental results showing calcite and dolomite addition to mafic magmas favor clinopyroxene crystallization (Iacono-Marziano et al. 2007). Friedrich (2019), based on detailed petrography of the inclusions and mineral chemistry, suggested rapid crystallization of large amounts of chromite due to wall-rock erosion adding fluids (H₂O and CO₂) and increasing the fO₂ during continuous inflow of hot primitive magma. The multiple sulfide inclusions in chromite also suggest addition of sulfur in the magma (Friedrich 2019).

IPGE (Ir, Os, Ru) minerals in chromite is common feature in other layered intrusions (Maier et al. 1999, Prichard et al. 2017), but mainly as isolated inclusions (Prichard et al. 2017). In the Jacurici Complex, PGM inclusions occur also in contact to base metal sulfides and hydrous and CO₂-rich minerals, interpreted as further evidence of combined fluids acting during chromite crystallization. Contamination may have caused S-saturation during chromite crystallization. This could explain the occurrence of laurite inclusions in close spatial relationship to base metal sulfides, isolated inclusions of irarsite and PPGE-enriched telluride, and sulfarsenide and alloys associated to composite inclusions in chromite.

In situ accumulation explains the gradational contacts at some sections and semi-massive intervals at the base of the chromite, but does not explain the thickness of the massive interval. Chromite crystallized along the roof, conduit-walls and margins of the chamber might have collapsed downward as slurry undergoing hydrodynamic sorting. The presence of CO₂ and H₂O bubbles in the magma/crystal mush are expected to help the downward influx considering it lowers the magma’s viscosity (Lesher and Spera 2015, Ghosh and Karki 2017). Chromite grains containing dozens of inclusions in different types of arrangement and also in spatial relation with inclusion-free chromite is another possible evidence of the suggested process. Friedrich (2019) interpreted the different types of inclusions arrangements as a result of chromite grains that crystallized under different fO₂.
5 Final remarks

Although, the trigger of chromite crystallization and the accumulation process still remain debated, the petrologic evolution of the Jacurici Complex mineralized intrusion suggests that a high volume of very hot magma flowed through a conduit-like chamber. Erosion and assimilation of metasedimentary country rocks is a reasonable process to be considered under such circumstance. Inclusions in chromite shed light to the process considering it is noticeable that fluids (H2O, CO2 and O2) due to crustal contamination favored chromite crystallization. We suggest that increasing O2 due to crustal contamination favored chromite crystallization. Chromite started crystallizing in situ, but fluids might have assisted chromite slurries to slump forming the thick chromitite.

Acknowledgements

Companhia de Ferro Ligas da Bahia is gratefully acknowledged. Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) is acknowledged for Friedrich’s scholarship (131133/2016-0), financial grant (436963/2018-3) and research fellow support to J. Marques (309519/2018-7).

References

Apatite-hosted melt inclusions from the Panzhihua gabbroic layered intrusion associated with a giant Fe-Ti oxide deposit in SW China

Christina Yan Wang, Kun Wang, Zhong-Yuan Ren
Guangzhou Institute of Geochemistry, Chinese Academy of Sciences

Abstract. The Panzhihua layered intrusion in SW China is unusual because it hosts a giant Fe-Ti oxide deposit in its lower zone. To examine the magmatic processes that resulted in the Fe enrichment of parental high-Ti basaltic magma, we carried out a detailed study of melt inclusions in apatite from a 500-m-thick profile of leucogabbro in the middle zone of the intrusion. These melt inclusions have variable compositions with contrasting end-members; one end-member being Fe-rich and Si-poor (40.2 wt.% FeO and 17.7 wt.% SiO₂) and the other being Si-rich and Fe-poor (74.0 wt.% SiO₂ and 1.20 wt.% FeO). This compositional range may be attributed to entrapment of immiscible Fe-rich and Si-rich components in different proportions over a range of temperature. Simulating results indicate that Si-rich droplets could be separated from Fe-rich melt within a crystal mush. Migration of Si-rich droplets caused the remaining Fe-rich melt to react with plagioclase primocrysts (An₅₉₋₆₀), as evidenced by lamellar intergrowth of An-rich plagioclase (An₇₉₋₆₄) + clinopyroxene in the oxide gabbro of the lower zone. Therefore, magma unmixing combined with gravitationally driven loss of the Si-rich component, resulted in the formation of melagabbro and major Fe-Ti oxide ores in the lower part of the intrusion.

1 Introduction

Conjugate immiscible Fe-rich and Si-rich melts in both natural rocks and experimental resultants are typically related to magma unmixing (McBirney 1975; Philpotts 1982). Separation of immiscible Fe-rich and Si-rich melts may contribute to the Daly gap along the tholeiitic liquid line of descent (Charlier et al. 2011), and can explain why felsic rocks usually occur at the top of layered intrusions such as Skaergaard in Greenland and the Bushveld Complex in South Africa (Jakobsen et al. 2011; Holness et al. 2011; Fischer et al. 2016).

The onset of unmixing in basaltic magma systems is traditionally considered to occur at late-stage differentiation, i.e., below 1040°C, equivalent to 90-95% crystallization (McBirney 1975; Philpotts 1982). New experimental studies demonstrate that magma unmixing may start at temperature > 1100°C, before 50-60% crystallization (Veksler et al. 2007). Unmixing at an earlier stage of differentiation in a slow-cooling magma chamber is important as it may play a key role in the Fe enrichment of basaltic magma and the separation of conjugate immiscible melts. However, the separation and migration of conjugate immiscible melts are poorly understood, as is their role in the production of voluminous, extremely Fe-rich melt.

The Panzhihua intrusion in SW China, hosts thick Fe-Ti oxide ore layers in the lower part. It has long been debated on how large amount of Fe-Ti oxides were accumulated. One early model invoked separation of immiscible oxide liquids from high-Ti basaltic magmas (Zhou et al. 2005), whereas a later model proposed gravitational settling and sorting of early cumulus Fe-Ti oxides from parental magmas (Pang et al. 2009). However, both models have been challenged due to lack of convincing petrographic and experimental evidence (Wang and Zhou 2013).

In this study, we document the compositions and characteristics of apatite-hosted melt inclusions in the middle zone, and replacive symplectites in the lower zone of the Panzhihua intrusion, putting forward a model of magma unmixing within a crystal mush to explain the formation of major Fe-Ti oxide ore layers in the lower part of the Panzhihua intrusion.

2 Panzhihua layered intrusion

The Panzhihua intrusion is 2 km thick with an outcrop area of 30 km², and contains ore reserves of 1,333 million tons at an average grade of ~33% FeO and ~12% TiO₂ (Zhou et al. 2005). It is divided into four zones by local geologists on the basis of internal structure and the extent of Fe-Ti oxide mineralization, which are from the base upwards; a marginal zone (MGZ), lower zone (LZ), middle zone (MZ) and upper zone (UZ). The LZ is subdivided into a lower MZA and upper MZB by the appearance of apatite in the MZB (Zhou et al. 2005). The MGZ is a thin, chilled margin composed of fine-grained gabbro. The LZ, MZ and the Fe-Ti oxide ore layers in the LZ are thought to have formed from one magma pulse, whereas the UZ is Fe-Ti oxide-barren and is assumed to have formed from a new magma pulse (Pang et al. 2009).

3 Replacive symplectites in LZ

Replacive symplectites are common in the oxide gabbro from the LZ of the Panzhihua intrusion. They include lamellar intergrowths of clinopyroxene + Ti-rich magnetite (Fig. 1a) and An-rich plagioclase + clinopyroxene (Fig. 1b). Clinopyroxene in the intergrowth have Mg# of 78.4 to 81.3, slightly higher than that for adjacent clinopyroxene primocrysts (Mg# = 75.3 to 76.9). Plagioclase lamellae in the intergrowth have An contents of 79-84, much higher than adjacent plagioclase primocrysts (An₅₉₋₆₀).
Figure 1. Backscattered electron (BSE) images showing the replacive symplectites in the oxide gabbro from the LZ of the Panzhihua intrusion. (a) an intergrowth of Ti-rich magnetite (Ti-Mt) and clinopyroxene (Cpx) replacing a clinopyroxene primocryst with an amphibole (Amp) substrate between Ti-rich magnetite and symplectite; (b) an intergrowth of An-rich plagioclase (Pl) and clinopyroxene replacing a plagioclase primocryst with an amphibole substrate between Ti-rich magnetite and symplectite.

4 Melt inclusions in apatite from MZb

Melt inclusions in apatite are light to dark brown, ranging from 5 to 50 um in width and 5 to 100 um in length. After heating and quenching, some melt inclusions became a single homogeneous phase with a bubble (Fig. 2a); and some others appear to have complex composites with overall Fe-rich compositions (Fig. 2b). Homogenized inclusions from the Panzhihua intrusion are more Si-rich than the unhomogenized ones which are more Fe-rich, and thus are termed as Si-rich melt inclusions and Fe-rich melt inclusions.

Overall, melt inclusions in apatite of the Panzhihua intrusion show a large range of SiO₂ and FeOt and make up a continuous trend on a plot of SiO₂ versus FeOt, comparable to apatite-hosted melt inclusions from the Skaergaard and the Bushveld Complex (Jakobsen et al. 2005; Fischer et al. 2016) (Fig. 3).

5 Discussion

5.1 High-temperature magma unmixing within a crystal mush

Many extremely Fe-rich melt inclusions with >18 wt.%
FeOt are trapped inapatite of the Panzhihua intrusion (Fig. 3), and many olivine- and plagioclase-hosted melt inclusions have similar compositions (Zhang 2014) (Fig. 3). Given that the parental high-Ti basaltic magmas of the Panzhihua intrusion contain ~14 wt.% FeO (Fig. 3), the extremely Fe-rich melt inclusions are considered to be indicative of a Fe-rich, immiscible melt.

The intergrowth of An-rich plagioclase and clino.pyroxene in the Panzhihua intrusion (Fig. 1b) is identical to Type 1 replacive symplectite in the Skaergaard intrusions, which is considered to form by the reaction between residual immiscible Fe-rich melt and primocryst plagioclase after the loss of a Si-rich component from the interstitial liquid (Holness et al. 2011). We attribute the replacive symplectites observed in the oxide gabbro from the lower zone of the Panzhihua intrusion to the same mechanism.

The formation temperatures of the symplectites in the Panzhihua intrusion are constrained to be 1012-1034 °C based on the substrate amphibole compositions using the amphibole thermometer by Putirka (2016). These may represent the lowest temperatures because amphibole is likely the last solidified phase in such symplectites. Plagioclase primocrysts adjacent to the intergrowth of An-rich plagioclase + clino.pyroxene in the Panzhihua intrusion have An contents of ~60, which are higher than the An54 plagioclase when magma unmixing began (~1100°C) in the Skaergaard intrusion (Jakobsen et al. 2011). We thus consider that the onset of unmixing at Panzhihua may have started at a higher temperature (>1100°C).

### 5.2 Separation of conjugate immiscible melts

Unmixing in a basaltic magmatic system can develop emulsified immiscible melts composed of low-viscosity, high-density Fe-rich melt along with small, viscous and lower-density Si-rich droplets (c.f. Holness et al. 2011). The separation of Si-rich droplets from Fe-rich melt might be approximated using the Stokes law:

$$h = \frac{2gt\Delta\rho r^2}{9\eta}$$

Where h is the migration distance of Si-rich droplet, g is the acceleration of gravity of 9.8 m/s², t is the time for separation, r is the radius of the droplet, Δρ is the density difference between Si-rich and Fe-rich melts, and η is the viscosity of the host Fe-rich melt.

The Δρ is set to be ~0.4 g/cm³ based on the average compositions of apatite-hosted, Fe-rich and Si-rich melt inclusions and the equation provided by Bottinga and Weill (1970). The viscosity (η) of the host Fe-rich melt is calculated using the method by Hui and Zhang (2007) to be in a range between 90Pa.s at 1100°C and 937Pa.s at 1000°C. The radius (r) of Si-rich droplets is set to be from ~2 to ~50 µm based on the sizes of melt inclusions in apatite. The Si-rich droplets were theoretically removable within the crystal mush for at least 2,400 years which is the timescale of the Panzhihua intrusion reaching 50% crystallization (Cheng et al. 2014). In this time interval, the migration distance of Si-rich droplets is highly variable from 0.28 to 1,831 m depending on the radii of the Si-rich droplets and the viscosity of the Fe-rich melt (Fig. 4).

Although the migration of Si-rich droplets may be decelerated by the crystal mush, it would be accelerated by the wetting properties of immiscible melts on suspended crystals and also by magma convection. In this scenario, Si-rich droplets of different sizes may have migrated and dispersed randomly within the crystal mush.

![Figure 4. Contour map showing migration distance of Si-rich droplets as a function of the radius (r) of Si-rich droplet and the viscosity (η) of the host Fe-rich melt. The calculation is based on the rising velocities or migration distance at extreme the radii of Si-rich droplets and the viscosities of the host Fe-rich melt (see the text).](image)

### 5.3 Metallogenic model

A conceptual cartoon in Fig. 5 illustrates a possible mechanism for the formation of Fe-Ti oxide ore layers in the lower part of the Panzhihua intrusion. Fractional crystallization of parental high-Ti basaltic magmas developed a crystal mush in the Panzhihua chamber (Fig. 5a). The interstitial liquid was enriched in Fe with the continued crystallization of silicate minerals and intersected the immiscible field at high temperatures (>1100°C). Then, emulsified immiscible melts that are composed of Fe-rich melt and Si-rich droplets were developed in the interstitial liquid (Fig. 5b). Because of density differences, different wetting properties of immiscible melts and magma convection, Si-rich droplets were separated efficiently from the host Fe-rich melt and migrated upwards (Fig. 5b). Progressive separation of the immiscible melts led to collection of the Fe-rich and Si-rich melts in the lower and upper part of the magma chamber, respectively (Fig. 5c). In this scenario, large amounts of Fe-Ti oxides crystallized from Fe-rich melt in the lower part to form the major Fe-Ti oxide ore layers, whereas some Si-rich melts may have coalesced into large Si-rich agglomerates, forming felsic veins and lenses in the MZb (Fig. 5d).

We note that the apatite-bearing leucogabbro occurs above the major oxide ore bodies in the Panzhihua intrusion, suggesting that apatite was not saturated in the Fe-rich melt at high temperature. The crystallization of Fe-Ti oxides may result in the enrichment of P in the
residual Fe-rich melt. Mixing of P-rich, residual Fe-rich melt with Si-rich melt could have led to formation of the apatite-bearing leucogabbro in the MZb.

6 Conclusion

Apatite-hosted melt inclusions in the MZb of the Panzhihua intrusion show a large and continuous range of SiO₂ and FeOt with contrasting Fe-rich and Si-rich end-members which is attributed to entrapment of Fe-rich and Si-rich components in different proportions over a range of temperature. It is proposed that emulsified immiscible melts composed of Fe-rich melt and small Si-rich droplets developed in the interstitial liquid. Si-rich droplets were separated from the remaining Fe-rich melt and migrated upwards due to gravitational instability. Large amounts of Fe-Ti oxides crystallized from the remaining Fe-rich melt in the lower part of magma chamber, forming the major Fe-Ti oxide ore layers of the Panzhihua intrusion.

Acknowledgements

This study was financially supported by the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (XDB18000000), and NSFC grants 41325006 and 41473037.

References

Field and geochemical constraints on the origin of massive magnetitite layers of the Bushveld Complex, South Africa

Willem Kruger & Rais Latypov

University of the Witwatersrand, South Africa

Abstract. One of the greatest enigmas of igneous petrology is the occurrence of monomineralic rocks in layered intrusions that are commonly thought to have formed from melts saturated in multiple phases. These rock types are crucial for the concentration of metals that are vital for modern society, such as Cr in chromitite layers and V and Ti in massive magnetitite layers. This study focusses on constraining the origin of magnetitite layers from the Upper Zone of the Bushveld Complex, South Africa, the largest preserved mafic magma chamber in Earth’s crust. New field observations and two-dimensional geochemical mapping of magnetitite layers provide important constraints and insights regarding their origin. These include field evidence for thermo-chemical erosion of the footwall rocks, Cr reversals indicating magma chamber replenishments, and high-Cr in situ growth nodes suggesting that the parental melt was likely saturated in magnetite alone. We propose that magnetite layers are adcumulates formed from evolved, Fe-rich melts derived from a deeper-seated staging chamber of the Bushveld Complex. The reason for the melt being saturated in magnetite only is not yet clear but possibly caused by decompression associated with its ascent towards the Earth’s surface.

1 Introduction

The immense size of the 2.054 Ga (Scoates and Friedman 2008) Bushveld Complex, with its world-class deposits of PGE, Cr, and V, has made it one of the most famous geological features on our planet. These deposits are commonly hosted by monomineralic igneous rocks, such as stratiform chromitites (exploited for Cr and PGE) and magnetitites (exploited for V) that may be up to several meters thick and can be traced for hundreds of kilometres along strike (Viljoen 2016). Despite their economic importance, petrologists are still baffled by the processes that led to their formation. In this study, we attempt to further constrain the origin of massive magnetitite layers that occur in the upper reaches of the Bushveld Complex.

Magasms of tholeiitic affinity (as is the case for the parental magmas of the Bushveld) require a significant degree of Fe-enrichment via crystal fractionation before magnetite becomes stable as a liquidus phase. By that time, magnetite is crystallizing in conjunction with several other minerals, such as pyroxene, plagioclase, and olivine. It is thus clear that to concentrate magnetite into monomineralic layers, some process is required to physically separate magnetite from the other crystallizing phases, or it should ensure the sole crystallization of magnetite from the magma. Exactly what this process (or processes) may have been debated for decades (e.g. Cawthorn & McCarthy 1980; Klemm et al. 1985; Kruger 1987; Harney and Von Gruenewaldt 1995; Scoon & Mitchell 2012; Maier et al. 2013; Bilenker et al. 2017; Yuan et al. 2017; Lesher et al. 2019).

In this study, we employ field observations to further constrain the formation of massive magnetitites; an approach that has been largely neglected in recent literature (e.g. Yuan et al. 2017). Furthermore, we combine our field observations with the two-dimensional distribution of Cr within magnetitite layers, obtained by geochemical mapping of the layers using a portable XRF spectrometer on closely-spaced grid patterns. Chromium’s extreme compatibility in magnetite (with a D value potentially exceeding 600; Irving 1974; Toplis and Corgne 2002; Castle and Herd 2017) makes it an ideal element to study the processes operating within magma chambers during their crystallization.

2 Field relations

This study focusses primarily on the prominent, 2 meter-thick Main Magnetite Layer from the Magnet Heights locality in the Eastern Limb of the Bushveld Complex, as well as numerous magnetitite layers from the lower portion of the Upper Zone from the Rhovan vanadium mine in the Western Limb. In general, massive magnetitite layers are characterized by sharp and planar basal contacts with their typically anorthositic footwall rocks, but they may also be locally underlain by gabbronorites. Upper contacts are typically gradational into the overlying lithology (Figure 1a). Undulations are also common in magnetitite layers and, in some instances, the contact with the footwall may become near-vertical (Figure 1b). On closer inspection, the contact between magnetitite layers and the footwall appears dimpled (Figure 1c), while larger (from a few to several tens of centimetres deep) depressions may also occur within the footwall (Figure 1d). Sub-angular to pod-shaped anorthosite inclusions are also frequently observed to occur within magnetitite layers.
Figure 1: Field photographs of exposures of massive magnetitite layers from the Bushveld Complex. (a) Magnetitite Layer 1 from the Eastern Limb of the Bushveld Complex, Magnet Heights area. Notice the planar basal contact and gradational upper contact. (b) The Main Magnetite Layer from the same locality with a pothole-like depression in its footwall. (c) A close-up picture of the Main Magnetite Layer revealing an uneven, dimpled contact with the footwall. (d) Pothole-like depressions in the footwall of the Main Magnetite Layer from the Rohovan vanadium mine in the Western Limb of the Bushveld Complex.

3 Distribution of Cr in magnetitite

The base of magnetitite layers is normally marked by strong reversals in the Cr content in pure magnetite. This trace element is also rapidly depleted upwards within magnetite layers, commonly exceeding 18,000 ppm at the base to less than 700 ppm after just 1 meter of crystallization. Significant lateral variations in the Cr content are also observed, as multiple dome-shaped structures occur at the bases of magnetitite layers with dramatically elevated Cr concentrations (up to 48,000 ppm compared to a typical concentration of 10,000 ppm at the base). Chromium concentration gradients may exceed 200 ppm/mm within these structures. Elevated Cr concentrations are recorded all along footwall contacts, even where the orientation of the footwall contact is near-vertical. The Cr concentration is also up to two times higher along the outer margin of anorthositic autolith inclusions compared to the surrounding magnetite and also occasionally host some of the dome-shaped high-Cr structures on their outer surfaces.

4 Discussion

The presence of high-Cr structures at the bases of magnetitite layers places great constraints on their petrogenesis. Their existence is most simply explained as the sites where magnetite first started nucleating and growing concentrically outwards directly on the footwall rocks (Cawthorn 1994). As these “growth nodes” grow outwards from their central point of origin, the Cr content of the magma is rapidly depleted. This depletion is recorded in the outward concentric decrease in the Cr concentration in the growth node. This interpretation has two important implications: magnetitite crystallized in situ and the melt was saturated in magnetite only. Models that have invoked crystal settling and/or sorting to explain the origin of these layers (e.g. Scoon & Mitchell 2012; Maier et al. 2013; Yuan et al. 2017) are not compatible with this interpretation.

Another constraint comes from the very rapid depletion of Cr upwards in magnetitite layers, which only appears to be possible if it crystallized from a relatively thin (approximately 20 to 60 meters high) column of magma, instead of the more than 1.5 km-thick magma chamber from which the Upper Zone is believed to have crystallized (Molyneux 1974; Kruger et al. 1987; Cawthorn et al. 1991). Clues regarding the origin of such a basal layer can be found in the field observations. A dimpled footwall contact, undulating layers and transgressive depressions in the footwall rocks (commonly referred to as potholes) are well-known to be associated with other rock types of the Bushveld Complex as well, such as the Pt-rich Merensky Reef and various chromitite layers, and are best explained by thermo-chemical erosion of the footwall rocks following magmatic recharge of the chamber (Campbell 1986; Latypov et al. 2015; 2017). This is further supported by the presence of Cr-reversals recorded at the bases of magnetitite layers. Elevated Cr concentration around anorthosite autoliths also indicate that they were surrounded by magnetite-saturated melt when magnetite started crystallizing, indicating that they are likely in situ remnants of thermochemical erosion of the footwall.
rocks.

A remaining question is how the incoming magma became saturated in magnetite only. It has recently been shown that it is possible to produce a chromite-saturated melt due to the pressure reduction associated with magma ascent from a deeper-seated staging chamber (Latypov et al. 2018). We assume that a similar mechanism may also be applied to magnetitite layers. A tholeiitic magma may have undergone significant silicate extraction at depth, leading to Fe-enrichment. When a pulse of this magma is released upwards to shallower regions of the crust, the boundaries on the phase diagram may shift in such a manner as to stabilize magnetite as the sole liquidus phase. This idea requires, however, rigorous phase equilibria testing.

5 Conclusion

Based on field and geochemical evidence, we propose the following sequence of events that led to the formation of massive magnetitite layers of the Bushveld Complex: (1) A mantle-derived tholeiitic magma ponded at a relatively deeper level in the crust or upper mantle. (2) During cooling of the melt it experienced significant silicate extraction, which led to Fe-enrichment typical of the tholeiitic differentiation trend. (3) A pulse of the evolved magma ascended to shallower levels in the crust until it intruded into the Bushveld magma chamber. The pressure decrease experienced by the magma during its ascent lowered its liquidus temperature and shifted the phase boundaries in such a manner as to move the magma composition into the magnetite field. This ensured the melt was in both thermal and chemical disequilibrium with its surroundings. (4) Due to the incoming magma’s high density (attributed to its high Fe-concentration) the magma formed a relatively thin basal flow on the chamber floor. (5) This was followed by thermo-chemical erosion of the chamber floor, producing irregularities such as depressions and undulations in the underlying cumulates. (6) After some degree of cooling of the new magma, magnetite started nucleating and growing in situ on its footwall, eventually forming a massive magnetitite layer.

Acknowledgements

The study was supported by several research grants to R.L. from DST-NRF CIMERA the National Research Foundation (NRF) of South Africa. Any opinion, finding and conclusion or recommendation expressed in this contribution is that of the authors and the DST-NRF CIMERA and NRF do not accept any liability in this regard. We would like to thank the personnel at Rhovan for granting us access to their site and their kind assistance with field work, Merrily Tau for his assistance in performing pXRF analysis in the Magnet Heights area, and Grant Cawthorn for providing us with samples and data used for calibration of the pXRF.

References


Geology and ophiolite complex-hosted magmatic Fe-Ni-Cu±Co-Au mineralization in Sebuku Island, Indonesia

Yoseph C. A. Swamidharma & Andhi Cahyadi
PT Sebuku Iron Lateritic Ores, Indonesia

Ade Kadarusman,
AKG Consulting, Indonesia

Ernowo Harjanto
Geological Agency of Indonesia

Arifudin Idrus*
Universitas Gadjah Mada, Indonesia

Abstract. Geological framework of Sebuku Island is predominantly occupied by ophiolite complex units including cumulate ultramafics, mafic volcanoclastics and gabbroic intrusions. Fe-Ni-Cu±Co-Au sulphides mineralization was discovered which is hosted by cumulus ultramafic rocks through exploration program of PT. Sebuku Iron Lateritic Ores. The thickness of the massive sulphide zone ranges 1-2.6 m and disseminated sulphide zone varies 1-3 m with the highest grade of 40% Fe, 1.3% Cu, 1.2% Ni, 0.51% Co and 1.8 ppm Au. Occurrence of mineralization is dictated by normal ultramafic rock but within complex structural zones due to tectonic events that produce specific mineralization styles on the island. Various phases of deposition are analyzed through: (i) major and trace element geochemical data derived from XRF, ICP-MS and (ii) petrography-mineragraphy by transmitted light microscopy, SEM and QEMSCAN. Phases of deposition are interpreted as follows: (i) Cr-Fe oxide mineralization in serpentinite, (ii) Fe-Ni-Cu sulphide mineralization in cumulus ultramafics (iii) enrichments through metasomatism and hydrothermal activity, and (iv) enrichment through lateritisation due to weathering. Trace metals are thought to be associated with the second mineralization phase. The occurrence of magmatic mineralization in Sebuku Island may imply the potential for more deposits in similar geological settings throughout Indonesia.

1 Introduction

Sebuku island is a small island located in the SE corner of South East Kalimantan, approximately 5 km east of Laut island. The island is administered by Kotabaru Regional District within South Kalimantan. The easiest access to the island from Jakarta, the capital city of Indonesia is through one and a half hours flight to Banjarmasin, followed by half an hour flight to Kotabaru and followed by one hour of speedboat from kotabaru port to Tanjung Nusantara port or Sungai Bali port.

PT. Sebuku Iron Lateritic Ores (PT.SILO) has produced iron ore since 2004 and is in the construction period to produce direct reduction iron and reduced nickel from detrital iron and Fe-Ni bearing laterite ores. Since 4th quarter of 2014, PT.SILO’s exploration and mining development team has explored for further mineral potential in both laterite and in the primary ultramafic complex unit. The mineral concession of PT.SILO is approximately 11,000 ha across the North East portion of Sebuku Island.

Sebuku Island is known to be host of numerous ore deposit types such as primary and lateritic iron ores, podiform chromite, W-Sb±Au quartz vein, REE, Sc and PGM-enriched iron ore and magmatic Fe-Ni-Cu±Co-Au mineralization (Swamidharma et al. 2016; Cahyadi et al. 2017; Swamidharma et al. 2018).

Currently PT. SILO focus activity on the development and exploration of the magmatic Fe-Ni-Cu±Co-Au deposit type. Deep drilling to confirm the best location for the Iron Ores deposit with guidelines from the distribution of high magnetic anomalies resulting from airborne magnetic survey. One drill holes of SDD 009 at Madang Belakang location penetrated a 2 m intercept at 56m depth of mineralization characterized by magnetite associated with Fe-Ni-Cu-sulphide minerals (pyrrhotite, pentlandite and chalcopyrite). The 2 m intercept at SDD 009 should be considered the first significant discovery Ni-Sulphides in Indonesia.

This paper is aimed to review the geological framework of Sebuku Island as well as to discuss the characteristics and origin of the magmatic Fe-Ni-Cu±Co-Au mineralization. This is a significant frontier work in discovering magmatic Fe-Ni-Cu±Co-Au deposit type, which could be a guideline and exploration model of the primary ore in Indonesia in the future.

2 Geology of Sebuku Island

Geology of Sebuku Island (Fig. 1) is covered by the youngest quaternary unconsolidated sediment materials in most of north west part and further south east by a coal bearing sediments of Eocene-age known as the Tanjung Formation. The rest is mostly occupied by the ophiolite complex unit that includes pelagic sediment, gabbro dykes, cumulus ultramafics and the detrital iron ore unit. These rocks are dated from late Triassic to early Cretaceous, except, to some extent, North South trending of volcanoclastic of late Cretaceous Haruyan formation in the central part of the island.
Throughout pre Tertiary, several plutonic rocks intruded the units, including gabbro, diorite and andesite plutons. Due to thick laterisation, limited accessible bedrock can be identified during surface mapping. Due to the same reason, soil sampling may fail to provide useful information. Also, limited active streams in the concession prevent stream sediment geochemical sampling from delineating the prospect area.

Best exposed lithologies are within the open pit perimeter although it also depends on Fe grade where depth of excavation is limited to top saprolitic material only. Second best bedrock observation is from drill core which is designed to target 3m below enriched saprolite.

3 Methodology

Six polished thin sections were studied under the microscope to describe the petrography, then carbon coated for scanning electron microscopy in attempt to obtain better quantitative information.

Major elements and trace elements concentration of 32 samples were analyzed using X-Ray Fluorescence (XRF) and Inductivity Coupled Plasma Mass Spectrometer (ICP-MS), respectively.

QEMSCAN analysis carried out to obtain higher degree of quantitative as well as to preserve original fabric and texture of petrology and mineralogy.

4 Tectonic Setting and Structures

Most of authors of early tectonic studies in the regions includes Koosesumadinata et al. 1989; Van der Weerd et al. 1992; Setyana et al. 1999; Wilson et al. 1999; Moss et al. 2000; Hall 2009 and so on, agreed that Sebuku island is part of the Laut Island ridge, oceanic crust material generated at a convergent boundary to Sundaland in NW and compressed toward WNW by Patenoster Platform, a microcontinent, from SE.

However, disagreements still exist, notably, whether the ridge is an exposed sub lithospheric continental material or the ridge is obducted material as part of accretionary wedge of subduction zone. Nonetheless, this tectonic activity forms geology and structure of Sebuku Island.

Airborne Magnetic data carried out by the last quarter of 2015. Interpretation of data from a 2015 airborne magnetic survey concludes an identification of a NNE major structural trend below 400m. Structural interpretation above 400m is influenced by brittle deformation of serpentinised ultramafics, therefore incapable to delineate any useful trends.

The magnetic data also provide the approximate location of intrusive bodies (dykes) and trend of potentially shallow high magnetic anomaly. This information was used to locate first potential target for primary mineralization (Fig. 2).

5 Host Rocks

Host rock ultramafic majorly comprises dunite and harzburgite with minor gabbro, anorthosite and troctolite which occasionally develops thin stratiform layers at the base, as indicator of in or near petrological moho boundary between cumulate and tectonized ultramafic. This cumulate is also altered to develop serpentine assemblage and or soapstone/talc assemblage, due to gabbro dyke intrusion cross cut this ultramafic to develop such as low-grade metamorphism.
5.1 Host rocks petrography

The ultramafic rocks mostly altered to serpentinite with minor to talc carbonate assemblage and some further altered to tremolite (Fig. 3a). Younger phases of serpentine and chlorite also are seen crosscutting older mineral in vein (Fig. 3b). Fe stringers are developed along serpentine grain boundaries, while euhedral opaque spinel is disseminated throughout this rock and sometimes zone out to magnetite or totally replaced by Fe oxide.

Figure 3. Photomicrograph of serpentine. a) Ca silicate with remnant serpentine, b) Serpentine with stringer Fe and euhedral spinel crosscut by chlorite.

5.2 Host rock geochemistry

Petrochemistry applied to host rocks is limited to gabbro due to alteration of ultramafic to serpentine and talc carbonate assemblages. REE plots indicate the unit is in cumulus mafic-ultramafic.

Plots normalized to primitive mantle (Fig. 4a) shows all elements are enriched relatively and normalized to normal mid oceanic ridge basalt (Fig. 4b) shows majorly slightly below reference value. The deficit to reference value of MORB is considered acceptable. This deficit is thought to be caused by volatiles (H2O, CO2, S etc.) introduced to this unit. Trace element scatter diagrams confirm data shown in the REE plots.

6 Fe-Ni-Cu Sulphide Mineralization

The first drillhole to intercept massive sulphide mineralization is SDD0009 at the depth of 50.80 - 52.65 m. Others intercept various concentration of disseminated and massive sulphide mineralization (up to 5m). Ni sulphide occurs as pentlandite (Fig. 5).

In massive sulphides, pentlandite is always in association with magnetite, pyrrhotite and with smaller amounts of pyrite, chalcopyrite and other unidentified trace minerals. All massive sulphides occur in fine grains and euhedral form, as belbs-veins-stockworks to or cut/scavange fractures/sheets of serpentiniised ultramafic host rock.

Disseminated sulphide zones ranging 1-3% up to 8-10% sulphide and occur as crystals (replacing cpx? or Cr?) in serpentiniised ultramafic rocks. Minor Ni-sulphides are disseminated throughout sample and tend to be higher concentrate in association with Fe oxide rather than in serpentinite.

Figure 5. SEM backscattered images showing a) Individual grain of pentlandite in serpentine and b) disseminated pentlandite in Fe oxide.

The massive sulphides consist of intergrown pyrite, pyrrhotite, chalcopyrite, pentlandite, Co-pentlandite, cobaltite with inclusion of gold. Palladium is the only PGE found in the sample even in low concentrations. The sulphides fracture fill and breccias matrices fill in serpentine and chlorite of ultramafic origin which has remnant euhedral chromite and Fe-oxide magnetite hematite.

Geochemistry of massive sulphide yields reasonable fit to mineralogy discussed above. Major elements composition i.e. Fe, MgO, SiO2, Al2O3, CaO, Na2O and K2O are still reasonable for mafic-ultramafic classification without acidic (continental crust) influence and or hydrothermal alteration.

Sulphur is at reasonably high (~18%) and corresponds to yields of Fe, Ni and Cu at 40%, 1.6% and 1,1% respectively. Co has positive correlation to Ni in sulphide condition. High Ni sulphide is accompanied by high Co thus Ni/Co ratio decrease. This relationship is expected in Co-pentlandite (Fig. 6).
Figure 6. Fieldscan image QEMSCAN of sample SDD 0009.2C 52-52.65 m section HG/I/4.

7 Discussion

The mineralogy is a set of minerals comprising of chalcophile elements which bounding chemically to construct sulphides, arsenides minerals within a magmatic sulphide deposit environment (Schulz et al. 2010). At present there is no economic magmatic sulphide deposit generated in pure MORB and ophiolite complex environment.

Further study is carried out particularly to follow up remnant metamorphism in talc carbonate assemblages in attempt to discover potential partial melting "plume" magmatism which responsible to magmatic sulphide occurrence in SILO.

Gabbro intrusion and other potentials within SILO i.e. stratiform chromite, hydrothermal As-Sb, detrital iron and lateritic Fe-Ni deposits are not covered in this paper and may be the subject of future research.

8 Conclusion

The Fe-Ni-Cu±Co-Au massive sulphides mineralization in Sebuku Island is hosted by cumulus ultramafic rocks of an ophiolite complex. The thickness of the massive sulphide zone ranges 1-2.6 m and disseminated sulphide zone varies 1-3 m with the highest grade of 40% Fe, 1.3% Cu, 1.2% Ni, 0.51% Co and 1.8 ppm Au. The magmatic Cu-Ni-sulphide deposit type is majorly developed by specific tectonic setting and structure so that the massive sulphide occurred in specific structural trap even in normal MORB-origin ophiolite environment and without any obvious sulphur source or sulphur saturated environment.

Advanced petrological–mineralogical tools and geochemical tools are proved to assist SILO to conduct problem solving map to optimize exploration program. The occurrence of magmatic mineralization in Sebuku Island may imply the potential of the similar deposit type in the similar geological setting in Indonesia.

Acknowledgements

Special thanks to the management of SILO for the permission to use their data for this study and the geologist who done most of hard works in the field. Sincere thanks goes to Dr Duncan Pirrie for advanced study in petrography and mineralogy. We also thank to anonymous reviewer for improvement of the manuscript.

References

Schulz KJ et al. (2010) Magmatic Sulfide-Rich Nickel-Copper Deposits Related to Picrite and (or) Tholeiitic Basalt Dike-Sill Complexes: A Preliminary Deposit Model.
Pathfinder mineral geochemistry for magmatic oxide and sulfide mineralization: insights from trace elements in Fe-oxides determined by laser ablation ICP-MS

Sarah. A.S. Dare,
Université du Québec à Chicoutimi, QC, Canada (Canada Research Chair in Geochemistry Applied to Ore Deposits)

Mark Grant, Matthew Polivchuk
University of Ottawa, ON, Canada

Erin Bethell
Carleton University, ON, Canada

Abstract. The trace element chemistry of magnetite, which is common in both magmatic oxide and sulfide mineralization, is distinctive in different ore deposit types. This means that magnetite chemistry could be used as a pathfinder during the exploration of mineral deposits, including magmatic ones, using detrital magnetite recovered in surficial sediments. However, this will only work if it is possible to first discriminate magnetite in mineralized from unmineralized rocks. We have investigated this for magmatic ore systems and their host intrusions from a range of tectonic settings and metamorphic conditions. We use a petrogenetic approach to better understand the processes (magmatic and sub-solidus) that control the trace element chemistry of magnetite in order to propose new discrimination diagrams for mineral exploration and sedimentary provenance. The origin of igneous magnetite can now be identified as coming from: 1) An intrusion of mafic-intermediate composition that could be prospective for magmatic oxide deposits, including an indicator of fertility for Ni-sulfide mineralization at depth; 2) Oxide-rich V mineralization itself, rather than disseminated oxides (uneconomic) in the host rock.

1 Introduction
The trace element chemistry of magnetite is currently under development as a pathfinder mineral for the exploration of mineral deposits using detrital grains in glacial till and sediments. This is because magnetite is: 1) A resistant mineral that is readily recovered from surficial sediments; 2) Common in a wide variety of ore deposits; 3) Has distinctive chemical signatures from different ore-forming environments (Dupuis and Beaudoin 2011; Nadoll et al. 2014; Dare et al. 2014). For example, using discrimination diagram of Dupuis and Beaudoin (2011) it is possible to distinguish magnetite in 1) massive Ni-sulfide ore (high Ni+Cr) and 2) massive Fe-Ti-V ore (high Ti+V) from all other hydrothermal deposit types. Furthermore, once the signature of magnetite from massive sulfide is identified, it is possible to determine, using the Cr-Ti-V content of magnetite, whether the massive sulfide is Fe-Ni-rich or Cu-Pt-Pd-rich (Dare et al. 2012; Boutroy et al. 2014).

However, magnetite is also a common accessory mineral in unmineralized rocks (igneous, metamorphic, hydrothermal and sedimentary) but there is currently no systematic way to discriminate magnetite in barren bedrock from magnetite associated with mineralization. Whereas hydrothermal magnetite is poorer in Ti (< 2 wt.%) than magnetite from mafic-intermediate igneous rocks, magnetite in felsic rocks is also low in Ti (Fig. 1). Therefore, in Duparc et al. (2016), we proposed that the Ti vs. Ni/Cr ratio readily distinguishes hydrothermal magnetite from that of igneous origin (Fig. 1). Therefore, in Duparc et al. (2016), we proposed that the Ti vs. Ni/Cr diagram should be used first to filter out detrital igneous magnetite, in particular low-Ti magnetite from felsic rocks, before using discrimination diagrams of Dupuis and Beaudoin (2011) and Nadoll et al. (2014). Otherwise low-Ti magnetite from felsic rocks would be misidentified as coming from a variety of hydrothermal

Figure 1: The Ti vs. Ni/Cr diagram to discriminate hydrothermal from magmatic magnetite. In igneous magnetite, Ni and Cr both decrease during differentiation of silicate magmas (lower Ni/Cr ratios). In hydrothermal systems, Cr is immobile compared to Ni (higher Ni/Cr ratios in magnetite). Modified from Dare et al. (2014). Additional data: Duparc et al. (2016); Nadoll et al. (2014).

In magmatic ore systems, Ni-Cu-(PGE) sulfide mineralization typically forms from magmas of ultramafic-mafic composition whereas Fe-Ti-V-P oxide
mineralization typically crystallizes from more evolved magma compositions (mafic-intermediate). Few have tried to distinguish magmatic ore from its host igneous intrusion (Ward et al. 2018). Given that the chemistry of magnetite is highly dependent on the conditions of formation (composition of magma/fluid, competition with co-existing minerals and physico-chemical parameters, such as temperature, redox, and partition coefficients; Dare et al. 2014; Nadoll et al. 2014) it could be challenging to discriminate magnetite in magmatic ore from its host rocks because magmatic conditions during their formation are similar, especially for oxide systems. Therefore, the aim of this study is to better distinguish magnetite in magmatic ore deposits from their host intrusions so that magnetite discrimination could be more realistically applied in mineral exploration of magmatic ore systems using detrital magnetite. We use a petrogenetic approach, rather than a statistical one, to better understand the processes that control trace element distribution in magnetite during both magmatic and post-magmatic processes in order to develop a robust series of discrimination diagrams.

2 Magmatic oxide systems

Magmatic Fe-oxide deposits are important sources of Ti (ilmenite), V (magnetite) and P (apatite). They typically crystallise from an evolved silicate melt (~ferrodiorite in composition) but the exact timing of magnetite crystallization can vary with fO₂ conditions and initial composition of the magma (Namur et al. 2010).

Dare et al. (2014) demonstrated that the trace element composition of magnetite from massive oxide layers varies with fractional crystallization (Fig. 2A). Magnetite from V deposits (i.e. lowermost layers) have a more primitive signature (enriched in compatible elements: Cr, Ni, V, Co, Mg) than magnetite from P deposits (i.e. uppermost layers), which are more evolved (depleted in compatible but enriched in incompatible elements: Ti, Mn, Sn, Mo and high field strength elements (HFSE – Nb, Ta, Sc, Zr and Hf). Granite represents extreme degrees of fractionation and its magnetite is extremely poor in Ti and HFSE due to crystallization of accessory phases (e.g., titanite and zircon).

2.1 Samples and methods

This research combines detailed studies on Fe-Ti oxide chemistry and petrography from several Fe-Ti-V±P oxide deposits (and their host intrusions), chosen to represent different degrees of metamorphism and tectonic settings. 1) The Upper Zone of the 2.06 Ga Bushveld Complex (unmetamorphosed), the world’s largest layered intrusion and part of a plume-related large igneous province in South Africa. 2) The 2.7 Ga Rivièrè Bell Complex (greenschist facies), a small-layered intrusion hosting V mineralization in the Abitibi greenstone belt, Canada. 3) The 1.1 Ga Lac-St-Jean Anorthosite Massif (granulite facies), Canada, hosting numerous small, sub-economic V and P deposits. A suite of 25 trace elements was determined in magnetite and co-existing ilmenite ± Al-spinel using laser ablation ICP-MS at the University of Ottawa following the method outlined in Dare et al. (2014). Major and minor elements were also determined using the electron microprobe at the University of Ottawa.

2.2 Magnetite chemistry as indicator of magmatic and post-magmatic processes

Magmatic magnetite in these intrusions are commonly Ti-rich (2 - 20 wt.% TiO₂, i.e. titanomagnetite) but during cooling its original composition is readily modified by post-magmatic processes, such as sub-solidus re-equilibration with silicates and oxy-exsolution of ilmenite ± exsolution of Al-spinel. The LA-ICP-MS results indicate that during oxy-exsolution Ti, HFSE, Mg, Mn, W, and Sn are preferentially enriched in ilmenite, Al, Mn, Zn, Ga (Co, Ni, Ge less so) are preferentially enriched in Al-spinel whereas only Cr, V, Mo are enriched in magnetite.
Our new data from the unmetamorphosed Bushveld Complex reveals that magnetite in disseminated samples (< 30% oxide) have consistently much lower contents of Mg and Co than oxide-rich samples, at the same stratigraphic level. This is quantified by the Mg/V ratio (Fig. 3). In contrast, other divalent cations, namely Ni and Zn, are less affected by re-equilibration with silicates. Magnetite in disseminated samples also have lower Ti and HFSE concentrations due to more extensive oxy-exsolution of ilmenite than in oxide-rich samples. Modification of magnetite by reaction with trapped liquid, which occurs only in oxide-poor samples (< 10%), is also recorded by an increase in incompatible elements (e.g., Zn) in magnetite.

Chemical modification of magnetite by the sub-solidus processes described above is enhanced during metamorphism. Magnetite in metamorphosed intrusions, such as those in greenstone belts (greenschist–amphibolite facies) show more extensive (oxy-) exsolution of ilmenite and Al-spinel that is typically fine-grained enough to be re-incorporated into magnetite during analysis by LA-ICP-MS. However, the depletion of Mg in magnetite during re-equilibration with silicates is extensive and is not just limited to disseminated oxides but also affects semi-massive oxides. The oxide deposits of the Lac St-Jean anorthosite massif, have remained hot a very long time at granulite facies. Many of these deposits show extensive (oxy-) exsolution and coarsening of both ilmenite and Al-spinel (< 1 cm in size) from the original titanomagnetite. In this case the composition of magnetite dramatically changes (Fig. 2B): magnetite is not only significantly poorer in Ti, Mn and HFSE, due to oxy-exsolution of ilmenite, but also in Al, Mg, Zn due to exsolution of Al-spinel. The amount of exsolution is highest in disseminated samples. The resulting ‘clean’ magnetite is extremely Ti poor (several 1000s ppm Ti: Fig. 4A), devoid of fine-grained exsolutions, but subsequently enriched in elements that prefer magnetite (i.e. Cr, V – Fig. 2B). Therefore, care must be taken in using Cr and V content of magnetite for tracking differentiation in highly metamorphosed intrusions that have undergone extensive exsolution and textural coarsening.

2.3 Magnetite chemistry as a pathfinder mineral for V mineralization

Based on a better understanding of how post-magmatic processes can modify the initial composition of magnetite during cooling and metamorphism, a sequence of new discrimination diagrams is proposed to better identify igneous magnetite that come from i) an intrusion of mafic-intermediate composition that could be prospective for magmatic ore deposits and ii) oxide-rich mineralization, rather than disseminated host rock.

---

**Figure 3:** Mg/V vs. V diagram to discriminate magnetite in igneous rocks containing massive (msv.) to semi-massive oxides (> 40% oxides), associated with V mineralization, from disseminated (diss.) oxides in the host intrusion due to loss of Mg during re-equilibration with silicates (indicated by arrow).

**Figure 4:** Discrimination diagrams to identify magnetite from intrusions of mafic-intermediate composition (prospective for V-P deposits) and of ultramafic-mafic composition (prospective for Ni sulfide deposits). A) First, identify magnetite of igneous origin using Ti vs. Ni/Cr diagram. B) Second, filter out magnetite of felsic composition from magnetite associated with ultramafic-mafic-intermediate intrusions using Ti/Zn vs Mg/V diagram. Additional data sources: Dare et al. (2014, 2015) and Duran (2015).
First, magnetite is identified as igneous in origin using the Ti vs Ni/Cr diagram (Fig. 4A). For cases of extreme modification of magnetite in granulite terrains, such as Anorthosite-hosted deposits, the resulting low-Ti magnetite still plots in the igneous field (i.e. low Ni/Cr ratio) as Cr is enriched relative to Ni. However, many anorthosite-hosted magnetite now plot in the felsic field (< 2 wt.% Ti). Therefore, a second diagram, Ti/Zn vs Mg/V (Fig. 4B), is proposed to discriminate (and filter out) low-Ti magnetite in felsic rock from low-Ti magnetite from mafic/intermediate intrusions, to negate the effect of post-cumulus modification. Magnetite from felsic rocks have high Zn contents, because the melt is highly evolved (Fig. 2A), and therefore have low Ti/Zn ratios. In contrast, low-Ti magnetite resulting from extensive exsolution of titanomagnetite in Anorthosite-hosted deposits have high Ti/Zn ratios, similar to less modified magnetite from mafic/intermediate intrusions. This is because both Ti and Zn are depleted together from magnetite during extensive exsolution of Al-spinel and ilmenite (Fig. 2B). The Mg/V ratio is used to help distinguish magnetite in oxide-rich mineralization (higher Mg/V ratios) from that in disseminated host rocks (lower Mg/V ratios), due to Mg diffusion during sub-solidus re-equilibration with silicates. Once a mineralized sample is identified, then its Ni-Cr content (Fig. 2A) can be used to identify if it is from a more primitive melt (i.e. early forming magnetite, typical of V mineralization, if redox conditions are suitable) or from an evolved melt (i.e. later forming magnetite, co-crystallizing with apatite and perhaps a P deposit). Ultimately, its V content is used to evaluate the V potential of the mineralization (Fig. 3).

3 Magmatic sulfide systems

Identifying the fertility of mafic-ultramafic intrusions to host Ni-Cu-PGE deposits can be a useful vectoring tool during exploration. Numerous tools exist to identify chalcopyhile depletion in host intrusions, that result during sulfide saturation and accumulation at depth, using whole rock ratios, such as Ni/Ni*, Cu/Zn and Cu/Pd (e.g., Darling et al. 2010). Dare et al. (2015) demonstrated the potential of magnetite and ilmenite to also record significant sulfide formation, via Ni and Cu depletion, in the igneous complexes that host world-class Ni deposits, such as Sudbury and Voisey’s Bay mining camps in Canada.

In the host intrusions of the Ni sulfide deposits studied, magnetite commonly co-crystallizes with ilmenite and is typically intercumulus at the stratigraphic level of sulfide mineralization but becomes cumulus (weakly disseminated only) higher up the sequence. Magnetic data from the disseminated host rocks of Ni deposits are plotted on Figures 3 – 4 to test the new discrimination diagrams. Some of the magnetite is low in Ti (<2 wt.% Ti) and plot in the felsic field on the Ti vs. Ni/Cr diagram (Fig. 4A). However, the new Ti/Zn vs. Mg/V diagram (Fig. 4B) is able to correctly identify them as: 1) Coming from mafic-intermediate intrusions rather than felsic intrusions; 2) Having low oxide content (disseminated host rock), although there is some overlap with the field of massive oxide. However, they correctly plot in the disseminated oxide field in the Mg/V vs. V diagram (Fig. 3). This highlights the fact that a combination of diagrams must be used together to optimize correct identification of magnetite from mineralization and barren host rock.

Acknowledgements

The research was funded by NSERC Discovery Grant (RGPIN-2015-05924) and the University of Ottawa start-up fund of S. Dare. Thanks are given to S. Morfin and G. Poirier for their technical support in the LA-ICP-MS and EMPA laboratories at the University of Ottawa.

References


Magmatic Sulfide and Oxide Systems
Reactivation and enrichment of a Gondwana margin Ni-Cu-PGE-(Te-Au) mineral system during the breakup of Pangea

Marco Fiorentini, Steve Denyszyn, Greg Dering
University of Western Australia

David Holwell, Daryl Blanks
University of Leicester, UK

Roland Maas
University of Melbourne, Australia

Marek Locmelis
Missouri University of Science & Technology

Crystal Laflamme
Universite Laval

Abstract. The lower crustal domains of the Ivrea Zone of NW Italy record the polyphase evolution of a Ni-Cu-PGE-(Te-Au) magmatic sulfide mineral system, which formed during multiple stages over an 80 Myr interval along the NW margin of Gondwana. Between 290-250 Ma, a series of hydrated and carbonated ultramafic alkaline pipes containing Ni-Cu-PGE-(Te-Au) mineralisation was emplaced in the lower continental crust of the Ivrea Zone. Subsequently, at 200 Ma Ni-Cu-PGE mineralisation was associated with emplacement of the La Balma-Monte Capio (LBMC) ultramafic intrusion. The composition and metal endowment of the LBMC reflects interaction and mixing between a deeply sourced juvenile and relatively dry primitive magma, most likely associated with the Central Atlantic Magmatic Province, with localised pods enriched in volatiles, metals, sulfur and tellurium, consistent with the composition of the Permo-Triassic pipes. The scenario depicted here may explain why ore deposits along the margins of lithospheric blocks are not distributed homogeneously along their entire extension but generally form clusters. As mineral exploration is essentially a search space reduction exercise, this new understanding may prove to be important in predictive exploration targeting for new mineralised camps, as it provides a way to prioritise segments with enhanced fertility along extensive lithospheric block margins.

1 Introduction

The Ivrea Zone, a well-known section of exhumed lower continental crust in the southern Alps of Italy, was deformed and metamorphosed during the ca. 420–300 Ma Variscan Orogeny, the result of collision between Laurussia and Gondwana during the formation of Pangaea. Following the peak of regional metamorphism, underplating and intrusion of voluminous mafic magmas formed the 287 Ma Mafic Complex (e.g., Peressini et al. 2007; Fiorentini et al. 2018). A series of alkaline pipes containing widespread Ni-Cu-PGE-(Te-Au) mineralisation intruded both the Mafic Complex and the metasedimentary host rocks from 287 Ma to 249 Ma (Fiorentini et al. 2018). Tectonic overprint of the Alpine orogeny from ca. 100 Ma onward was relatively minor and mainly resulted in tilting of the entire section and subsequent exhumation along a major lithospheric boundary marked by the Insubric Line (e.g., Wolff et al. 2012).

Extending north from the Mafic Complex are mafic and ultramafic bodies that have historically been considered as attenuated intrusions emplaced in the lower to middle crust. The largest ultramafic body among these is the La Balma-Monte Capio (LBMC) intrusion, which contains significant Ni-Cu-PGE-(Te-Au) mineralisation. Ferrario et al. (1983) suggested that it formed by in situ differentiation of a high-Mg magma emplaced coevally with the Mafic Complex (i.e., at 287 Ma). However, new isotopic and geochronological data presented in Denyszyn et al. (2018) reveal that the LBMC intrusion represents a distinct magmatic event in the Ivrea Zone, with major implications for our understanding of the emplacement of one of the largest large igneous provinces (LIPs) in the geological record, and for the development of a significant mineralisation event.

Mafic and ultramafic magmas that intrude into the lower crust can preserve evidence for transfer of metal and S from the lithospheric mantle into continental crust. The Ni-Cu-PGE-(Te-Au) mineral system archived in the Ivrea Zone illustrates how the lower continental crust can be locally fertilised with mantle-derived metals and volatiles, which are available for later remobilisation into a range of ore systems at various lithospheric depths. It has previously been proposed that the spatial correlation of world-class mineral deposits with the margins of lithospheric blocks is the result of crustal architecture that promotes focused flux of fluids and mantle-derived magmas (Begg et al. 2010). In addition to favourable pathways, our work suggests that localised volatile and metal enrichment of the lower crust related to mantle-derived hydrous (and carbonate) metasomatism plays a role in the distribution of mineral deposits along lithospheric boundaries.
2 The Permo-Triassic Ni-Cu-PGE-(Te-Au) mineral system related to post-collisional gravitational collapse of the Variscan Orogen

Early mineralization is associated with a series of ultramafic, alkaline pipes emplaced after formation of the Mafic Complex, a major crustal underplating event precisely dated via U/Pb CA-IDTIMS on zircon at 286.8 ± 0.4 Ma (Fiorentini et al. 2018). The ultramafic pipes are 100 to 300 m wide and form cumulate-rich conduits that intrude gabbrro and dioritic rocks of the Mafic Complex at mid-crustal depths (Demarchi et al. 1998). They are hydrated and carbonated, have unusually high incompatible element concentrations and contain blebby and semi-massive Ni-Cu-PGE sulfide mineralisation.

The sulfides occur as coarse intergranular nodules (> 10 mm) and as small intragranular blebs (< 1 mm) hosted in olivine (Vukmanovic et al. 2018), and have homogeneous, mantle-like δ34S (Fiorentini et al. 2018). This homogeneity suggests that the pipes reached sulfide supersaturation without addition of crustal sulfur, and that the δ34S signature is representative of the continental lithospheric mantle. One of the pipes, the 249 Ma Valmaggia pipe, carries a very distinctive Sr-Nd-Hf-Pb isotopic composition, which requires a source with long-term (2500 to 1500 Myr) U-, Th- and Rb-depletion and LREE enrichment (Fiorentini et al. 2018). During post-collisional gravitational collapse of the Variscan Orogen, this source produced the alkaline mafic–ultramafic magma enriched in Ni-Cu-PGE-(Te-Au) and volatiles (H2O, CO2, S), which formed the deep-crustal intrusion at Valmaggia. U/Pb dating of other chemically and geologically comparable pipes in the area show that this process was active over at least 40 Myr (Fiorentini et al. 2018).

3 The Jurassic Ni-Cu-PGE mineral system related to emplacement of magmas of the Central Atlantic Magmatic Province

The LBMC intrusion is a north-striking tabular body, approximately 400 m thick and > 3 km long that dips steeply east, concordant with the overlying metasedimentary rocks. Regional tilting effectively exposes a cross section of the intrusion, with basal dunes grading to plagioclase pyroxenites at the top (cf. Ferrario et al. 1983). Magmatic Ni-Cu-PGE mineralization occurs as disseminated, blebby, and locally net-textured sulfides in horizons throughout the intrusion, in places reaching 10% in volume. The roof of the body displays metre-scale intrusive relationships with the overlying high-grade metasedimentary rocks, referred to as the Kinzigite Formation (Garuti et al. 1980). The base of the intrusion is strongly modified by southeast-vergent thrust faults in the footwall of the Insubric Line (Denyszyn et al. 2018). Across this faulted footwall contact, migmatites of the Kinzigite Formation are interlayered with a belt of garnet-bearing gabbros of Permian–Carboniferous age, previously referred to as the Monte Capio sill (Klötzli et al. 2014). The original lateral extent of the LBMC intrusion is unconstrained because of faulting and younger cover.

The LBMC intrusion differs from other mafic-ultramafic bodies in the Ivrea Zone in its geometry and mineralisation style (Garuti et al. 1990). It is ~400 m thick and mostly dunitic, compared to the < 30-m-thick pyroxenitic sills in the lowermost Mafic Complex or the Permo-Triassic < 300-m-wide alkaline pipes emplaced within the Mafic Complex and Kinzigite Formation.

The recent precise U/Pb CA-IDTIMS age of 200 Ma led Denyszyn et al. (2018) to suggest the LBMC intrusion is a deep and distal expression of the Central Atlantic Magmatic Province (CAMP), which is related to the opening of the central Atlantic Ocean and thus the breakup of Pangaea (e.g., Ruiz-Martinez et al. 2012). The driver for CAMP magmatism may be a mantle plume (e.g., Wilson 1997), though thermal anomalies inducing mantle melting in the absence of any deeper mantle source have also been proposed (e.g., McHone 2000).

New information from trace element geochemistry as well as stable and radiogenic isotopes indicates that the composition of the LBMC intrusion reflects interaction and mixing between a deeply sourced juvenile and relatively dry primitive magma, most likely associated with the CAMP (Denyszyn et al. 2018), with localised pods enriched in volatiles, metals, S and Te, consistent with the composition of the Permo-Triassic pipes (Fiorentini et al. 2018).

The results presented in this study, which include new field observations integrated with petrological, geochemical and isotopic data, constrain the internal architecture of the LBMC intrusion and question the existing interpretation of formation as a layered sequence produced by in situ fractionation (Ferrario et al. 1983). New mapping and structural analyses combined with thermodynamic modelling of this largely dunitic body have implications for emplacement dynamics and the geodynamic setting of intrusion and mineralisation. The outcome of our work supports the hypothesis of Fiorentini et al. (2018) that enhanced potential for ore formation at lithospheric margins may be due not only to favourable architecture conducive to focussing of magmas and fluids (e.g., Begg et al. 2010; Mole et al. 2013), but also to localised enhanced metal and volatile fertility (cf. Laflamme et al. 2018).

4 The lower crust as a key to fertility

At the time of emplacement of the LBMC intrusion, the physical and chemical structure of the crust in the Ivrea Zone had been strongly modified by emplacement of the Mafic Complex > 80 Ma earlier. The process of magmatic underplating in the Ivrea Zone (e.g., Quick et al. 2009) has been compared to layering and densification of lower continental crust in other extensional terranes, such as the central Basin and Range province (western North America; Rutter et al. 1993), yet the long-term effects of these physical changes on crustal evolution and the effects on later magmatic episodes are poorly known.
As Denyszyn et al. (2018) discussed, the LBMC intrusion seems to have exploited the transition in the lower crust where the Permian underplate (i.e., the Mafic Complex) is in contact with metasedimentary host rocks (i.e., the Kinzigite Formation). Studies of the structural position of the LBMC intrusion with respect to such petrological and rheological boundaries may yield insight into mechanisms of magma ascent and arrest in the lower crust.

The proposed temporal and genetic link between 200 Ma magmatism in the Ivrea Zone and the CAMP is supported by the position of the Ivrea Zone near a major lithospheric suture, the Insubric Line, which separates the European and Adria plates. Emplacement of mantle-derived magmas is commonly localised along lithospheric boundaries (Gorczyk et al. 2017), as is the occurrence of magmatic Ni-Cu-PGE mineralisation (Begg et al. 2010), preferentially in areas where previous S and metal enrichment of the lower continental crust may enhance localised sulfide saturation in ascending mantle-derived magmas (Fiorentini et al. 2018). The crustal suture represented by the Insubric Line may have created pathways that promoted interaction of CAMP-related magma with pre-existing metal- and volatile-enriched pipes stored in the lower crust.

The scenario depicted here may explain why ore deposits along the margins of lithospheric blocks are not distributed homogeneously along their entire extension but generally form clusters. As mineral exploration is essentially a search space reduction exercise, this new understanding may prove to be important in predictive exploration targeting for new mineralised camps, as it provides a way to prioritise segments with enhanced fertility along extensive lithospheric block margins.

Acknowledgements

This work is funded by the Australian Research Council grant “Metal Sources and Transport Mechanisms in the Deep Lithosphere” Centre of Excellence for Core to Crust Fluid Systems (CCFS, CE11E0070) and by NERC grant NE/M010848/1 “TeaSe: tellurium and selenium cycling and supply” awarded to the University of Leicester.

References


Ferrario A, Garutti G, Rossi A, Sighinolfi GP (1983) Petrographic and metallogenic outlines of the “La Balma–M. Capio” ultrama c c body (Ivrea-Verbano basic complex, NW Italian Alps), in


Formation and disruption of Cu-Ni-PGE deposits in a giant deep-seated mafic-ultramafic conduit system

Rune B. Larsen, Bjørn E. Sørensen, Even Nikolaisen

Department of Geosciences and Petroleum, NTNU, Trondheim, Norway

Abstract. The Central Iapetus Magmatic Province (CIMP, Ma 610-560) is a prominent worldwide LIP, well known from Greenland, Labrador, North America, the Baltic shield and South Africa. The Seiland Igneous Province (SIP) forming at Ma 570-520, in NW-Norway comprises the most deep-seated parts of the CIMP event (0.6-1.0 GPa). The SIP is a high yielding, mafic-ultramafic-alkaline conduit system conveying thousands of km³ of melts from the asthenosphere to the continental lithosphere. In the SIP, we have located several meter’s wide sub-horizontal Cu-Ni-PGE occurrences in the Reinfjord ultramafic conduit system (Fig. 1). The deposits carry up to 1.7 g/t total PGE with c. 75% PPGE+Au and 25 % IPGE including 0.2 g/t osmium. Other deposits have c. 0.1 wt% Cu and up to 0.4 wt% Ni i.e. they are not particularly rich, however, with thicknesses of 10-20 meters over >0.5 Km², they represent considerable tonnages. The PGE and Cu+Ni occurrences are decoupled. The PGE-horizons are mostly situated in dunitic cumulates, which formed from picritic melts in the most primitive parts of the intrusion. The sulphides as well as the PGMs are closely associated with carbonated as well as hydrous mineral assemblages that formed from immiscible alkaline melts that are co-genetic with and/or dissolved in the picritic melts and may play an important role in both formation and remobilization of the immiscible sulphide droplets.

1 Significance of large deep-seated conduit system

The upper crustal expressions of large magmatic events are documented in several well-exposed Large Igneous Provinces (LIP’s) (e.g., Ernst and Bell, 2010). Problematically, the shallow intrusive and extrusive products of LIP magmatism represent a system that has lost many of its key components during ascent through 30-50 km of crust and during surface eruptions. Not least when melts and volatile-rich phases pass through and become altered in intermittent magma-chambers en route to the shallow crust or the surface. Therefore, lavas and shallow sills provide a biased and distant record of the primary magmas and deep crustal processes that likely govern composition, tempo, and outgassing (e.g., Cox et al. 1980). Equally important, the transfer of economic metals such as Cu, Ni and the PGE’s from the mantle to the lower crust is poorly constrained.

This is a very serious gap in our knowledge because the primary chemical as well as physical properties of lower lithospheric melts mostly are known from theoretical modelling. It is in the magma-chambers and conduit systems at the mantle-crust transition that the parental melts are closest to their juvenile compositions. However, in situ studies of products and processes at these great depths of the continental lithosphere are very rare in deed. Particularly the origin, properties and significance of volatile-rich phases are lost during decompression from the deep lithosphere to the surface.

This knowledge-gap can be resolved by studying the few rare localities preserving lower crustal conduit system such as those preserved at Ivrea in NW Italy (Fiorentini et al. 2018) and the large volcanic conduit systems of the Seiland Igneous Province (SIP) in N. Norway (Fig. 1). SIP is the focus of this communication.

At the depths of SIP and Ivrea (Fiorentini et al. 2018) we are observing distinctive properties of melts, fluids and ore-deposits compared to the well-known equivalents at the shallow locations of LIP’s. We observe a large range of enigmatic melt compositions, as well as mixing and un-mixing of diverse magmas and volatile phases and the formation and disruption or ore-deposits. It is clear that C-O-H-S volatile-rich phases here are omnipresent and highly enriched compared to shallow parts of LIP-forming systems (Fiorentini et al. 2018; Larsen et al. 2018). Arguably, it appears that volatile-rich melts aid in transporting dense ultramafic melts and in disrupting, mobilizing and upgrading PGE-Cu-Ni deposits.

2 The Seiland Igneous Province (SIP) – a giant volcanic conduit system

The Seiland Igneous Province (SIP) consists of >5,000 km² of mafic, ultramafic and alkaline melts that, for the majority of the intrusions, were emplaced into the lower continental crust (30-40 km’s depth) in <10 Ma (570-560 Ma) and with alkaline as well as ultramafic magmatism spilling in to the L. Cambrian. As the SIP was a deep-seated conduit system co-forming with the Central Iapetus Magmatic Province (CIMP), it represents the deepest parts of CIMP, representing a key locality in which to study the ascent, emplacement and modification of dense mantle melts enroute to more shallow igneous systems. Here, in SIP, we may study igneous processes that relates to asthenosphere deep-lithosphere interaction processes prior to the melt-modifying processes that influence the parent melts during ascent towards the shallow crust.

Ultramafic complexes dominated by peridotitic cumulates occupy 1/3 of SIP and comprise the main volcanic conduits along which ultramafic magma migrated upwards in the continental lithosphere. The Reinfjord Complex is an excellent example of one of these conduit systems.
It was recently confirmed that SIP may have a significant ore-forming potential of Cu-Ni-PGE deposits (Schanche et al. 2012). Equally important for the formation of SIP, the ore-forming processes in the Reinfjord Complex document the importance of volatile fluxing of sulphur and carbon during emplacement of the ultramafic magmas (Nikolaisen 2016; Larsen et al. 2018), similar to observations in the Ivrea conduits (Fiorentini et al. 2018). Accordingly, minute but conspicuous assemblages of magmatic carbonate and sulphide are common throughout the Reinfjord Complex, particularly where Cu-Ni-PGE deposits occur.

Reinfjord also features contact deposits (Larsen et al. 2018) but the largest and richest deposits are hosted in the dunitic cumulates (Schanche et al. 2012; Larsen et al. 2018). Only the dunitic hosted deposits are described here because of their clear economic potential.

### 3.1 Dunite hosted deposits

The largest deposits appear as a 5 Ohm conductor providing an excellent contrast to the 3000 Ohm Central Series dunitic cumulates (Schanche et al. 2012). Modelling implied a conformable saucer-shaped body at a depth of c. 40 to 100 metres covering an area of 600 x 400 metres. A late magmatic normal fault runs through the centre of the deposit and downthrow the eastern block 50-60 metres. Exploratory drilling confirmed the presence of weakly disseminated deposits at 85 and 110 m (eastern block) below the surface with 1.6 and 1.2 wt% total sulphides, respectively. Here, the upper reef comprises 5 metres of dunite with an average of 0.4 wt% sulphide-bound Ni, 0.14 wt% Cu and 70 ppb PGE+Au whereas the lower reef comprises 5 metres with 0.23 wt% Ni and 715 ppb PGE+Au. Importantly, most of the PGE+Au is confined to a 1 m dunite section with 1635 ppb PGE+Au including 750 ppb Pd, 430 ppb Pt, 220 ppb Au and, 235 ppb IPGE with an Os-peak at 200 ppb. The Ni peak actually occurs 7 metres higher up, hence the PGE-ref is clearly decoupled from the Ni-ref and the Ni-ref is decoupled from the Cu-ref. Mineralogically, c. 50 % of the sulphides are pentlandite and chalcopyrite, the remaining part being pyrrhotite. Detailed studies demonstrated that peak values are associated with dunitic cumulates belonging to the third major recharge event (Nikolaisen 2016; Larsen et al. 2018).

The sulphide rich horizons were also discovered in two recent (RF-3 and 4 on Fig. 2) drill holes sampled c. 600 metres north of the two discovery holes. Here, the deposits occur from 40-80 metres below the surface in the dunites. Cu peaks with values of c. 0.1 wt % Cu in two 10 m thick reefs separated by 20 metres of dunite (Fig. 9). Finally, there is a deep-seated Cu-horizon at 349 m with 0.1 wt% Cu over 20 metres occurring at the transition between dunites and pyroxenites (RF-4 in Fig. 2).
Figure 2. Geological setting of the Reinfjord ultramafic conduit showing main igneous lithologies, position of drillholes (RF-1 to RF-4) and location of the main Cu-Ni-PGE deposit. 1-3 marks the three main recharge events forming the Reinfjord Complex.

The PGE deposit contain 0.3 ppm PGE over 5 metres and is decoupled from the Cu-deposits in occurring at 64 metres between the two Cu-maxima. None of the Cu deposits are associated with significant Ni-sulphide anomalies. The highest Ni values occur 5 metres above the PGE-horizon.

There are 4 more PGE horizons with c. 0.1 ppm PGE, but none of them are close to the Ni and/or Cu sulphide deposits.

It is clear that the main PGE-horizons are decoupled from both Cu and Ni horizons, and that the Ni-horizon, that occur 5 and 7 metres above the PGE’s, is Cu-poor. Furthermore, PGE deposits coincide with relatively Sulphur poor segments of the igneous stratigraphy.

The Pt/Pd ratios at all anomalous horizons in the drill-cores are between 1:1 and 1:2 whereas, “barren” sections have an average of 2:1. The PPGE/IPGE ratios are comparable to the Merensky Reef (S. Afr. Rep.) with typical values of 2-10. Platinum Group Minerals (PGM) are dominated by tellurides mostly Moncheite ((Pt, Pd)Te$_2$) and Merenskyite ((Pd, Pt)(Bi, Te)$_2$) whereas Au varies from pure gold to electrum with 40 % Ag (Nikolaisen 2016; Larsen et al. 2018). However, we also found several IPGE minerals including hollingworthite ((Rh,Ir,Os,Pt)AsS) and irarsite ((Rh, Ir)AsS$_2$).

Most of the PGMs occur together with sulphides that are commonly intimately intergrown with pentlandite exsolution in pyrrhotite (Fig. 3), whereas gold-rich phases show a close association with carbonate-sulphide assemblages (Nikolaisen 2016; Larsen et al. 2018).

Similarly, the PGE-mineralised sections normally contain high concentrations of carbonates and hydrous minerals (Fig. 3) that we have interpreted to represent alkali melts that co-existed with the ultramafic melts that formed.
the dunitic cumulates and/or, alternatively, were dissolved in the ultramafic parental melts prior to the formation of the dunitic cumulates.

In situ ion probe sulphur isotope analysis of sulphides yielded bulk $\delta^{34}S$ values around -2 to +2 $\permil$ for dunite hosted deposits as well as for sulphides in barren parts of the dunites whereas the host gabbro and paragneisses gave average values of +4 $\permil$ and +11 $\permil$, respectively (Larsen et al. 2018). Accordingly, the parental melts forming the ultramafic cumulates gained its sulphur from a distinctively different source region than both the paragneisses and the layered gabbros.

4 Origin and significance of PGE-Cu-Ni deposits in lower crustal conduit systems

Our studies at the Seiland Igneous Province is a rare probe in to the igneous processes pertaining to the deep-seated parts of a LIP-forming igneous system. An important lesson is that the diversity and composition of juvenile igneous melts is considerably more complex than the upper crustal formations of LIP-magmatism may imply. Not least, in SIP, we observe that ultramafic melts of picritic/komatiitic composition are close to or at sulphide saturation, are emplaced in the lower crust together with alkaline carbonated hydrous-rich melts and are themselves enriched in volatiles.

This is comparable to observations from the Ivrea Zone in NW Italy, where the parental melts forming deep-seated (c. 0.8 Gpa) conduit systems are also enriched in volatile constituents and show a characteristic alkaline signature (Fiorentini et al. 2018). The Ivrea conduits are also enriched in Cu-Ni-PGE mineralized sulphides and with an average of +1.35 $\permil$, the $\delta^{34}S$ values fall in the same range as at SIP and support that the likely isotopic range for the sub continental mantle is a narrow interval close to nil (Fiorentini et al. 2018).

The genesis of the sulphide deposits in the Reinfjord conduit system involves liquid immiscibility of a sulphide liquid at or shortly after emplacement of the dunite forming melts. The irregular distribution of the sulphides, sometimes over 10-20 metres of cumulates at several horizons in the dunites, imply multiple episodes of deposition and remobilisation in an open conduit system exposed to repetitive recharge events. The PGE-rich horizons are sulphide poor (<1 wt.% S) and decoupled from the Cu-Ni maxima. Contrary to the Cu-Ni-rich horizons, the PGE-rich zones are narrow occurring over only 1-2 metres of the cumulate stratigraphy.

Apparently, most of the PGE-Cu-Ni deposits at Reinfjord occur in a swelling structure forming a side chamber along the main conduit (Fig. 2, profile 1 and 2). Arguably, potential deposits forming in the actual conduit may have been remobilised hence migrated towards higher crustal levels.

Finally, we have the high contents of carbonates and hydrous phases throughout all cumulate types as well as in early and late dykes, i.e. it may be concluded that mafic as well as ultramafic parental melts were strongly enriched in dissolved volatile constituents.

The significance of the volatile-rich phases for asthenosphere-lithosphere transfer of mafic-ultramafic melts and ore-forming processes is not currently resolved. However, the fact that both SIP and the Ivrea conduits (Fiorentini et al 2018) show a high abundance of volatile-rich phases indicates that mafic-ultramafic melts in the deep-seated parts of volcanic conduit-systems may be the norm rather than an anomaly. During decompression towards the surface, this volatile-rich signature may be lost when the carbonate-component becomes immiscible in the silicate melts under the formation of shallow alkaline complexes.

Acknowledgement
Generous funding from the Nordic Council of Ministers, the Directorate for Internationalisation in Higher Education (DIKU) and NTNU made this study possible. Inspiring reviews from Prof. Fiorentini are highly appreciated.

References
Ernst, R.E., Bell, K. (2010) Large igneous provinces (LIPs) and carbonatites. Mineralogy and Petrology, 98:55-76
Ni-Cu-(PGE) fertility of the Zambezi belt rift magmatism: source and temporal controls

Ward A. Laura, Holwell A. David
School of Geography, Geology and the Environment, University of Leicester, UK

Tapster Simon
NERC Isotope Geosciences Laboratory, British Geological Survey

Abstract. Magmatic Ni-Cu-(PGE) sulphide deposits are the world’s most valuable source of Ni and PGEs. It is widely recognised that many major Ni-Cu-(PGE) sulphide deposits are spatially associated with craton or palaeocraton margins; a surface manifestation of the channelisation of plume magmas into zones of thinning lithosphere. Whilst many aspects of the ore system are well-constrained, the occurrence of mineralised and unmineralised intrusions within the same geological setting cannot yet be adequately explained. Understanding why unmineralised intrusions form within otherwise prospective terrains is the ‘holy grail’ of the Ni exploration industry and highlights a number of substantial research challenges. This study represents the first of its kind in the Zambezi belt in testing the temporal and isotopic characteristics of a suite of mineralised and unmineralised intrusions along this prospective belt. Using high precision dating techniques (CA-ID-TIMS) and a range of isotopic tracers (Lu-Hf, Sm-Nd, Rb-Sr), a suite of variably mineralised intrusions from the Zambezi belt are assessed in order to try and better understand the interplay between magma fertility and geodynamic controls.

1 Introduction

Magmatic Ni-Cu-(PGE) sulphide deposits represent some of the world’s most valuable metal accumulations, accounting globally for ~56% of Ni and ~96% of PGE production. Many of the world’s largest and most lucrative Ni-Cu-(PGE) deposits exhibit a well-defined spatial relationship with craton margins (e.g. Voisey’s Bay, Noril’sk, Jinchuan; Begg et al. 2010). In fact, there are few major Ni-Cu-(PGE) deposits for which there is no documented relationship (Begg et al. 2010; Maier and Groves 2011). Based on this observation, these regions are frequently targeted as corridors of enhanced prospectivity. Craton margins comprise zones of relatively thin lithosphere which become focal points for regional strain during tectonism, creating points of dilation along former deep-rooted fault systems (Begg et al. 2010; Barnes et al. 2015). Large and sustained magma volumes are able to ascend through these established crack networks, becoming channelised in the upper crust into high-flux magma conduits: prime conditions for ore genesis (Barnes et al. 2015; Lightfoot and Lamswood 2015). Particularly well-mineralised cratons include those in central-southern Africa (e.g. Kaapvaal, Zimbabwe and Congo cratons), though some are seemingly more PGE (e.g. Kalahari) than Ni-Cu rich (e.g. Congo; Maier and Groves 2011).

The ore-forming processes responsible for Ni-Cu-(PGE) sulphide mineralisation are relatively well constrained. The generally supported hypothesis is that parental ultramafic-mafic magmas must saturate with sulphide in the near surface environment (Naldrett 1999). The magmatic plumbing networks which feed these systems need to sustain dynamic magma flows in order to successfully scavenge chalcophile elements from their parental melts and upgrade metal tenors to economic concentrations. Whilst process models for Ni-Cu-(PGE) mineralisation are seemingly robust, less understood are the province/ regional geodynamic controls on magma fertility before the influences of shallow upper-crustal interactions. This point is largely founded on the observation that within a number of well-explored terrains, mineralisation is unevenly distributed amongst superficially similar intrusions. For example, in the Voisey’s Bay district, northern Canada, the Voisey’s bay intrusion hosts a giant ore-body whilst the apparently similar surrounding intrusions are sub-economic. Likewise, in the Yunnan and Sichuan Provinces of SW China, a number of heavily mineralised intrusions are surrounded by superficially similar intrusions, containing sub-economic to uneconomic accumulations of low tenor sulphide (Lightfoot and Lamswood 2015).

A substantial challenge to research and exploration lies in understanding the cryptic processes resulting in the occurrence of unmineralised intrusions in otherwise prospective regions. Using a suite of variably mineralised (economically mineralised, weakly mineralised, unmineralised) mafic-ultramafic intrusions from across the Zambezi belt, southern Zambia, this study aims to investigate the geodynamic and temporal influences on regional magma fertility and how these relate to the source and source characteristics of a deposit prior to the influences of upper crustal processes/interactions.

2 Case study area: The Zambezi belt

The Zambezi belt represents an example of a classic continental rift system and hosts abundant mafic-ultramafic rift magmatism, including the economic Munali Ni deposit. The Zambezi belt forms a key component in the network of Neoproterozoic tectonic belts in central-southern Africa that formed during the amalgamation of the supercontinent Gondwana (Johnson et al. 2007).

2.1 Geochronology of the Zambezi belt

The Zambezi metamorphic belt is situated between the
Congo-Kalahari cratons and forms part of the Pan-African orogenic system (Johnson et al. 2007). The Neoproterozoic Zambezi belt is characterized by abundant mafic-ultramafic magmatism exclusively hosted in high-level basin sediments as outlined in the classic ‘craton-margin’ setting defined by Begg et al. (2010). The belt is comprised of sediments belonging to the Zambezi Supracrustal sequence (ZSS), which are largely made up of sedimentary, volcanic and volcanoclastic rocks unconformably resting on a basement of gneiss (~1106 Ma) and granite (~1090 Ma). They are thought to represent a full tectonic cycle from continental rifting to subduction (Vinyu et al. 1999; Johnson et al. 2007).

Johnson et al. (2007) constrained much of the temporal evolution of the Zambezi basin where the onset of continental rifting and sedimentation is constrained by basal rhyolite flows as clasts in conglomerates at the base of the overlying ZSS units. A maximum depositional age of the ZSS at 879 ± 19 Ma has been proposed (Johnson et al. 2007). The main phase sedimentation is thought to have ceased by 820 Ma, marked by the emplacement of two geochemically similar A-type granitoids (820 ± 7 Ma Ngoma Gneiss and 821 ± 9 Ma Lusaka granite). Whilst the exact tectonic implications of the emplacement of these granitoid bodies is yet to be fully established, they are thought to mark the final stages of basin development and onset of basin convergence (Katongo et al. 2004; Johnson et al. 2007).

2.2 Mafic magmatism in the Zambezi belt

The Zambezi belt is characterised by hundreds of superficially similar mafic-ultramafic intrusions emplaced into a common stratigraphic succession within the Zambezi belt stratigraphy, independent of the degree of mineralisation. The Munali Intrusive Complex (MIC) is hosted within the upper carbonate sequences of the ZSS and comprises two main units: the Central Gabbro unit (CGU) and the Mafic-Ultramafic-Breccia-Unit (MUBU; Fig. 1). High-precision CA-ID-TIMS U-Pb dating of zircons from the Munali CGU and MUBU yields ages of 857 ± 0.84 Ma and 857 ± 1.9 Ma, respectively, and thus likely correlate with emplacement during early stages of basin extension and rifting (Holwell et al. 2017). Associated with the MIC are several, apparently similar intrusions (Chikani, Chibuku, Termite and T1B; see Fig. 1) thought to be genetically related to the MIC based on spatial associations and whole rock geochemistry. The Chibuku, Termite and T1B intrusions are known to contain Ni-sulphide mineralisation, though to what economic extent is still to be established. Dating of the Chibuku intrusive body in this study suggests emplacement occurred around ~855 Ma, strengthening the genetic association with the MIC and early extensional relationships.

Figure 1. Map of the Zambezi Supracrustal Sequence and location of the Lusaka West intrusions and MIC. Insert map of the MIC and surrounding intrusions (Chibuku, T1b, Termite, Chikani).

Fifty five kilometers NE of the MIC are the Lusaka West intrusives (Fig. 1), which appear both superficially and geochemically similar to the Munali Ni-Cu-(PGE) deposit. The Lusaka West intrusions comprise numerous small differentiated mafic-ultramafic intrusions emplaced into the same meta-sedimentary succession as the MIC, ranging from sub- to uneconomic. Whilst some of the Lusaka West intrusions show evidence of localised sulphide segregation based on whole rock Cu/Zr ratios, no primary-magmatic Ni-sulphides are observed and PGE concentrations are around that of average mantle compositions.

Traditionally, these intrusions have been assigned either a Pan-African (~520 Ma) or Munali (~860 Ma) emplacement age. However, high precision dating conducted in this study suggests intrusions are much older (~737 Ma), around 100 Ma prior to peak Pan-African metamorphism in the Zambezi belt, and ~123 Ma younger than Munali emplacement, overlapping with reported magmatism in the Copperbelt.

2.3 Preliminary findings and further work

Preliminary data currently alludes to a temporal distinction between the apparently fertile Munali hills and barren Lusaka West intrusives. We suggest that is during discrete early extensional phases of the Zambezi basin evolution (~880 to ~820 Ma) that magmatism was particularly capable of segregating economic accumulations of sulphide. Furthermore, data suggest that later intrusion emplacement during periods of regional convergence (after ~820 Ma) are seemingly less...
fertile. The source characteristics of these temporally distinct episodes will be assessed using isotopic tracers to reconstruct the 4D evolution of Ni-Cu-(PGE) mineralisation in craton margin settings. We aim to continue testing the hypothesis that the geodynamic evolution of the Zambezi Mobile Belt exerted a fundamental control over magma fertility, with a view to framing findings in the context of basin evolution and potential magma sources.

Acknowledgements

The management and staff at Mabiza Resources and Consolidated Nickel Mines are thanked for their technical and logistical support during fieldwork in Zambia.

References


Insights into the origin of the Munali magmatic sulfide deposit: evidence for a hidden Cu orebody?

Daryl Blanks, David Holwell
University of Leicester, UK

Stephen Barnes, Louise Schoneveld
CSIRO Mineral Resources, Perth, Australia

Abstract. The Munali magmatic sulfide complex is an enigmatic mafic-ultramafic breccia deposit, comprised of atypical Cr-poor magmatic host rocks and an unusual Ni-rich/Cu-poor carbonate-apatite-magnetite sulfide assemblage. Mineralisation is present as a sulfide matrix breccia, in which the clasts are present as an array of lithologies and sizes ranging from < 0.5 cm to > 5 m and is mined principally for its Ni resource, with Cu, PGE and Co as supplementary by-products. Several mineralisation styles have been identified which contain a similar sulfide mineralogy (pyrrhotite >> pentlandite > chalcopyrite ± pyrite), but display differences in sulfide abundance, gangue mineralogy and geochemical characteristics. Additionally, variations of Pd and Co within pentlandite and pyrite between the styles, suggest complexities in emplacement timing and/or sulfide melt interactions. The bulk sulfide at Munali displays high Ni/Cu ratios and an extreme negative Au anomaly, which is atypical for a mafic-ultramafic complex. Therefore, Munali may represent a sulfide system where the primary sulfide melt that crystallised was unusually low in Cu and Au or may instead suggest that syn-to-post magmatic processes may have altered or displaced the Cu(-Au)-rich component of the orebody and that these may now reside elsewhere in the system.

1 Introduction

The Munali magmatic sulfide deposit is a highly complex Neoproterozoic Ni-Cu-Co-PGE mafic-ultramafic breccia located within the Zambezi Belt in southern Zambia.

The deposit represents a multi-phase dynamic system comprised of an early unmineralised gabbroic core, surrounded by a later marginal mafic-ultramafic breccia unit that is host to a sulfide matrix (Holwell et al. 2017). The mafic-ultramafic breccia clasts in this unit comprise dolerite, weakly mineralised poikilitic gabbro and a suite of atypical ultramafic rocks that include olivinite (Cr-poor olivine cumulates) and phoscorite (olivine-magnetite-apatite rock). The intrusive complex is steeply dipping and exhibits typical characteristics of a magmatic-conduit system located along a transliithospheric fault zone. Mineralisation is open at depth with the ore zone comprised of a massive sulfide breccia ore composed of an unusual Ni-rich but Cu-poor sulfide assemblage with associated carbonate-apatite-magnetite. The carbonate is of mantle origin and has carbonatitic affinities that are consistent with the presence of phoscorites.

2 Sulfide characteristics

The sulfide matrix of the mafic-ultramafic breccia forms the main stage of mineralisation with the sulfide comprised of multiple styles, characterised by differences in sulfide abundance, ore and gangue mineralogy and textural associations and include:

1) Massive sulfide;
2) Semi-massive sulfide;
3) Semi-massive sulfide with apatite;
4) Apatite-rich pyritic sulfide;
5) Carbonate-rich sulfide;
6) Talc-carbonate associated sulfide.

All styles comprise the typical magmatic sulfide assemblage of pyrrhotite, pentlandite, and chalcopyrite ± pyrite and magnetite in variable abundances. Geochemically, the sulfides are very primitive, Fe-rich monosulfide solid solution (mss) cumulates with variable Pt/Pd ratios that are nearly always < 1, with a high Ni/Cu ratio of approximately 7.5 to 10 (Fig. 1). As a result of the low Cu tenor, the sulfide at Munali plots towards the lowest extent for the mafic associated field and overlaps with the field for sulfides associated with komatiite magmatism.

Figure 1. Ore compositions and bulk metal tenors of Cu and Ni in 100% sulfide showing the fields for mafic, komatitite, komatitite basalts and the red field for Munali, exhibiting a Ni/Cu ratio of around 7.5 to 10 (after Barnes et al. 2017).
Massive and semi-massive sulfide (mineralisation styles 1 and 2), represent the most voluminous sulfide styles of the ore-body and exhibit the lowest Cu tenors. In contrast, styles 3, 4 and 5, where mineralisation is associated with gangue minerals apatite and carbonate, display relatively high Cu tenors.

Sulfides display striking loop textures, comprising pentlandite and lesser chalcopyrite forming continuous rims around pyrrhotite crystals. These are very similar to textures observed in the Nova deposit (Barnes et al. this volume) and are interpreted similarly as the result of peritectic growth of high-T pentlandite from residual sulfide liquid.

Platinum-group mineral (PGM) assemblages are present almost exclusively as Pd>Pt tellurides, with slight variations between styles. PGMs are present solely as Pd-tellurides in the apatite and carbonate styles whereas massive to semi-massive sulfide without these gangue appear to show much more variable mineralisation of variations between styles. PGMs are present solely as 0.03 ppm) most were below detection limit. detected low Au in pyrite, chalcopyrite and pentlandite (< in solid solution within pyrrhotite, whilst several analyses pyrrhotite in any style. Additionally, Au was not detected present in notable quantities within chalcopyrite and enrichment during talc-carbonate formation. No Co was identified that include 1) a positive correlation of Ni and pentlandite and pyrite where four major trends have been identified that include 1) a positive correlation of Ni and Co in pentlandite; 2) high Co with low Ni in pentlandite associated with semi-massive sulfide with apatite; 3) high Co in pyrite and 4) moderate Co in As and Ni enriched pyrite hosted within talc-carbonate associated sulfide, with the latter likely formed from later hydrothermal enrichment during talc-carbonate formation. No Co was present in notable quantities within chalcopyrite and pyrrhotite in any style. Additionally, Au was not detected in solid solution within pyrrhotite, whilst several analyses detected low Au in pyrite, chalcopyrite and pentlandite ( < 0.03 ppm) most were below detection limit.

### 2.1 Sulfide geochemistry

The concentrations of PGE and other chalcophile elements have been determined by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) in pyrrhotite, pentlandite, chalcopyrite and pyrite from all mineralisation styles, where present. Although Pd is present as Pd-tellurides associated with sulfide, there are significant levels of Pd hosted in solid solution in pentlandite, ranging from < 1 to 500 ppm, whilst Pt, not present in significant quantities as PGMs was not found to be elevated in any of the sulfides analysed. The high Pd content of the loop-textured pentlandite is evidence for its peritectic origin (Mansur et al. 2019).

No Co-minerals have been identified as part of the base metal sulfide mineral assemblage, although Co is an economic by-product of the deposit. Cobalt is instead present in notable quantities (up to 4 wt. %) within pentlandite and pyrite where four major trends have been identified that include 1) a positive correlation of Ni and Co in pentlandite; 2) high Co with low Ni in pentlandite associated with semi-massive sulfide with apatite; 3) high Co in pyrite and 4) moderate Co in As and Ni enriched pyrite hosted within talc-carbonate associated sulfide, with the latter likely formed from later hydrothermal enrichment during talc-carbonate formation. No Co was present in notable quantities within chalcopyrite and pyrrhotite in any style. Additionally, Au was not detected in solid solution within pyrrhotite, whilst several analyses detected low Au in pyrite, chalcopyrite and pentlandite (< 0.03 ppm) most were below detection limit.

### 2.2 PGE Geochemistry

Bulk PGE profiles from the different mineralisation styles at Munali highlights two key trends within the sulfide (Fig. 2). Massive sulfide and semi-massive sulfide without carbonate and/or apatite show a moderate steepening trend from IPGE to PPGE with an average (Pd/Ir)N ratio of 265. Sulfide associated with apatite and carbonate appear relatively more fractionated with an average (Pd/Ir)N ratio of 3374, and is slightly more enriched in Cu. However, although overall the system appears to be fractionated with respect to the PGE, there is a distinct negative Au anomaly along with relatively low Cu contents in the system.

**Figure 2.** Primitive mantle normalised bulk PGE profiles for the main sulfide mineralisation styles.

### 3 The loss of Cu?

The sulfide at Munali represents a magmatic system that is depleted in Cu and Au in relation to similar deposits worldwide, representing an unusual, fractionated Cu-poor sulfide system, with moderate to high Pd/Ir and high Ni/Cu ratios. As such, this may indicate that the Cu-poor nature of the orebody may reflect an inherent characteristic of the initial sulfide liquid composition, representing a sulfide system retaining the mss cumulate portion. This may be due to sulfide at Munali reflecting a new subclassification of sulfide mineralisations systems, potentially linked to phoscoritic/carbonatitic magmas. However, it is possible that the Cu and Au depletion may be due secondary processes and does not represent the primary sulfide liquid composition. Although the sulfide is Cu-poor, there is textural evidence for Cu-rich sulfide liquid migration within the deposit on a cm scale, whereby chalcopyrite is present within cracks and fractures in the brecciated host rocks. As such, it may be possible that on a larger scale, the Cu portion of the orebody, which may be additionally enriched in Au and PGE, may have migrated via pre-existing structures or as a result of syn- to post-tectonic processes. Thus, there remains the possibility of discovering a Cu-rich portion of the orebody a depth.

An alternative explanation may be that hydrothermal fluids interacted with the sulfides and stripped them of their most mobile metals such as Cu and Au via, for example, Cl-rich fluids (Aird and Boudreau 2013; Hanley et al. 2005). These may have been meteoric and derived from evaporitic sediments (for which there is evidence in the immediate host rocks), or magmatic-metamorphic in origin, due to the depletion in both Au and Cu within the orebody.
Overall, Munali represents an enigmatic deposit with unusual host rocks, gangue mineralogy and sulfide composition. These associations could represent primary features and a new style of magmatic sulfide deposit, or may be indicative of another process involving the modification of the sulfide mineralisation during or post emplacement.

Acknowledgements

DB was funded by Consolidated Nickel Mines and the University of Leicester. This work is additionally funded by NERC SoS Minerals consortium grant NE/M010848/1 “TeaSe: tellurium and selenium cycling and supply” awarded to the University of Leicester. Consolidated Nickel Mines are gratefully acknowledged for financial and logistical field support and permission to carry out and present this research.

References

Barnes SJ, Taranovic V, Miller JM, Beresford SW, Rennick S (2019) Sulfide-silicate textures and emplacement mechanisms of the Nova-Bollinger ores, Fraser Zone, Western Australia, this volume.
Fluorine and PGE-Au elevated signature of alkaline magmas from the Yilgarn Craton: insights into mantle fertility

Eunjoo Choi, Marco Fiorentini
Centre for Exploration Targeting, ARC Centre of Excellence in Core to Crust Fluid Systems (CCFS), University of Western Australia

Andrea Giuliani
KiDs (Kimberlites and Diamonds), School of Earth Sciences, University of Melbourne

Stephen Foley
ARC CCFS, Department of Earth and Planetary Sciences, Macquarie University

Abstract. Our current understanding of the nature of the mantle, under the Archean Yilgarn Craton, Western Australia is predominantly based on the image provided by a number of geophysical datasets and on the radiogenic isotope (e.g., Lu-Hf, Sm-Nd) composition of granitoid and ultramafic rocks. The PGE-Au signature of deeply sourced alkaline magmas may provide key insights into the metallogenic fertility of the mantle underlying the Yilgarn Craton. The Yilgarn Craton contains various types of alkaline rocks, including calcalkaline lamprophyres (CAL), ultramafic lamprophyres (UML), carbonatites, orangeites and kimberlites. The PGE patterns of the CAL exhibit elevated (Pd/Ir)N ratios, whereas the other rock types are characterised by less fractionated PGE patterns, with lower (Pd/Ir)N ratios. In general, most alkaline magmas from the Yilgarn Craton appear to be anomalously enriched in Au. Furthermore, their key constituent magmatic minerals, such as amphibole, mica and apatite are anomalously enriched in F, and S. These volatiles may play a crucial role in the transport and concentration of precious metals from the mantle into the crust, contributing to explaining its exceptional metal endowment.

1 Introduction

The Yilgarn Craton in Western Australia is a world-class metallogenic Archean craton hosting considerable metal resources, including komatiite-associated Ni-sulfides and orogenic Au. Interest in the geodynamic evolution of the crust and upper mantle in the craton has increased greatly over the last decade through various studies, which mainly relied on regional scale geophysical datasets, as well as geochemical, isotopic and geochronological information of subalkaline felsic, mafic and ultramafic magmas (e.g. Blewett et al. 2010; Mole et al. 2013). However, these studies provided limited information on the composition of the lithospheric mantle, which may hold the key to understanding the exceptional metal endowment of this craton (Griffin et al. 2013). This knowledge gap may be at least partially addressed through the study of the metal and volatile nature of a serious of poorly characterised alkaline magmas, which are distributed throughout the eastern part of the Yilgarn Craton as well as along its northern and southern margins. This study represents the first comprehensive characterisation of the precious element signature of alkaline magmas in this craton.

2 Geologic Settings

2.1 Evolution of the Yilgarn Craton

The Yilgarn Craton mainly consists of metavolcanic and metasedimentary rocks, granitoid complexes, and greenstone belts, which formed principally between ~3050 and 2600 Ma, with minor older components >3700 Ma in age (e.g., Wilde et al. 1996; Myers 1995; Pawley et al. 2012; Griffin et al. 2004). It can be subdivided into the Western Yilgarn and Eastern Goldfields Supercraton based on stratigraphic, structural, geochemical and geochronological data, each comprising a number of domains, terranes and superterrane (Cassidy et al. 2006). The Eastern Goldfields Superterrane dominantly consists of ~2710-2690 Ma tholeiitic and komatiitic units and the ~2690-2660 Ma felsic volcaniclastic units (e.g., Cassidy et al. 2006; Barley et al. 2003). Craton-wide felsic magmatism from ~2650 to 2620 Ma is thought to reflect the cratonisation of the Yilgarn Craton into its current form and size (Cassidy et al. 2006; Czarnota et al. 2010; Mole et al. 2014).

2.2 Alkaline rocks in the Yilgarn Craton

The Yilgarn Craton contains various types of alkaline magmas, including CAL, UML, carbonatites, orangeites, and kimberlites. The spatial distribution of the alkaline rocks in the craton can be subdivided into three groups. The alkaline rocks on the northern boundary of the craton comprise orangeites and kimberlites with ages of 1324 ± 4 Ma (Phillips et al. 1997) and 1900-1700 Ma (Shee et al. 1999). The eastern part of the Yilgarn Craton includes older UML, carbonatites and kimberlites with an age of 2025 ± 10 Ma (Graham et al. 2004) and the late Archean CAL with ages of 2684 - 2640 Ma (Perring et al. 1989; McNaughton et al. 2005). Finally, UML at Norseman in...
the southern margin of the craton occur with an age of 849 ± 9 Ma (Robey et al. 1989).

3 Results

3.1 Volatile elements (mineral chemistry)

Amphibole, mica and apatite are common minerals in alkaline rocks and can be used as an important indicator to reveal magma evolution. In the alkaline rocks of the Yilgarn Craton, amphibole is the dominant phenocryst phase in the CAL, whereas mica (phlogopite and tetraferriphlogopite) is the dominant phenocryst and macrocryst in UML, carbonatites, and orangeites. Apatite occurs as inclusions in amphibole phenocrysts of the CAL, as well as a groundmass phase in the other studied rock types.

Amphibole phenocrysts in the CAL contain F contents up to 0.6 wt.%, which is similar to or higher than magmatic amphibole from global lamprophyre occurrences (Tappe et al. 2004; Rock 1991). Phlogopite phenocrysts in the UML exhibit F contents (~ 1.5 wt.%), higher than those found in the global UML (Rock 1991; Tappe et al. 2004). The carbonatites contain both phlogopite and tetraferriphlogopite, displaying the highest F contents (~2.6 wt.%). Fluorine contents in tetraferriphlogopite grains from the orangeites are moderate (up to 0.5 wt.%). Overall, both amphibole and mica phenocrysts of the studied rocks are generally enriched in F.

Apatite grains in the studied CAL and carbonatites are enriched in F up to 5.1 wt.%, which is higher than average F contents in magmatic apatite from global silicate magma occurrences (Webster and Piccoli 2015). Fluorine contents in apatite from the UML and orangeites are similar or less than the average contents (~2.3 wt.%; Webster and Piccoli 2015). Sulfur contents in apatite from the examined CAL and one UML are enriched (~ 2 wt.%), which are much higher than average S concentrations found in global magmatic apatite occurrences from silicate and carbonate magmas (Belousova et al. 2002; Webster and Piccoli 2015).

3.2 Major, trace, volatile elements (whole-rock geochemistry)

Whole-rock data exhibit different geochemical characteristics for the different alkaline rock types. The CAL show distinct geochemistry and have higher SiO₂ and Na₂O (~ 60 and 8 wt.% respectively) with lower contents of K₂O (~ 3 wt.%), MgO (~ 12 wt.%) and TiO₂ (~ 1 wt.%) compared to the other alkaline rocks. They show significant primitive mantle-normalised negative Nb-Ta anomalies, whereas their CO₂ contents are highly variable (~11.6 wt.%), with relatively higher SO₃ contents (~ 0.5 wt.%) than the other rock types.

On the other hand, the UML, carbonatites, orangeites and kimberlites are generally characterised by low SiO₂ contents (< 42 wt.%) and high MgO, TiO₂ (~ 17 and 7 wt.% respectively) contents, similar to global UML (e.g., Tappe et al. 2008; Rock 1991) as well as orangeites (e.g., Mitchell 1995). In the primitive-mantle normalised patterns, the positive F anomalies are observed in these rocks. Their Ni and Cr contents are commonly high (up to ~1500, 2000 ppm).

3.3 PGE-Au (whole-rock geochemistry)

Primitive-mantle normalised PGE patterns of the CAL show strong fractionation with highly elevated (Pd/Ir)ₚ ratios up to ~44. The CAL display highly variable Pt/Ir (up to ~58) with moderate Pt/Pd (mostly less than ~1.5) and Ru/Ir (~ 2.0) ratios. These features are also observed in the global CAL (Rock 1991; Gan and Huang 2017), however, the studied CAL contain higher Ir, Ru and Rh contents than the CAL from China (Gan and Huang 2017).

On the other hand, the UML, carbonatites, orangeites, and kimberlites are characterised by less fractionated PGE patterns, with (Pd/Ir)ₚ ratios as low as ~11, which is similar to those found in kimberlites from South Africa and Finland (Maier et al. 2017). These rocks have similar Pd/Pl (~1.7) ratios to the CAL, whereas contain much lower Pt/Ir (~ 18) and higher Ru/Ir (up to ~2.8) ratios. In particular, the UML and carbonatites display lower Ir, Ru and Rh contents than other rock types, whereas the kimberlites and orangeites have higher Ir, Ru and Rh contents.

Interestingly, all the examined samples in this study exhibit primitive-mantle normalised positive Au-anomalies, with absolute values generally higher than the average contents of the primitive-mantle (McDonough and Sun 1995). These elevated Au contents are higher than any reported contents in kimberlites (Maier et al. 2017; McDonald et al. 1995).

4 Discussion

4.1 PGE distribution in the mantle

The alkaline rocks analysed in this study were most likely generated by small degrees of partial melting of the mantle and probably from different source depths. The variably fractionated but ubiquitously enriched PGE signature of all studied alkaline systems may reflect an inherited difference in the metallic endowment of the source, which would in turn point to the presence of spatially defined different pre-existing metasomatised domains in the mantle underlying the Yilgarn Craton.

4.2 Fluorine, sulfur and gold enrichment

The alkaline rocks from the Yilgarn Craton consistently display a strong positive Au anomaly in their primitive-mantle normalised patterns as well as higher Au contents than the primitive-mantle. These features are also observed in kimberlites and orangeites from Finland and South Africa (Maier et al. 2017; McDonald et al. 1995). This observation is potentially consistent with studies suggesting that spatially constrained metasomatised portions of the lithospheric mantle may be relatively enriched in Au (Maier et al. 2017; Tassara et al. 2018; Tassara et al. 2017).
In general, the key constituent magmatic minerals, such as amphibole, mica and apatite, of alkaline magmas from the Yilgarn Craton are anomalously enriched in F and S. It is argued that these volatiles may play a crucial role in the transport and concentration of precious metals from the mantle into the crust, and may go some way to explaining the metal endowment of the Yilgarn Craton.

Figure 1. Primitive-mantle normalised PGE patterns of the various alkaline rock types in the Yilgarn Craton. Note that each line represents the average PGE contents of the different rock types: the bright green line (CAL; N = 21), blue line (UML and orangeites; N = 10), red line (kimberlites; N = 5), and dark green line (carbonatites; N=4).

Acknowledgements

This study is supported by the Australian Government through an Australian Government Research Training Program Scholarship and the Minerals Research Institute of Western Australia Postgraduate Scholarship, and by Australian Research Council Centre of Excellence for Core to Crust Fluid System.

References

Gan T, Huang Z (2017) Platinum-group element and Re-Os geochronology of lamprophyres in the Zhenyuan gold deposit, Yunnan Province, China: Implications for petrogenesis and mantle evolution. Lithos.
Perring CS, Rock NM, Golden SD, Roberts DE (1989) Criteria for the recognition of metamorphosed or altered lamprophyres: a case study from the Archaean of Kambalda, Western Australia.


Widespread PGE depletion in the Tarim CFBs of NW China and implications for the ore potential in the Tarim LIP

Yin-Qi Li, Zi-Long Li, Shu-Feng Yang, Han-Lin Chen
Zhejiang University, China
Ya-Li Sun
Chinese Academy of Sciences

Abstract. The Early Permian Tarim Large Igneous Province (LIP) in northwestern China consists of voluminous continental flood basalts (CFBs) that can be classified into three groups. All of them exhibit extreme depletion in platinum group element (PGE; ΣPGE < 1 ppb). Such widespread PGE depletion indicates that their parental magmas were likely to have been S-saturated before final eruption and/or there are residual S remaining in the mantle source during melting. The almost identical PGE depletion in both the more crustal contaminated and the least crustal contaminated basalts suggests that crustal contamination did not trigger the S saturation in the Tarim CFBs. Sulfur concentration at sulfide saturation estimation suggests that low-degree (ca. 5%) partial melting of the Tarim LIP’s mantle source may play an important role on the widespread PGE depletion in the Tarim CFBs, residual S in the mantle takes most PGE from the basaltic magma. Furthermore, the evidence of magma mixing by magma chamber replenishment during the basalt eruptions in the Keping area supports secondary S-saturation for the basaltic magmas in the crust, which may cause PGE enrichment in some parts of the magma conduit. Therefore, it is still possible to discover the magmatic sulfide deposit in the Tarim LIP, which will probably be similar to the Voisey’s Bay magmatic sulfide deposit in Canada.

1 Introduction

As one of the five Large Igneous Province (LIP) events occurring during Permian, the ca. 290 Ma Tarim LIP in the Tarim basin of northwest China comprises a diverse range of magmatic rocks from ultramafic–mafic to felsic compositions, and has been widely regarded as being genetically linked to a mantle plume (Li et al. 2012; Xu et al. 2014). Many LIPs around world possess world class Ni–PGE magmatic ore deposits, such as the Siberian Traps and Bushveld Complex. Although by far no Ni–Cu–PGE deposits are found in the Tarim LIP, a number of coeval Ni–Cu–(PGE) magmatic ore deposits have been reported around the Tarim Basin (Chai et al. 2008; Yang 2011). Whether the Tarim LIP has the potential of Ni–Cu–PGE magmatic ore deposits has also generated considerable interest among geologists leading to a number of recent investigations (e.g., Pirajno et al. 2009; Qin et al. 2011). PGEs (Os, Ir, Ru, Rh, Pt and Pd) are highly siderophile elements that provide valuable information on the petrogenesis of mantle-derived igneous rocks. The PGE abundances in the CFBs are much lower as compared to lithophile elements, usually at ppb or even ppt level. Nevertheless, they are potential markers of the magmatic process and source nature of the basalts. They are particularly sensitive for the extent of sulfur saturation and sulfide segregation (Barnes et al. 1985; Keays 1995). In addition, variations in the concentrations and ratios between different PGE can provide important information relating to the genesis of magmatic Ni–Cu–PGE sulfide mineralization. A number of studies have proposed that the giant Noril’sk–Talnakh Ni–Cu–PGE sulfide ore is associated with the PGE-depleted basalts of the Nadezhhdinsky Formation in the Siberian Traps (Naldrett et al. 1992).

In this study, PGE geochemistry of the Tarim continental flood basalts (CFBs) are systematically studied to address the sulfur saturation and evolution process of the Tarim CFB magmas and evaluate the Cu–Ni–PGE mineralization potential of the TLIP.

2 Geological background

The Tarim Basin in the northwest China, surrounded by the Tianshan, Kunlun and Altn–Tagh orogenic belts, mainly consists of Precambrian crystalline basement and Phanerozoic strata from the Ordovician to Neogene. Some important tectonothermal activities from the Archean to Paleozoic have been identified in this area, in which the early Permian magmatic event (known as the Tarim LIP) was regarded as the most important one. The Tarim LIP is widely distributed in the Tarim Basin. Large scale continental flood basalt lavas were erupted during the Early Permian, constituting the main part of the Tarim LIP. Systematic geochronological studies have concluded that the main eruptions of the Tarim CFBs occurred in a period of ~5 Myr close to 290 Ma (Li et al. 2011). A diverse assemblage of coeval intrusive rocks, such as layered mafic–ultramafic intrusions, mica–olivine pyroxenite breccia pipes, diabase and ultramafic dykes, quartz syenites, diorite, quartz syenite porphyry and bimodal dykes, were also emplaced in the Tarim Basin (Li et al. 2012).

The Tarim CFBs are mostly high-Ti basalts (TiO2 > 2.5 wt.% and Ti/Y > 500) belonging to the alkaline series. In general, they exhibit significant enrichments of large-ion lithophile and light rare-earth elements on the primitive mantle-normalized spidergram, which are similar to the ocean island basalts (OIBs) except the slight Nb–Ta depletion (Fig. 1). Their high Ti/Y and Zr/Y ratios support
a within-plate petrogenetic affinity.

Based on their geochemical distinctions, the Tarim CFBs can be subdivided into three. Groups 1a and 1b basalts are widely distributed within the Tarim Basin. They have many similar petrological and geochemical characteristics, but the earlier erupted Group 1b basalts show higher Th/Nb ratios (mostly >0.2), and exhibit fairly low Nb/U (<21) and Ce/Pb (<12) ratios, indicating more crustal contamination than the latter group 1a basalts (Li et al. 2014). Conversely, Group 2 basalts so far are only identified from four drill holes in the Northern Tarim Basin. They show a clear depletion on the heavy rare-earth elements, have higher Nb/Yb ratios (≥15) that approach those of OIB. These geochemical features indicate that Group 2 basalts are less crustally contaminated and more similar to OIB in composition than both Groups 1a and 1b basalts. Differences among the three group basalts can also be discerned from their distinctive Sr and Nd isotopic compositions and variable crustal contamination during the generation of the Tarim CFBs.

Figure 1. Primitive mantle normalized element abundance patterns for the three group basalts in the Tarim LIP.

3 PGE geochemistry of the Tarim CFBs

Twenty-five basalt samples from different locations in the Tarim LIP were selected to analyze their PGE contents. Among them, 19 samples are Group 1a basalts from the Northern, Southwestern and Central Tarim Basin; 2 samples are Group 1b basalts from the Northern Tarim Basin; and 4 samples are Group 2 basalts from the drill holes in the Northern Tarim Basin.

All the three group basalts from different locations in the TLIP exhibit extremely low PGE contents (Os 0.001–0.106 ppb, Ir 0.000–0.067 ppb, Ru 0.004–0.253 ppb, Rh 0.001–0.078 ppb, Pt 0.031–0.376 ppb, Pd 0.026–0.168 ppb and ∑PGEs = 0.078–0.723 ppb; Table 1). Apart from PGE, the Tarim CFBs also display low Cu contents (mostly < 100 ppm). On the primitive mantle normalized plot, basalts from the same section (or the same location) display similar PGE pattern. Except those from the Keping area (12 Group 1a basalts and 2 Group 1b basalts), they generally show an enriched trend from Os to Pd in Pt and Pd than the other PGEs, similar to other CFBs around the world (Barnes et al. 1985).

Table 1. PGE and Cu concentrations of basalts from the TLIP, Siberian Traps, ELIP, East Greenland CFBs and Deccan Traps.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Ir (ppb)</th>
<th>Pd (ppb)</th>
<th>Cu (ppm)</th>
<th>Pd/Ir</th>
<th>Cu/Pd (×10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tarim LIP</td>
<td>36</td>
<td>0–0.015</td>
<td>0.275–24.7</td>
<td>0.067–223</td>
<td>0.34–39.9</td>
<td>0.078–0.723</td>
</tr>
<tr>
<td>Siberian Traps</td>
<td>15</td>
<td>&lt;0.01</td>
<td>0.07–20.46</td>
<td>0.01</td>
<td>0.07–9</td>
<td>1.55–32.9</td>
</tr>
<tr>
<td>ELIP (high Ti basalts)</td>
<td>115</td>
<td>0.009–0.3</td>
<td>3.88–292</td>
<td>0.08–32.6</td>
<td>0.03–6.11</td>
<td>1.58–1.60</td>
</tr>
<tr>
<td>Deccan</td>
<td>31</td>
<td>0.05–2.35</td>
<td>17.4–105</td>
<td>0.49–31.8</td>
<td>0.03–12.6</td>
<td>0.44–0.68</td>
</tr>
<tr>
<td>East Greenland</td>
<td>35</td>
<td>0.05–3.04</td>
<td>43–105</td>
<td>1.58–346</td>
<td>0.03–2.07</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Note: N is the number of samples. The Tarim LIP basalts data are from this study and Yuan et al. (2012), the Siberian Traps basalts data are from Lightfoot and Keays (2005), the ELIP high-Ti basalts data area from Qi et al. (2008) and Song et al. (2009), and the East Greenland basalts data are from Momme et al. (2002).

4 Discussion

4.1 S-saturated Tarim CFB magmas

Compared with other CFBs around the world, the PGE concentrations (represented by Ir and Pd) in the Tarim CFBs appear to be strongly depleted, only similar to those PGE-depleted basalts in the Nadezhdinsky Formation in the Siberian Traps (Table 1). PGEs are generally partitioned into immiscible sulfide liquids during sulfide segregation due to their extremely high sulfide liquid/silicate melt partition coefficients (Fleet et al. 1991), causing their concentrations to decrease in the residual silicate magma. Cu, Pd and Ir are often used to judge the magma’s sulfur saturation state. Pd and Ir show compatible behavior in sulfide phase when a suite of lavas undergoes S-saturated differentiation, due to their sulfate liquid/silicate melt partition coefficients (D_sulfate) of the order of 10^3 to 10^5 (Song et al. 2009). The D_sulfate of Cu (10^2 to 10^3) is much lower than the PGEs, which indicates that the Cu/Pd ratio will strongly increase once sulfide liquids segregate from the silicate magma (Campbell and Barnes 1984). In contrast, both Cu and Pd behave as incompatible elements in S-undersaturated systems, but the Pd/Ir ratio increases during S-undersaturated differentiation (Momme et al. 2002). This is because Pd is an incompatible element whereas Ir behaves as a compatible element during silicate fractionation of a basaltic magma (Keays 1995). The Tarim CFBs have extremely high Cu/Pd ratios (>10^5) with a narrow range of lower Pd/Ir ratios (<50),
which can be easily distinguished from the S-undersaturated and PGE-undepleted basaltic suites from the Siberian Traps, ELIP, East Greenland CFB and Deccan Traps (Fig. 2a). Besides, the Tarim CFBs also exhibit generally lower Cu/Zr ratios than the PGE-depleted PGE-depleted basalts in the Nadezhdinsky Formation in the Noril’sk region in the Siberian Traps (Fig. 2b), reflecting Cu depletion (Keays and Lightfoot 2010). These features, combined with the extremely low PGE and Cu contents, suggest that the parental magmas of the Tarim CFBs have been S-saturated before final eruption.

4.2 Possible reason for S-saturation in the Tarim CFB magmas

Crustal contamination is commonly considered as the main reason to cause S-saturation in mantle-derived magmas (Keays and Lightfoot 2010). The Tarim CFBs in different locations have suffered variable degrees of crustal contamination, whereas both more contaminated Group 1 basalts and less contaminated Group 2 basalts show strong depletion in PGE. Therefore, crustal contamination during the Tarim basalt eruptions may not trigger S-saturation in their parental magmas. The S-saturation process are more likely to be related to the magma source region.

Although the Tarim CFBs in different locations may have variable source compositions, calculations based on trace element geochemistry from the Tarim CFB suggest that their parent magmas were derived from <5% partial melting of the mantle source (Yu et al. 2011; Zhou et al. 2009), consistent with their alkaline nature and LILE- and LREE-enriched trace element signature. The S content of the mantle reservoir is generally about 150–250 ppm, and therefore melts derived by ca. 5% partial melting would contain 3000 to 5000 ppm S from a columnar melting regime (Keays 1995). Whereas the estimated sulfur concentration at sulfide saturation (SCSS) for the Tarim CFB magmas range from 859 to 1929 ppm, which is much lower than the S content produced by their partial melts. In this scenario, a substantial amount of residual sulfide would be left behind in the mantle, and only a small portion of the PGEs would be released to the silicate partial melts, which may account for the significant PGE depletion of all the Tarim CFBs. The fact that all the known Tarim CFBs in the TLIP are exclusively PGE-depleted also indicates that their parent magmas have been S-saturated at the same stage, probably when they emerged from the mantle.

Furthermore, Fig. 3 shows that there is a negative correlation between the PGE concentrations and εNd(t) values for the basalt sequence in the Keping area, indicating that a continuously influx of relatively primitive and uncontaminated magma of the same lineage into a chamber occupied by evolved residual magma. Mixing of an evolved magma with appropriate amounts of a primitive magma is capable of achieving sulfur saturation in the hybrid (Li et al. 2001), which may trigger a certain extent of sulfide segregation and PGE depletion in the basalt sequence, although the feature is not so prominent due to their extremely low PGE contents. Such a magma chamber replenishing process is also supported by the general decreasing trend of the (La/Yb)_N ratios from the base to the top basaltic units in the Yingan section, which eventually led to multiple basaltic flows in the Keping area (Yu et al. 2011).

5 Implications for the Cu–Ni–PGE mineral resource potential in the TLIP

The above considerations indicate that the degree of partial melting plays an important role on the Cu–Ni–PGE mineralization in the TLIP. Due to very low degrees of
partial melting, the Tarim CFBs are extremely PGE-depleted, which may account for the absence of Cu–Ni–PGE sulfide deposit in the TLIP. Mafic–ultramafic rocks formed by high-degree partial melting from the mantle source in the TLIP should receive more attention in terms of their Cu–Ni–PGE mineralization potential. In fact, a number of similar deposits are reported in the Eastern Tianshan and Beishan area, and recent studies suggest that they may also be a part of the TLIP (Pirajno et al. 2009; Qin et al. 2011). It is also noted that the PGE geochemistry of basalts in the Yingan section indicates that magma replenishment in the magma chamber may trigger S-saturation in the evolved magma. The latter may cause the magma become S-saturated again and segregate the saturated sulfide in the crust before final eruptions (Naldrett 2004), which may be possible to develop a Cu–Ni–PGE sulfide deposit in the Tarim LIP.

Acknowledgements

This study was jointly funded by the National Natural Science Foundation of China (41603029 and 40930315) and the National Basic Research Program of China (973 Program: 2011CB808902 and 2007CB411303).

References


Using Platinum Group Element geochemistry to determine magma fertility of Mount Hagen, Papua-New Guinea

Monika Misztela, Ian Campbell
Research School of Earth Sciences, Australian National University, Canberra, Australia

Abstract. Mount Hagen is a Mid-Pleistocene stratovolcano located in Papua-New Guinea Highlands. The tectonic setting of the volcano has been a matter of considerable debate, with its complexity leading to different conclusions regarding magma source and classification. Two key questions remain unanswered: (i) is this “arc-like” magma related to a subduction zone and therefore part of an arc system and, (ii) can it be related to potential porphyry style economic mineralisation? Occurrence of porphyry deposits is strongly related to subduction zones, so the identification of tectonic setting is important for mineral exploration. If Mount Hagen is part of an arc system, is it barren or ore-bearing? Assuming that sulfide saturation, relative to volatile saturation, is one of the main factors controlling magma fertility, PGE, Re and Au concentrations were measured by fire-assay isotope dilution method in 18 samples, to determine its potential to form an Au-Cu deposit. PGE were chosen to investigate the timing of S saturation because of their low solution mobility in hydrothermal fluids and their high partition coefficient into sulfide melts. Analyses showed that S saturation occurred early in the system (at 8 MgO wt%), which make it unlikely that the system will produce an Au-Cu deposit.

1 Background

Porphyry deposits are large, low grade, epigenetic, intrusion-related deposits that form in magmatic arcs above subduction zones in both oceanic and continental margins (Wilkinson 2013). These systems are the primary resource world’s Cu (nearly three-quarters) and Au (almost a half) (Sillitoe 2010). Even though their metal grades are low, their economic significance is compensated by their size, which makes them desirable for exploration companies.

Most of these systems occur in recent or old subduction zones, so the prospectivity is strongly determined by this factor. Every year, exploration companies invest millions of dollars in discovery of locations of new porphyry systems. The process of identification whether they are barren, or ore-bearing is time- and funds-consuming. Intrusion shape, the mineral phases and even the alteration haloes around both types can be the same, which makes the prospecting problematic. Money and time could be saved, if barren systems could be distinguished from ore-bearing ones at an early stage of exploration.

The starting hypothesis for this study is that the timing of sulfide saturation, relative to volatile saturation, plays a key role in porphyry system fertility. If S saturation starts early, all of the chalcophile elements, including Cu and Au, are trapped in sulfide phases in a deep magma chamber, and are unable to enter a fluid phase. The result is a barren system. However, if the S saturation occurs late, after or shortly before the volatile saturation, metals will be able to enter the fluid phase and form a deposit (Park 2012). To precisely identify timing of sulfide saturation in the samples, platinum group elements (PGE) concentrations were measured in rocks of varying MgO content, assuming that they are related by fractional crystallization. PGE were chosen because their partition coefficients into sulfides are higher than Cu (1000 times higher) and Au (100 times higher), which makes them very sensitive indicators of the S saturation. Furthermore, their solubility in hydrothermal fluids is 1000 to 100 times less than Cu and Au, so they are more reliable indicators of magmatic processes. PGE occur in rocks in very low concentration, so it is necessary to apply a suitable method that can measure these elements with the required precision. Recent advances in the NiS fire assay-isotope dilution method make it possible to detect the PGE at ultra-low levels (ppt) and apply it to rock suites associated with porphyry Cu deposits (Park 2012).

A known quantity of spike (a solution with a known, unnatural isotope composition) is added to a sample to determine the concentration of an element. It can be calculated by measuring spike-sample mixture at the end of the process by using the formula (Stracke et al. 2014):

\[ A_{\text{mix}} = A_{\text{sa}} + A_{\text{sp}} \]
\[ B_{\text{mix}} = B_{\text{sa}} + B_{\text{sp}} \]

(Where: \( A_{\text{mix}} \) – a mixture of a sample \( A_{\text{sa}} \) and spike \( A_{\text{sp}} \), \( B_{\text{mix}} \) – a mixture of a sample \( B_{\text{sa}} \) and spike \( B_{\text{sp}} \))

2 Geological setting

Mount Hagen is a Pleistocene stratovolcano located in Western Highlands and Enga Provinces in Papua New Guinea (Mackenzie and Johnson 1984). It is the second highest volcano on both the island and on the Australian continent (3,778 m) and was formed during a magmatic period around 230,000 years ago. It is considered extinct with the last eruption taking place around 50,000 years ago (Mackenzie and Johnson 1984). The mountain lies on a folded Mesozoic and Cenozoic sedimentary sequence, which overlies late Palaeozoic granitic and metamorphic basement (Mackenzie 1972).

For many years, the tectonic setting of this very complex area of Papua New Guinea, and the formation of the Mount Hagen volcano were topics of discussion. Mackenzie (1972 and 1980) classified the volcano as belonging to an arc-like system, with no evidence for Benioff zone but with many geochemical similarities to arc systems. As most of the theories about formation of
porphyry deposits involve arc magmas, which are strongly associated with active subduction zones, there was no tectonic evidence to support the hypothesis that Mount Hagen could be related.

New theories suggest that porphyry deposits form even after tectonic activity on subduction zones stops (Richards 2009). Most likely, these magmas are products of remelting a previously subducted slab, activated during the post-subduction processes. Magmas formed this way normally do not host large amounts of sulfides. Recently, a number of porphyries have been related to magmas that were not associated with any contemporaneous subductions, however they are overlapping with the post-subduction processes or collisions between plates. This type of event is, in many ways, similar to subduction related calc-alkaline magmatism.

Recent reconstructions of Papua New Guinea microplate tectonics show that at around 4 Ma ago convergence between New Guinea and South Bismarck microplate led to a collision between Australian plate and an early Tertiary island-arc that later caused anticlockwise rotation of the New Britain arc (Hill and Hall 2003; Holm and Richards 2013; Koulali et al. 2015). This event eventually led to a subduction of Solomon Plate from northern and southern sides, creating a U-shape slab (Pegler 1995). This movement resulted in orogenesis, that is continuing to today, and formation of the New Guinea Mobile Belt. This, in turn, led to a series of thrusting and faulting at the continental margin (Jaques et al. 1977). Building on this hypothesis, Pegler (1995) suggested that the Solomon Plate’s southern slab is no longer active, and instead it is sinking under its own gravitational forces. Further uplift of Highlands triggered magmatic activity and formation of Mount Hagen from a subducted previously, partially melted slab (Jaques et al. 1977).

3 Samples and analytical methods

Forty-five whole-rock samples from Mount Hagen, which had previously been analysed for major elements by Mackenzie (1980), were obtained from the Australian National University and the University of Melbourne rock collections. Eighteen samples with a range of 2.04 to 11.5 MgO wt% were selected for further analysis.

The trace-element concentrations of all samples were measured by LA-ICP-MS at Research School of Earth Sciences at the Australian National University. Glass discs used for the analysis were prepared by mixing 0.5 g of rock powder and 1.5 g of flux (consists of 65% of lithium metaborate and 35% lithium tetraborate), and fused in an induction furnace. Calcium was used as an internal standard for the data reduction, NIST 610 as the primary standard, and NIST 612 and BCR-2G for quality control.

PGE, Re and Au concentrations were determined by the Ni-sulfide fire assay-isotope dilution method, described in detail by Park et al. (2012). Concentrations of these elements were measured by ICP-MS in solution mode at RSES. Selected samples were analysed in duplicate to monitor heterogeneity. To test the accuracy of the method, the standard TDB-1 was run during each analysis.

Chemical analyses of mineral phases were obtained by LA-ICP-MS at RSES and JEOL 8530F Plus Electron Probe Microanalyser at Centre for Advanced Microscopy (CAM), ANU. Eleven element and mineral distribution maps were also obtained by FEI Quanta QEMSCAN at CAM, ANU, using a step size of 15μm.

4 Results

4.1 Petrography and mineral composition

All the samples collected from Mount Hagen are moderately to strongly porphyritic, with phenocrysts of augite, olivine (samples with high MgO wt%) and hornblende (rocks with low MgO wt%) up to 4 mm, smaller plagioclase (1-2 mm), rarely biotite and microphenocrysts of Fe-Ti oxides. The groundmass in general consists of plagioclase (increasing with decreasing MgO content), alkali feldspar (decreasing with decreasing MgO content), ortho- and clinoxyroxene, fine-grained Fe-Ti oxides, hornblende and apatite (Fig. 1).

Most of the plagioclase and pyroxene phenocrysts show oscillatory zoning. Plagioclases tend to have slightly more calcic cores and sodic rims. In general, pyroxenes show enrichment in Mg with slightly more calcic cores whereas olivines show enrichment in Mg in the cores and Fe in the rims. Often, olivine phenocrysts with diopside or ferrosilite rims can be observed in high-MgO samples.

Figure 1. QEMSCAN image of 1707 thin section (11.5 MgO wt%). Cpx = here augite; Ol = forsterite; Plag = anorthite, Chr = chromite.

Most of the sulfides found in thin sections and polished mounts occur as rounded inclusions in pyroxenes of 5 to 20 μm in diameter (Fig. 2). Microprobe analysis of 6 of them show that they consist of 55 to 57 Fe wt%, 38 S wt%, 2.5 to 4 Ni wt% in high MgO samples (referred as pyrrhotites Fe$_{2.8}$Ni$_{0.3}$S$_{8}$) and 33 to 41 Fe wt%, 34 S wt%, 17 to 29 Cu wt% and up to 5.5 Ni wt% in low MgO ones (referred as chalcocyprites Cu$_{0.5}$Fe$_{1.1}$Ni$_{0.2}$S$_{2}$).

Figure 2. Rock thin section in optical microscope with reflected light.
4.2 Major- and trace-element geochemistry

Based on the alkali and silica content in samples, most of them were classified as basalts or andesites and form part of a calc-alkaline to high-K calc-alkaline series, typical of magmas from island arcs. (Fig.3).

Most of the primitive mantle-normalized rare earth element (REE) patterns of 18 samples are parallel to each other, suggesting that they come from the same system and are related by fractional crystallisation (Fig. 4).

Plots of Cu (Fig. 5), Sc and V, together with total Fe as Fe$_2$O$_3$ (Fig. 6) and TiO$_2$ show that sulfide saturation coincides with the onset of magnetite crystallization (the magnetite crisis) and occurred at about 8 MgO wt%. This conclusion is consistent with the previous studies reporting that the crystallisation of magnetite often triggers sulfide saturation in the system (Jenner et al. 2012).

Disagreement between duplicate analyses for both Pt and Pd indicate the presence of nuggets before and after sulfide saturation (Fig. 7). In this case, disagreement after 8 MgO wt% was expected, as it had been seen in previous studies (Park 2012; Hao et al. 2017), but finding it in pre-sulfide saturation samples was a surprise. It is suggested that this nugget effect is due to the presence of sulfide inclusions in phenocrysts carried into the sulfide unsaturated magma. These were seen as sulfide inclusions in pyroxene phenocrysts during microprobe analysis of thin sections of high MgO samples (Fig. 2). It is suggested that sulfide saturation occurred in two
stages. The first took place at early phase of magma evolution, probably in the magma chamber at the crustal level, where the fractionation occurred (>12 MgO wt%) and pyroxene phenocrysts grew. It involved precipitation of a small amount of sulfide, which affected the PGE due to their high partition coefficient into sulfides but did not affect Cu. The second stage of sulfide saturation occurred later in the magma evolution process, at around 8 MgO wt%, this time affecting all the chalcophile elements, including Cu.

Figure 7. Plot of Pt vs MgO for samples from Mount Hagen suite. Green arrows show variations in Pd. SS show the point of sulfide saturation. Blue circles are results of the first analysis, empty ones of duplicates.

5 Conclusions and implications for the ore-forming process

Recent studies of Papua New Guinea microplate tectonics, together with geochemical data suggest that Mount Hagen magma resulted of post-collision remelting of a previously subducted slab. As a consequence, the Mount Hagen suite could potentially be related to a porphyry system.

Major- and minor elements imply that fractional crystallization was the main factor controlling the geochemistry of the studied suite. Some scattering is attributed to presence of phenocrysts and minor alterations.

The PGE in Mount Hagen volcanics show that S saturation occurred early in the system, which agrees with previous studies, suggesting that metals such as Cu and Au were trapped in the crystallizing magma chamber and were unable to enter a fluid phase (Hao, 2017). As a consequence, the residual magma would be depleted in these elements the suite unlikely to produce a Cu or Au deposit despite the favourable tectonic setting.

Acknowledgements

This work was supported by an ARC Discovery Project to Ian Campbell. We would like to thank prof. Richard Arculus and prof. Jon Woodhead for providing samples used in this study. The authors acknowledge the facilities, and the scientific and technical assistance, of Microscopy Australia at the Centre for Advanced Microscopy, The Australian National University.

References

Wilkinson JJ (2013) Triggers for the formation of porphyry ore deposits in magmatic arcs. Nature Geoscience, 6:917-921
Abstract. The ~60 m thick Northern Irish Magilligan Sill is a dolerite and olivine gabbro intrusion, thought to be connected to the Irish dyke swarm plumbing system that is part of the British Palaeogene Igneous Province (BPIP) in the North Atlantic. The sill has received interest as an exploration target for Ni-Cu-PGE sulphide mineralisation due to its morphological similarity to Noril'sk-Talnakh (Russia). We present new petrological, geochemical and S-isotope data for the sill, to assess its prospectivity and detail the underlying magmatic plumbing system. Most sulphides in the dolerite portions of the sill contain negligible PGE. In the olivine gabbros, sulphides contain significant PGE, Cu, Ni, Co and Ag. Pyrite from the dolerites have δ34S ranging from -10.0 to +3.4 ‰ and olivine gabbro sulphides range from -2.5 to -1.1 ‰, suggesting widespread crustal contamination. The S/Se ratios of sulphides in the dolerites and olivine gabbros range from 3,500 to 19,500 and from 1,970 to 3,710, respectively, indicating that olivine gabbro sulphides may have come from upstream in the magma plumbing system. The Magilligan Sill records multiple injections of mafic magma into a single intrusive package, each with distinct mechanisms towards S-saturation. The divergence in S-saturation histories and metal contents suggest that a larger volume of olivine gabbro sulphides at depth may be prospective.

1 Geological Setting

The Magilligan Sill is a mafic intrusion injected into Mesozoic sedimentary rocks on the north coast of County Londonderry, Northern Ireland. It crops out close to the western edge of the Antrim Plateau, and is part of the BPIP in the North Atlantic Igneous Province (NAIP) (GSNI, 2004). Given its setting within a large igneous province, injected through a thick sequence of S-rich crustal sediments (akin to the Siberian Noril’sk Talnakh Ni-Cu-PGE deposit; Arndt et al. 2003), it is an interesting metal exploration target. Lonmin (Northern Ireland) Ltd. and now Walkabout Resources have been investigating the area since 2014. This study is the first published in-depth petrological and geochemical account of the sill since its first documentation (BGS, 1964).

2 Methods

A total of forty-seven half or quarter diamond drill core samples were collected for this study from three Lonmin boreholes in 2017 that intersect the sill and the overlying/underlying Mesozoic sedimentary rocks. The samples were analysed using electron microprobe analysis and laser ablation inductively coupled plasma (LA-ICP-MS) for in-situ major and trace element abundances, including PGE. Sulphur isotope (δ34S) analyses by mineral picking and conventional analysis of sulphides from the sill and sediment samples provide an indication of the S-saturation regime within the sill.

3 Results

New petrological logging of the drill core samples defined two major lithologies in the Magilligan Sill package. The first, which made up the majority of the intrusion thickness (~60 m), is a dolerite to gabbro (referred to herein as ‘dolerite’ for brevity). Laser ablation work revealed sulphides in the dolerites have a significant or complete lack of base and precious metals including PGE. The second lithology, which occurred as multiple ~1 m horizons within the main lithology, is an olivine gabbro. Chalcopyrite and pentlandite in the olivine gabbro contain up to 4 ppm total PGE, 1,460 ppm Co and 88 ppm Ag. Pyrite from the dolerites display δ34S ranging from -10.0 to +3.4 ‰, whereas sulphides in the olivine gabbro display signatures ranging from -2.5 to -1.1 ‰, S/Se in the different lithologies varies significantly, with the dolerites recording ratios an order of magnitude higher than the ‘mantle-like’ values of 2,850 to 4,350 (Eckstrand and Hulbert, 1987). Geochemical data are summarised in Fig. 1.
4 Distinct S-saturation histories

Discrete pulses of at least two chemically distinct magma generations were emplaced into the Magilligan sill within a single intrusion. Sulphur isotope signatures in the sill suggest widespread crustal contamination, given that ‘mantle-like’ $\delta^{34}S$ should be $0.1 \pm 0.5$ ‰ (Sakai et al. 1984). The large discrepancy in S/Se among the various horizons suggests that despite widespread contamination, their S-saturation mechanisms were different. The olivine gabbros (with low S/Se) are likely to have had less S added than the dolerites or even had S removed from sulphides through time. Ultimately, the sill appears to be made up of two distinct pulses of magma each with their own petrology, geochemistry, S-saturation pathways and mineralisation potential. The first magmatic generation crystallised to form most of the sill – olivine-deficient dolerites and gabbros with barren sulphide minerals. The second generation crystallised to form olivine gabbro horizons within the pre-existing sill, and contained metal-enriched sulphides. In order to form younger, more primitive magmas, the feeder chamber must have mixed with a new magma between the emplacements of the two different units in the sill, in a similar fashion to the overlying Antrim Plateau Lavas, in which more mafic Upper Basalts postdate less mafic Lower Basalts.

Overall, the $\delta^{34}S$ of the Magilligan Sill indicates that crustal S contamination is present throughout the entire intrusion. S/Se ratios in second-generation (olivine gabbro) sulphides are similar to that of published average ‘magmatic’ values of 2,850-4,350 (Eckstrand and Hulbert, 1987; Queffurus and Barnes, 2015), indicating a deeper/earlier S-saturation event perhaps with smaller degrees of crustal contamination. We propose that the second generation of sulphides belonging to the olivine gabbros were originally mineralised ‘upstream’ in the plumbing system that fed the Magilligan Sill. They were cycled through subsequent pulses of second-generation magma before being entrained and emplaced into the Magilligan Sill via ‘cumulative R-factor’ (Kerr and Leitch, 2005), in which subsequent magma pulses remove S from sulphides caught in the pulse while leaving metals (e.g. Se and PGE).

Figure 2 summarises the perceived development of the Magilligan Sill in 2 phases. The pre-existing dolerites and gabbros formed during Stage A most likely shielded this second pulse of magma (Stage B) from further S absorption from the local country rocks, preventing dilution or addition of late-stage magmatic-hydrothermal S. The possible controls on this deep S-saturation include: the changing initial composition of the magma at source; the amount of sedimentary S available to the magma via assimilation, and the degree of shielding from these sediments enforced by pre-existing layers of the sill; and the geometry of the magmatic plumbing system. Through a combined approach of S-isotopes, S/Se ratios and detailed petrography, the pathways to S-saturation may be determined within plumbing systems and valuable information fed back into the exploration industry with regards to vectoring towards orthomagmatic sulphide mineralisation, both in the BPIP and more generally for large igneous provinces.
Figure 2. Stage A in the magmatic development model for the Magilligan system, showing the formation of the dolerites and gabbros, and their barren sulphides. Stage B in the magmatic development model for the Magilligan system, showing the formation of the olivine gabbros, and their cycled base/precious metal sulphides. Model constructed with reference to similar systems in Barnes et al. (2016)

Acknowledgements

The authors would like to thank Gavyn Rollinson, Peter Frost, Joe Pickles, and Charlie Compton-Jones at the Camborne School of Mines laboratory facilities for their guidance during SEM and EPMA analyses. Thanks are also extended to Alison McDonald of the Scottish Universities Environmental Research Centre (SUERC) for her assistance on sulphur isotope analysis, and to Lonmin (Northern Ireland) Ltd. for access to core and previous studies on the sill. Walkabout Resources are thanked for their support in publishing this work and for access to company data.

References


Thermal modelling of the Paleoproterozoic Fedorova layered intrusion, Kola Region, Russia: implications for the origin of contact-style PGE mineralisation

Nikolay Yu. Groshev, Dmitriy G. Stepenshchikov, Geological Institute, Kola Science Centre, Russian Academy of Sciences, Russia

Bartosz T. Karykowski
Fugro Germany Land GmbH, Resource Consulting, Germany

Malte Junge
Institute of Earth and Environmental Sciences, University Freiburg, Germany

Artyom M. Sushchenko
Murmansk State Technical University, Russia

Abstract. This contribution presents the results of thermal modelling of the Paleoproterozoic Fedorova intrusion located in the central part of the Kola Peninsula, NW Russia. The intrusion hosts a large contact-style platinum-group elements (PGE) deposit in its basal 300-m-thick unit (Fedorova Tundra). This basal unit is composed of varied-textured gabbro-norite and is believed to be an additional injection of sulphide-saturated magma, representing a second intrusive phase. The irregular distribution of sulphides across the entire basal unit and the absence of sulphide liquid migration into the underlying basement rocks suggest that this second injection exploited the cooled down contact between the first intrusive phase and the basement. The hiatus between the first and the second intrusive event allowed for some cooling of the former, however, the duration of the hiatus remains unknown. Assuming an average geothermal gradient of 30°C/km and a basement temperature of approx. 400°C due to preheating, thermal modelling indicates that the hiatus may have lasted for some 600–700 thousand years. These results are in agreement with a classic contact-style PGE mineralisation model for Fedorova Tundra and suggest an out-of-sequence formation of the layered succession.

1 Introduction

A critical factor in the formation of contact-style low-sulphide platinum group elements (PGE) mineralisation in layered mafic-ultramafic intrusions is the preheating of host rocks due to magmatic activity, preceding the emplacement of sulphide-saturated magma (Karykowski et al. 2018). Preheating of the basement to 400 °C due to the intrusion of, for example, a series of dikes or sills that precede the main intrusion, creates conditions for the effective accumulation of sulphide droplets at the bottom of the magma chamber as well as for the percolation of sulphide droplets into the partially molten basement rocks. The Paleoproterozoic Portimo and Monchegorsk layered complexes on the Fennoscandian Shield are typical examples of intrusions where this factor played a crucial role (Iljina 1994; Karykowski et al. 2018).

The Fedorova intrusion represents the western block of the Paleoproterozoic Fedorova-Pana Complex located in the central part of the Kola Peninsula, NW Russia. The intrusion forms a 4-km-thick lens-like body that is steeply dipping to the southwest (Fig. 1a). Three zones are distinguished in the sequence of the Fedorova intrusion (from the bottom upwards): a Norite-Gabbro-norite Zone (or ‘basal unit’), a Leucogabbro-Gabbronorite Zone, and a Leucogabbro Zone (Staritsina 1978). It is suggested that the Leucogabbro-Gabbronorite and the Leucogabbro zones comprise an early magmatic phase (2526-2515 Ma) with reef-style PGE mineralization, whereas the contact-style PGE mineralisation-hosting basal unit belongs to a later intrusive phase (2493-2485 Ma) (Schissel et al. 2002; Groshev et al. 2009; Groshev and Savchenko 2011). The 300-m-thick basal unit is composed of varied-textured melanorite and gabbronorite containing abundant orthopyroxenitic autoliths and irregular patches of disseminated sulphide enriched in PGE (2–5 vol. %) (Fig. 1, b). Evenly disseminated sulphide accumulations (20–30 vol. %) are generally rare, whereas massive sulphides are absent. The PGE mineralisation is only hosted by the basal unit of the intrusion, showing no evidence for sulphide liquid percolation into the basement rocks. These sulphides form the Fedorova Tundra deposit with a total resources of more than 400 t of PGE (Rasilainen et al. 2010).

It is believed that the first intrusive phase of the Fedorova intrusion preheated the basement before the second phase intruded along the lower contact of the first intrusive phase (Fig. 1). A thermal contact aureole of the first phase reaches several hundred meters as evidenced by partially molten two-pyroxene diorites observed in some drill holes (Groshev et al. 2009). In spite of this the second intrusive phase does not practically show features of sulphide accumulation within the basal unit or sulphide percolation into the basement rocks. Consequently, the time gap between the intrusive phases was long enough for cooling of the basement below.
400 °C (temperature supporting sulphide migration and accumulation). The purpose of this study is to estimate the time gap between the two intrusive phases comprising the Fedorova intrusion using thermal modelling and to discuss the results in the context of the crystallization duration of layered intrusions as well as the formation of a contact-style PGE mineralisation.

\[ T_i^{n+1} = T_i^n + k\Delta t \left( \frac{T_i^n - 2T_i^n + T_i^{n-1}}{(\Delta x)^2} \right), \]

where \( k \) – thermal diffusivity \( (k = 2 \times 10^{-6} \text{ m}^2\text{s}^{-1}) \), and \( T_i^n \) – temperature at a depth of \( i \Delta x \) m in \( n \Delta t \) years. A detailed derivation of the equation is given in (Karykowski et al. 2018). To eliminate boundary effects, the depth of modelling was increased to 20 km.

The thermal modelling was carried out using a FPC-based software (Stepenshchikov and Groshev 2019). Intrusive bodies are defined by four parameters: the boundary of the roof (m), thickness (m), temperature (°C) and the point in time of intrusion (years). One can set a number of intrusive bodies at different moments of time. For each body, the modelling parameters are printed in a single line in window 1 of the software interface (Fig. 2). During the simulation, the current time and the moments of emplacement are comparing and when they match, temperature of intrusive body assigns to corresponding depths. Then the calculation procedure continues.

To track the temperature profile with depth and time, one can set a list of depths (window 2 in Fig. 2) and time points (window 3 in Fig. 2). They will be automatically reordered and rewritten in the corresponding windows. Based on these data, a table of temperatures is created (window 5 in Fig. 2). This table can then be exported into an .xls-file. The temperature-depth plot for time points from window 3 are showing in window 4. This window may also be useful for testing the validity of the input parameters. The simulation time is limited by the last time point in window 3. An early stop of simulation is provided and after an interruption of the calculation, the modelling will start anew without saving previous results.

3 Thermal modelling results

The simulation shows that the emplacement of the Fedorova first phase will lead to a significant heating of
the underlying rocks (Fig. 3 a–c; Table 1). The partial melting temperature of the basement (≈ 700 °C) will be reached approx. 250 m away from the lower intrusion contact after some 25 thousand years (Fig. 3 c, blue circle). This is in agreement with the thickness of two-pyroxene diorite below the intrusion (Fig. 1 b).

Since the magma of the second intrusive phase was sulphide-saturated, as a result of its emplacement in the preheated by the first phase contact with the basement the sulphides would have been concentrated near the bottom of the intrusion forming sulphide-rich layers and locally percolating into the Archean gneissic basement. Fig. 1 b shows that sulphides distributed unevenly and the migration of sulphide liquid is not observed at the Fedorova Tundra deposit. Consequently, the basal unit consisting of varied-textured gabbronorite that postdate the first intrusive phase were emplaced after the temperature at the lower contact of the first phase reached less than 400 °C. Under these boundary conditions, the minimum time separating the different intrusive phases is some 600–700 thousand years, as can be seen in Fig. 3 e–f (green circle) and Table 1.

4 Discussion

4.1 Duration of the Fedorova intrusion crystallization

The example of the Fedorova intrusion shows that the duration of crystallization under open-system conditions can be hundreds of thousands of years (Fig. 3). At the same time, the latest data on systematic isotope dating of open-system layered intrusions, show that the duration of their crystallization ranges from 1 to 3 Ma with an error of individual age determinations of up to 0.26 Ma modulo (Scoates and Wall 2015; Zeh et al. 2015; Wall et al. 2018). In this regard, it is worth noting that the currently available geochronological data on the Fedorova intrusion suggest a duration of crystallisation spanning some 40 Ma (Groshev et al. 2009), which appears to be greatly overestimated due to the likely inclusion of secondary zircon in the calculation of U-Pb ages (Groshev and Karykowski 2019).

<table>
<thead>
<tr>
<th>t (years)</th>
<th>Temperature, T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d=5 km</td>
</tr>
<tr>
<td></td>
<td>d=9 km</td>
</tr>
<tr>
<td>1</td>
<td>839</td>
</tr>
<tr>
<td>10</td>
<td>732</td>
</tr>
<tr>
<td>100</td>
<td>692</td>
</tr>
<tr>
<td>1000</td>
<td>677</td>
</tr>
<tr>
<td>10000</td>
<td>663</td>
</tr>
<tr>
<td>100000</td>
<td>517</td>
</tr>
<tr>
<td>200000</td>
<td>415</td>
</tr>
<tr>
<td>300000</td>
<td>350</td>
</tr>
<tr>
<td>400000</td>
<td>306</td>
</tr>
<tr>
<td>500000</td>
<td>276</td>
</tr>
<tr>
<td>600000</td>
<td>254</td>
</tr>
<tr>
<td>700000</td>
<td>236</td>
</tr>
<tr>
<td>800000</td>
<td>223</td>
</tr>
<tr>
<td>900000</td>
<td>211</td>
</tr>
<tr>
<td>1000000</td>
<td>202</td>
</tr>
</tbody>
</table>

Thus, the Fedorova Tundra deposit most likely represents a separate 'out-of-sequence'-type of contact-style PGE mineralization. The advancement of the isotope age determination on the intrusive phases of the Fedorova intrusion is possibly one of the most important unresolved problems in the petrology of layered intrusions on the Fennoscandian Shield.
4.2 Similar contact-style PGE mineralization in other layered intrusions

The presence or absence of sulphide liquid migration from the basal mineralised zones into the basement rocks is an important genetic feature of contact-style PGE deposits, revealing their thermal history. Except the Fedorova intrusion it can be shown by thermal modeling for the Nyud-Poaz massif (Monchegorsk Complex), which has two ore-bearing intrusive phases both containing disseminated sulphides, extending beyond the intrusion in the basement (Karykowski et al. 2018; Groshev and Pripachkin 2018). An additional phase (Gabbro-10), emplaced along the basal contact of the Nyud-Poaz intrusion hosts PGE mineralisation that percolates into the Archean basement for 30 m. Consequently, the additional injection of sulphide-saturated magma occurred at a time when the basal contact of the Nyud-Poaz massif was characterised by elevated temperatures. The time gap between these two phases, according to the thermal modelling of the Nyud-Poaz massif, is no more than 150 thousand years. The accuracy of isotope dating cannot resolve such small time differences at the moment (Scoates and Wall 2015). This is also shown by the isotope dating of the Gabbro-10 intrusion whose age coincides with the age of the Nyud-Poaz massif within the error limits (Amelin et al. 1995; Groshev et al. 2018).

The South Sopcha intrusion of the Monchegorsk Complex is another example of contact-style PGE mineralisation that was likely formed out-of-sequence (Chashchin and Mitrofanov 2015; Pripachkin et al. 2015). The South Sopcha intrusion has an orthopyroxenitic lower unit, which is extensively intruded and brecciated by sill-like gabbro-pegmatites and coarse-grained gabbro-norites containing PGE-rich disseminated sulphide. The issues of sulphide migration from the gabbro-norites into the basement rocks as well as the duration of the South Sopcha crystallisation are to be solved in future research.

Acknowledgements

This research was carried out under the scientific theme No. 0226-2019-0053.

References

Ilijina M (1994) The Portimo layered igneous complex: with emphasis on diverse sulphide and platinum-group element deposits. University of Oulu Oulu, Finland
Sulfide textures, chalcophile element distribution, and timing of mineralization within the Crystal Lake intrusion, 1.1 Ga Midcontinent Rift

Jennifer W. Smith, Wouter Bleeker, Duane Petts
Geological Survey of Canada

Mike Hamilton
Jack Satterly Geochronology Laboratory, University of Toronto

Abstract. Magmatic Ni-Cu-PGE deposits of the ca. 1.1 Ga Midcontinent Rift (MCR) occur in association with a diverse range of ultramafic-mafic intrusions. High precision U-Pb dating throughout the MCR is critical for constraining the various magmatic pulses, the temporal and spatial controls on metal enrichment, and improving our general understanding of the rift's evolution. The 1099 Ma Crystal Lake layered intrusion is an olivine rich, Cr-spinel bearing, vari-textured gabbroic body, that hosts extensive low-grade Ni-Cu-PGE mineralization, and is broadly comparable to the nearby Duluth Complex. The Ni-Cu-PGE mineralization shows some similarities to other deposits such as Marathon (Coldwell Complex), Voisey's Bay and Norilsk. Segregation vesicles are common and show a close association with globular sulfides. The timing, cause and significance of degassing for ore genesis is yet to be fully explored but appears to be a feature of many Ni-Cu deposits.

1 Introduction

North America’s Midcontinent Rift (MCR) represents one of the best preserved and accessible intra-continental rift systems of late Mesoproterozoic age. The ca. 1.1 Ga failed rift system hosts a range of mafic-ultramafic, carbonatitic and alkaline intrusions, many of which are actively being explored for a range of commodities (e.g. Ni, Cu, PGE, Co, Cr, V, Nb). The magmatic Ni-Cu-PGE sulfide deposits occur in association with a diverse range of mafic and mafic-ultramafic intrusions. Like many other world-class Ni-Cu deposits (e.g. Norilsk, Voisey’s Bay, Raglan), this mineralization shows a close spatial and temporal relationship with large volumes of magma erupted at or near the margins of Archean cratons (Begg et al. 2010; Barnes et al. 2016) and a local prolific sulfur source.

Within the MCR, the most prospective Ni-Cu-PGE targets (e.g. Eagle, Tamarack) are hosted by small, ‘early-rift’ (ca. 1117–1106 Ma; Miller and Nicholson 2013), mafic-ultramafic intrusions. These deposits are developed within the magmatic plumbing system of the rift, an environment known to be favourable for the development of high-grade massive sulfides (Song et al. 2011; Barnes et al. 2016). The ca. 1099 Ma Duluth Complex and similar large, sill-like, mafic layered intrusions (e.g. Sonju Lake, Mellen Complex, Echo Lake, Crystal Lake, Coldwell Complex) are also known to host Ni-Cu-PGE sulfide mineralization (Good and Crocket 1994; Joslin 2004; Ripley 2014). Although these intrusion types are characterized by disseminated sulfides and often have lower grades than the conduit deposits, they remain prospective targets and are favourable settings for the development of stratiform reef-style PGE-Ni-Cu mineralization (e.g. Sonju Lake: Joslin 2004; and Duluth Complex: Miller 1998).

Although the MCR system has a rich legacy of past and on-going research, the fundamental controls pertaining to the localization and timing of mineralization remain poorly understood. In order to understand why significant Ni-Cu-PGE mineralization is not developed within all rift-related mafic-ultramafic intrusions a better temporal framework in addition to an improved understanding of source characteristics and geometry is required.

2 Crystal Lake intrusion

A detailed geochemical and isotopic study is underway on the 1099.1 ± 1.2 Ma (Heaman et al. 2007) Crystal Lake intrusion, which has previously been compared to the proximal Duluth Complex (Thomas 2015). The aim of this study is to gain further insights into the controls on ore genesis within the ‘main-rift’ intrusions (Miller and Nicholson 2013).

The Crystal Lake intrusion, located 47 km southwest of Thunder Bay, Ontario, Canada, outcrops as a prominent Y-shaped body (Fig. 1) within the Paleoproterozoic Animikie basin, intruding sulfur-bearing shale, argillite and greywacke of the Rove Formation (Geul 1970, 1973). Geochemically, the Crystal Lake intrusion can be distinguished from the more primitive conduit-type bodies by its olivine composition (Fo51-79), lower Ni/Cu and Pt/Pd ratios (<1), higher rare earth element (REE) abundances, light REE enrichment and minimal fractionation of heavy REEs (Gd/Yb <2; Thomas 2015; O’Brien 2018).

Although a number of dating studies have been undertaken on the MCR (see Heaman et al. 2007, for a relatively recent compilation), many of the intrusions either lack the precision that is now possible with routine chemical abrasion U-Pb geochronology or are yet to be dated. Consequently, the relationship between various rift-related intrusions remains poorly constrained. We are currently undertaking a comprehensive geochronology study on the Crystal Lake intrusion.
study throughout the MCR, this includes detailed dating of the Crystal Lake intrusion. In addition to refining Heaman’s et al. (2007) baddeleyite age of 1099.1 ± 1.2 Ma we aim to constrain the relationship of the northern and southern limbs of the intrusion. Furthermore, we plan to untangle the timing of the Crystal Lake intrusion relative to other MCR intrusive events including the NE-trending Pigeon River dykes, the NW-trending Cloud River dykes and the sulfide-bearing Mount Mollie intrusion developed to the east (Fig. 1).

Crystal Lake has previously been suggested to be coeval with the Mount Mollie dyke (Smith and Sutcliffe 1987; O’Brien 2018). This however is not supported by the current baddeleyite age date of 1109.3 ± 6.3 Ma (Hollings et al. 2010). Due to limited exposure, the timing relationships of the Crystal Lake intrusion with the Pigeon River, Mount Mollie and Cloud River dykes has not been successfully established from field observations.

3 Ni-Cu-PGE mineralization

Ni-Cu-PGE sulfide mineralization is developed within the northern and southern limbs of the Crystal Lake intrusion in association with vari-textured gabbros and irregular Cr-spinel-bearing horizons (Fig. 2). The association of sulfides and metal enrichment with pegmatic/taxitic units is also observed within other Ni-Cu-PGE deposits such as the ca. 1108 Ma (Heaman and Machado 1992) Coldwell Complex, Merensky Reef, Norilsk and Voisey’s Bay. The upper troctolite and magnetite-bearing olivine gabbro of the northern and southern limbs, respectively, appear to be barren of sulfides.

Sulfide mineralization is largely disseminated, with massive sulfides (<50 cm in thickness) developed locally within the northern limb (Fig. 2). The disseminated ores are variable in texture with globular (capped and uncapped), blebby and interstitial sulfides identified. Within the Crystal Lake intrusion, globular sulfides have been identified within the mineralized zones of the southern limb, where they occur in association with both the vari-textured gabbros and Cr-spinel-bearing ores. Disseminated sulfide ores within the northern limb appear to be more interstitial and blebby in morphology.

Silicate-capped sulfide globules have been recognized in other Ni-Cu sulfide deposits (e.g. Norilsk, Insizwa Complex; Barnes et al. 2017; Le Vaillant et al. 2017) and are interpreted as being the remnants of former segregation vesicles that attached to an immiscible sulfide melt (Mungall et al. 2015). Within the Crystal Lake intrusion, the morphology of the caps, which are comprised of amphiboles, clays, chlorite and calcite, is variable. Convex silicate caps, identical to those modelled by Mungall et al. (2015), are present along with very irregular silicate attachments (Fig. 3).

The ores are dominated by the primary magmatic assemblage pyrrhotite, pentlandite, chalcopyrite and cubanite with minor magnetite. Minor nickel arsenides are recognized within the massive sulfide assemblage, where they reside as rounded grains (<150 µm in diameter) within the primary phases. Within the disseminated ores, sulfide grains are composed primarily of either pyrrhotite or chalcopyrite. Pentlandite occurs as granular grains within pyrrhotite, around the margins of the composite grains or along the contact between pyrrhotite and chalcopyrite. Exsolution flames of pentlandite within pyrrhotite are also observed and are preferentially
concentrated along fractures. In areas where chalcopyrite and cubanite occur adjacent to pyrrhotite, rounded relics of pyrrhotite are observed within the Cu-rich phases.

Figure 2. Photographs from the Crystal Lake intrusion. a. Vari-textured gabbro. b. Horizons rich in Cr-spinel with disseminated and blebby sulfides. c. Massive sulfides.

A low temperature alteration assemblage characterized by pyrite, chalcopyrite and magnetite is recognized in both the disseminated and massive sulfide ores. The degree of replacement of the primary assemblage is variable throughout the intrusion although alteration does appear more pervasive in the disseminated ores of the northern limb.

A detailed elemental deportment study is currently in progress, focused on characterizing the distribution and mineralogy of platinum-group minerals (PGMs). Element mapping of sulfides by LA-ICP-MS has been used to further investigate the controls on the distribution of the chalcophile elements during sulfide fractionation. Preliminary observations indicate that Pd resides in solid solution within pentlandite (1-150 ppm) and as small As-Bi and Sb-bearing PGMs. Within the massive sulfides, Pd-bearing minerals show a strong association with nickel arsenides resulting in lower concentrations of Pd (~1 ppm) in the pentlandite than typical of other sulfide assemblages (10–150 ppm). Platinum is not compatible in any of the sulfide phases, instead occurring as discrete As and Sb-bearing PGMs. A close spatial association is observed between the PGMs and the sulfides. The PGMs are found either enclosed or attached to sulfides or within secondary silicates around the altered margins of the sulfides. It is yet to be established whether the crystallization of Cr-spinel and/or low-temperature alteration of the sulfides has had any control on the mineralogy and distribution of PGEs.

Figure 3. Silicate capped sulfides within the Crystal Lake intrusion, showing a range of sulfide and cap morphologies.

Element mapping of the sulfides by LA-ICP-MS has revealed some interesting structural and/or mineralogical controls on the distribution of chalcophile elements. Although not observed throughout the primary sulfide assemblage, some unaltered sulfides are characterized by a strong microfabric (Fig. 4). This fabric is defined by several elements including As, Mo, Bi, Pb, Pd and Re which appear to be preferentially concentrated along thin, parallel linear features within the pyrrhotite-pentlandite-chalcopyrite assemblage. The molybdenum map also shows thicker banding and elevated concentrations within pyrrhotite (Fig. 4). Interestingly this fabric is not confined to a particular sulfide phase. This is best shown by As, Mo and Re which clearly cut across the boundaries of pyrrhotite, pentlandite and chalcopyrite, which suggests that this fabric was developed subsequent to crystallization of all three sulfide phases. For other elements such as Pd and Pb, the fabric is restricted to the pyrrhotite and pentlandite (Fig. 4). Silicate infilled fractures appear to cut the fabric as shown in the As map. Further work is in progress to determine the controls on selected element mobility (i.e. low temperature alteration or deformation) and to gain an understanding at what scale this remobilization is occurring. If various elements are remobilized over long distances then it could have implications for vectoring of Ni-Cu ore systems.
4 Implications

The MCR provides a superb laboratory to study the differences between mineralized and unmineralized intrusions within a single tectonic setting and provides the opportunity to assess key controls on metal endowment within a LiP-scale magmatic system. Refining and expanding the existing age database for the MCR is fundamental if we are to improve our understanding of the rift's evolution and decipher whether there are temporal and/or spatial controls on metal enrichment. Improved geochronology for intrusions such as Crystal Lake, may also have direct implications for exploration within the area, and help in identifying new prospective intrusions.

Segregation vesicles associated with globular sulfides have recently been recognized in numerous Ni-Cu-PGE bearing mafic intrusions. Those documented at Crystal Lake show a striking resemblance to those described in the Norilsk ores (Le Vaillant et al. 2017; Barnes et al. 2017). The implications of degassing, which appears to be a common process within the Ni-Cu ore systems, for sulfide transportation and deposition is yet to be constrained. Furthermore, the cause (e.g. contamination, pressure changes) and timing of degassing relative to crystallization is not well understood.

Element mapping by LA-ICP-MS is an extremely powerful tool, providing unparalleled detail at the micro scale. This technique provides insight into the behavior and mobility of chalcophile elements during sulfide fractionation, low temperature alteration and/or deformation and may provide a link to larger element haloes associated with some Ni-Cu-PGE deposits.

![Element maps of primary sulfide assemblage](image)

**Figure 4.** LA-ICP-MS element maps of primary sulfide assemblage.

Acknowledgements

This study was supported by the Geological Survey of Canada’s Targeted Geoscience Initiative Program (TGI). The authors thank our partners at Rio Tinto, North American Palladium, Transition Metals, Panoramic, Stillwater Canada and Lakehead University for their help, access to data and constructive discussions. The Ontario Geological Survey are also thanked for their logistical support throughout the 2017/2018 field season. Sarah Davey is thanked for assistance in the field.

References


Petrological characteristics of mafic-ultramafic intrusions of the Khangay upland (Mongolia)

Maria Shapovalova, Roman Shelepaev, Nadezhda Tolstykh
VS Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia

Abstract. New data on the petrology and geochemistry of lithologies from the mafic-ultramafic massifs of Oortsog, Dulaan, Mankhan and Yamat (Khangay upland of the Central Asian Orogenic Belt, CAOB) are presented. The petrological characteristic of the massifs, together with their inherent positive anomalies of Cs, Sr and negative anomalies of Ta, Nb, indicates that magmatism stemmed from two different mantle source regions – a mantle plume interacting with the lithospheric mantle portions of a subduction zone. The received characteristics are comparable with the data of massifs of East Kazakhstan and Western Baikal described earlier. The aim of study is identification of typomorphic features of these massifs to understand the type of mantle magmatism and geodynamic environment of region.

1 Geological setting and relationships

The Oortsog, Dulaan, Mankhan and Yamat mafic-ultramafic massifs are located in the Khangay upland of Mongolia (Fig. 1). The Khangay upland belongs to the Central Asian Orogenic Belt. A Late Paleozoic and the Early Mesozoic 0.5 million km² batholite forms the central portion of the CAOB. This comprises the Angara–Vitim in the Western Baikal region (Litvinovsky et al. 1992), Khangay in the Central Mongolia (Fedorova 1977), Hentey in East Mongolia and the Central Baikal region (Koval et al. 1978). The batholite comprises a spectrum of lithologies, from gabbroids to leucogranites and alkaline granites. Dykes, subjacent intrusives and small massifs occur in association with granitoids (Yarmolyuk et al. 2016). The mafic-ultramafic massifs formed in the earliest stages of the Khangay batholite (Izokh et al. 2011) with the majority in the southern part of the batholite being Permian in age. The massifs are likely a thermal source for the partial melting and formation of granitoids (Izokh et al. 2011; Shelepaev et al. 2016).


2 Analytical methods

All analysis were carried out in the Analytical Centre for multi-elemental and isotope research of the VS Sobolev
Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia. Major element oxides (70 samples) were determined by XRF using an ARL 9900. Trace elements and REE (38 samples) were analysed by ICP-MS using an Element-I Finnigan MAT. Argon isotope ratios of biotite were measured using a GV Instruments ARGUS. SHRIMP-II zircon dating was carried out in VSEGEI’s Centre of Isotopic Research (St. Petersburg). Sm-Nd isotopic analyses of whole rock samples were determined using TIMS at the Geological Institute Kola Science Centre (Apatity).

3 Petrological characteristics

The layered Oortsog massif is approximately 5 km² and located on the northern slope of the Khangay uplands, on the left bank of the Tamiryn-Gol River in Western Mongolia (Izokh et al. 1990). The massif hosts two intrusions (Shapovalova et al. 2018): a rhythmically-layered peridotite with biotite-free gabbro (Intrusion 1); and a massive biotite-bearing amphibole gabbro with olivine gabbro (Intrusion 2). Geochemically, Intrusion 2 differs from the Intrusion 1 due to its higher content of incompatible elements (Ti, Rb, Ba et al.), including the content of alkali (Na, K). The positive anomalies of Cs, Sr and negative anomalies of high field strength elements (HFSE) such as Ta, Nb for the Intrusions 1 and 2, and also Zr, and Th (only the Intrusions 1) are observed on mantle-normalized spidergrams (Fig. 2). Results of Sm-Nd isotope analysis showed that rocks from the Intrusion 1 have positive value of εNd of +13.5 (at 270 Ma) while rocks from the Intrusion 2 have negative εNd of -4.3 (at 270 Ma). Such compositions of εNd demonstrate the existence of two sources of melts from which the Oortsog massif was formed: (1) a depleted source and (2) an enriched source (White and Hofmann 1982). Overall, the melt composition of Intrusion 2 cannot be the product of fractionation of a melt from Intrusion 1, but instead that the two intrusions are products of partial melting from at least two distinct mantle source regions (Bogatikov et al. 1987). The Cu-Ni-PGE mineralization in the both Intrusions was found (Shapovalova et al. 2015, Mao et al. 2018). The Ar-Ar age of Intrusion 1 is 278.7 ± 2.5 Ma. A U-Pb zircon age of Intrusion 2 is 272 ±2 Ma (SHRIMP II) (Shapovalova et al. 2018).

The Dulaan massif, located 1.5 km west of Oortsog (Fig. 1) is composed of a highly altered olivine gabbro. The massif has a similar REE composition to the Oortsog massif (Fig. 3). The Mankhan massif located to the north of the Khangay upland (Fig. 1) is composed of gabbro and gabbronorite and has positive anomalies for Ba and Sr, and negative anomalies for Ta and Nb on mantle-normalized spidergrams (Fig. 4). The Yamat peridotite-gabbro-monzogabbro massif is located in the south of the Khangay uplands and contain three intrusions (Shelepaev et al. 2015). The youngest intrusion is composed of a monzogabbro and is enriched with alkalis and incompatible elements, indicating an enriched mantle source. The age of the Yamat massif is 255.8±2.9 Ma (Intrusion 1, U-Pb) and 262.6±3.1 Ma (Intrusion 2, U-Pb) (Shelepaev et al. 2015).

Trace element spidergrams of the Yamat massif correlate well with the patterns of the Oortsog, Dulaan and Mankhan massifs: a flat negative slope, positive Cs, Ba, Sr anomalies and negative Ta and Nb anomalies (Fig. 5). Such geochemical characteristics appear to be inherited from a source of subduction origin.

4 Discussion

There are two hypotheses about the formation of the mafic-ultramafic massifs of the Khangay upland: 1) the magmatism was caused by the activity of the Khangay mantle plume and these massifs relate to a large igneous province (LIP) (Yarmolyuk et al. 2013b); 2) the magmatism is due to subduction processes at active continental margins (Ernst 2014). REE characteristics of the gabbroid of the Khangay upland are ambiguous and cannot be used to distinguish the paleo-geodynamical genesis of their region’s basic magmatism. On the one hand, the studied mafic-ultramafic massifs have the characteristics of an IAB (e.g., the enrichment by large ion lithophile elements, LILE, and Sr, and the negative anomalies of Nb, Ta, Zr, Hf). On the other hand, geochemical characteristics of plume-derived basalts are also evident (e.g., enriched in alkalis, Ti and PGE). Hence, we proposed a model of mantle plume and subduction lithosphere interaction. The model explains the duality of geochemical characteristics of the basic massifs, as early intrusions of Khangay batholith.
Magmatic Sulfide and Oxide Systems

Magmatic Sulfide and Oxide Systems 563

Figure 4. Primitive mantle normalized trace elements patterns for the gabbroid of the Mankhan massif.

Figure 5. Primitive mantle normalized trace elements patterns for the gabbroid of the Yamat massif.

Similar massifs with enriched (plume-related) and depleted (subduction-related) characteristics have been identified in other regions of CAOB – for example, (1) in the Surovsko-Talovsky gabbro massif (East Kazakhstan) (Khromykh et al. 2016) and (2) the mafic-ultramafic massifs of the Krestovsky zone (western Baikal region) which are composed of two geochemically distinct yet synchronous gabbroids (Lavrenchuk et al. 2017).

Overall, the gabbroids of the later intrusions in this suite have higher concentrations of incompatible elements than gabbroids of the earlier phase of intrusion (for rocks of equivalent MgO). In particular, the distinct negative Ta-Nb anomalies and positive Sr anomalies in the gabbroids of the later intrusions could provide evidence of a subduction-related component in a magma-generating source (Khromykh et al. 2016, Lavrenchuk et al. 2017).

The volume of granitoid magmas of the Khangay batholite exceeds 0.5 million km$^3$ (Turutanov et al. 2006, 2007). This is requiring the equivalent amount of the mafic magmas for the implementation of large-scale melting (Dobretsov et al. 2005). Thus, all granitoid and mafic-ultramafic massifs of the Khangay upland are considered as fragments of the large igneous province (Bryan and Ernst 2008).

The described earlier other massifs of Khangay upland (Nomgon and Nariyntolburiyngol) (Izokh et al. 1998, Izokh et al. 1990) are also Permian in age and host the Cu-Ni-PGE mineralization. Therefore, they as well the studied massifs are related to Khangay LIP.

5 Conclusions

1) The activity of the Khangay mantle plume is the factor of magmatic activity in Perm. Consequently, mafic-ultramafic massifs of the Khangay upland (Oortsoog, Dulaan, Manikhan and Yamat) with dual geochemical characteristics were formed as a result of the interaction of plume and a lithospheric mantle.

2) The Permian mafic-ultramafic massifs enriched in Cu, Ni and PGE together with granitoids of the Khangay batholite are the parts of LIP.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant 19-05-00181 and integration project of SB RAS “Carbon-Permian-Triassic granitoid batholites and mafic-ultramafic complexes of the southern border of the North Asian craton: age boundaries, numerical models of formation, metallogeny”) and by the Ministry of Education and Science of the Russian Federation (project no. 14.Y26.31.0018).

References


Yarmolyuk VV, Kuzmin MI, Kozlovskiy AM (2013b) Late Paleozoico- Early Mesozoico intraplate magmatism of northern Asia: trap, rifts, batholite giants and geodynamics of their formation. Petrology 21(2): 115-142.

Yarmolyuk VV, Kozlovskiy AM, Kuzmin MI (2016) Zoned magmatic areas and anorogenic batholith formation in the Central Asian Orogenic Belt (by the example of the Late Paleozoico-Khangai magmatic area). J Geol Geophys 57(3): 457-475.
Genesis of PGE-rich ophiolitic chromitites by assimilation of orthopyroxenite in the ophiolitic mantle of Loma Las Cabirmas, Dominican Republic

Júlia Farré-de-Pablo, Joaquín A. Proenza
Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona, Spain

José María González-Jiménez, Antonio García-Casco
Departamento de Mineralogía y Petrología, Universidad de Granada, Spain

Lisard Torró
Geological Engineering Program, Faculty of Sciences and Engineering, Pontifical Catholic University of Peru (PUCP)

Francisco Longo
Universidad Católica Tecnológica del Cibao, Dominican Republic

Abstract. This communication provides the first report of ophiolitic chromitites hosting clots of orthopyroxenites. These are Cr-rich chromitite (Cr# = 0.81–0.83) hosted in mantle peridotite from the Loma Las Cabirmas locality, Dominican Republic. A qualitative estimation of the composition of the melt in equilibrium with chromitite suggests that they were likely precipitated from a mantle melt with boninitic affinity, consistent with the abundance of inclusions of Ru-Os-Ir minerals (mainly laurite) and a lack of Ni-Fe-Cu sulfides. A distinctive feature of the chromitites from Loma las Cabirmas is the replacive contact between chromitite and the hosted clots of orthopyroxenites. We suggest a model in which orthopyroxenite and chromitite were formed as a result of the metasomatic reaction of mantle peridotite with infiltrating basaltic melt of boninitic parentage.

1 Introduction

Ophiolitic chromitites are monomineralic rocks of Cr- and Al-rich magnesian spinel (chromite) often hosted in mantle peridotites within the upper-mantle portion of an ophiolite or near the crust–mantle boundary. Most ophiolitic chromitites have dunite envelopes of variable thickness that separate them from the host harzburgite or lherzolite, although some chromitites are found in direct contact with the host peridotite with no dunite envelope. Pyroxenite has also been described in the form of dykes cross-cutting chromitite bodies or being assimilated by them.

During the past few decades many researches have focused on unravelling the genesis of the ophiolitic chromitites. A general assumption is that most ophiolitic chromitite form at low pressures (< 1 GPa) in the upper portions of the oceanic upper mantle in supra-subduction zones (González-Jiménez et al. 2014). Progressive reaction of sub-arc mantle peridotite with infiltrating basaltic melts (mid-ocean ridge basalts, back-arc basin basalts or island-arc tholeiites) may lead to the formation of dunite, corresponding to former higher permeability melt-conduit channels where batches of these types of melts, with different degrees of fractionation, may mingle to form the chromitites (Arai and Yurimoto 1994).

In this model, reaction of mantle peridotite and infiltrating melt at different melt/rock ratios is responsible for the variety of textures of the chromitites in ophiolites. Globally, textures of massive chromitite are found in the central part of the chromitite bodies, where the melt dominates. Conversely, when the melt/rock ratio is low at the margins of the chromitite bodies, disseminated or antinodular textures are more likely to be found. In antinodular chromitites, the chromitite surrounds relatively large ovoid masses of dunite, usually corresponding to former dunite channels that are being replaced.

Some authors described isolated lenses of the host rock within massive chromitites. In these cases, the clots are considered to be clear evidence of chromitite intrusion into the host peridotite. The composition of the clots is typically dunite and/or harzburgite/lherzolite (González-Jiménez et al. 2014). For example, Payot et al. (2013) described dunite clots located at the center of massive chromitite bodies at the Zambales Ophiolite Complex (Philippines). González-Jiménez et al. (2013) described clots of ortho- and clino-pyroxenites within podiform-like chromitites hosted in subcontinental dunite-harzburgite from the Ronda ultramafic massif in southern Spain. Here we provide the first example of ophiolitic chromitite hosting clots of orthopyroxenite and discuss their possible origin in relation with the formation of the chromitite deposit.

2 Geological background and description of the chromitites

Loma Las Cabirmas chromitite body is hosted in peridotites of the Loma Caribe massif, in the central part of the Dominican Republic (Fig. 1). The Loma Caribe peridotite is a NW–SE belt, which extends 95 km and 4 to 5 km wide along the Cordillera Central. Interpreted as remnants of a Mesozoic ophiolitic complex, the peridotite belt consists of small amounts of lherzolites associated...
with spinel-bearing harzburgites hosting small (< 10 m long) dunite bodies. These peridotites show variable degrees of serpentinization (40% to 90%; Marchesi et al. 2016). The Loma Caribe peridotites were emplaced as the result of collision of the oceanic Duarte plateau terrane with the primitive Caribbean island arc in the Aptian (Draper et al. 1996; Lewis et al. 2002). After its emplacement, the Loma Caribe peridotite experienced numerous cycles of weathering and lateritization, ultimately forming the largest Mg silicate-type Ni-laterite deposit in the Greater Antilles (Aiglsperger et al. 2015; Lewis et al. 2006).

The Loma Caribe peridotites contain frequent lenses of massive chromitite (up to 10 m in length and < 1 m thick) hosted in heavily serpentinized dunites (Proenza et al. 2007). These occur widespread in different locations through the whole peridotite belt. At Loma Las Cabirmas, the chromitites form small elongated pods (up to 4 m) of massive chromite, characterized by the presence of frequently altered ultramafic clots ranging in diameter from 2 mm to 4 cm (Fig. 2). The smaller clots exhibit irregular morphologies while the larger ones are sub-angular to oval-shaped. The chromitites are also characterized by PGE enrichment (up to 6.5 ppm; Farré-de-Pablo et al. 2017) and for being crosscut by veins of uvarovite.

3 Analytical techniques

Polished thin sections were prepared from four chromitite samples from Loma Las Cabirmas and subsequently investigated using a Quanta 200 FEI XTE 325/D8395, and a field-emission scanning-electron microscope (FE-SEM) Jeol JSM-7100 at the Serveis Científics i Tecnològics, University of Barcelona, Spain. Quantitative EMP analyses were obtained with a JEOL JXA-8230 electron probe microanalyzer in the wavelength-dispersive spectroscopy (WDS) mode, operating with an accelerating voltage of 20 kV, a beam current of 10 nA and a beam diameter of 1 μm.

4 Petrography

The Loma Las Cabirmas chromitites display massive textures consisting of euhedral crystals of chromite showing triple junctions. These samples of massive chromitites are frequently crosscut by veins of uvarovite, with thicknesses between 100 μm and 1 mm. Despite the fractures and alteration, chromite grains are homogeneous and show no chemical variation towards their edges or fractures. Primary matrix minerals are not preserved but have predominantly been replaced by serpentine and accessory Fe-Ni alloys (up to 10 μm). The chromite grains often host inclusions of serpentine and clinopyroxene as well as accessory platinum-group minerals (PGM) and Ni-Fe sulfides. Silicate inclusions form negative crystal shapes and are frequently altered to serpentine. The inclusions cluster in specific domains of the chromite grains (Fig. 2).

Most clots of silicate found in the chromitite are altered, although one of the clots identified still preserves an unaltered core composed of orthopyroxene (70%) and minor amounts of olivine, and accessory chromite also hosts inclusions of clinopyroxene and phlogopite. Locally, the olivine grains host aligned rounded-to-elongated microscopic inclusions of Fe-(Ni) alloys.

Figure 1. Geological map of central Dominican Republic, showing the location of Loma Las Cabirmas chromitite. Modified from Aiglsperger et al. (2015).

Figure 2. Top: Photomicrograph of the clot-chromitite contact (transmitted cross-polarized light). Bottom Photomicrograph of the massive chromitite with silicate inclusions. (up to 3 μm long and 2 μm in thickness). In the core of the clot, orthopyroxene shows alteration to amphibole along
its boundaries and along exfoliation planes whereas olivine grains are altered to sepiolite. Olivine is also crosscut by serpentine veins hosting abundant < 1 μm grains of awaruite. In contrast, close to the contact between the clot and chromitite, orthopyroxene is bastitized. The clot–chromitite contacts (Fig. 2) are irregular with interlocking textures defined by chromitite replacing orthopyroxene grains.

5 Mineral chemistry

Chromites from the Loma Las Cabirmas chromitites are unaltered, with SiO$_2$ contents invariably low (< 0.1 wt.%) and homogeneous in composition, and Cr# [Cr/(Cr + Al), atomic ratio] between 0.81 and 0.83, corresponding to 60.05–62.25 wt.% Cr$_2$O$_3$ and 8.46–9.52 wt.% Al$_2$O$_3$ contents (Fig. 3). The Mg# [Mg/(Mg + Fe$^{2+}$), atomic ratio] ranges from 0.61 to 0.65, corresponding to FeO contents between 12.44 and 14.30 wt.%. The chromites exhibit heterogeneous TiO$_2$ contents, from 0.09 to 0.27 wt.%, and relatively high NiO contents from 0.11 to 0.29 wt.%. Minor amounts of MnO (0.09–0.16 wt.%) and ZnO (0.04–0.14 wt.%) were also detected.

Accessory chromites within the clots show Cr# similar to the chromitite chromite (0.79–0.82). However, they are richer in FeO and NiO (15.62–20.90 wt.% and 0.20–0.47 wt.%, respectively) and poorer in MgO (7.87–11.59 wt.%). Their composition also varies depending on the degree of alteration of the clot. Accessory chromites within clots with a higher degree of serpentinization exhibit higher contents of MgO and NiO, and lower FeO content than the ones within unaltered clots. In all cases, chromite compositions are compositionally distinct from accessory chromite from the associated peridotite (Fig. 3).

Olivine is richer in Mg and Ni in the clots (Fo = 93–94; NiO = 0.79–2.04 wt.%) than in the associated peridotite (Fo = 90–91; NiO = 0.35–0.48 wt.%). Orthopyroxene is magnesian (En = 91.92–93.65) with low Al$_2$O$_3$ content (0.41–0.74 wt.%) and high Cr$_2$O$_3$ and NiO contents (0.21–0.42 wt.% and 0.32–0.46 wt.%, respectively). The orthopyroxene from the peridotite is compositionally different from that of the clot: 2.67–4.06 wt.% Al$_2$O$_3$, 0.40–0.98 wt.% Cr$_2$O$_3$, and 0.04–0.14 wt.% NiO. Interstitial serpentine and serpentine within clots have high concentrations of NiO (up to 4.15 wt.%) with variable amounts of Al$_2$O$_3$ from 0.05 to 1.61 wt. % depending on the mineral being altered: olivine reacts to form Al-poor serpentine and orthopyroxene to Al-rich serpentine.

6 PGE mineralogy

A total of 17 grains of PGM were found scattered in the studied chromitites. These comprise small inclusions, < 15 μm in diameter, of Ru, Os, Ir and Pt predominantly located inside chromite crystals and to a lesser extent in fractures or the interstitial serpentinized matrix. Laurite is the most abundant PGM and occurs as euhedral grains up to 10 μm in diameter within unaltered chromite forming isolated single-phase grain or biphasic with pentlandite or Ir–(Os–Ru) alloys. Laurite contains Os and Ir up to 15.98 wt.% and 8.57 wt.% respectively, as well as minor amounts of Rh, Ni, Fe and Cu (up to 1.54 wt.%, 0.36 wt.%, 0.12 wt.% and 0.12 wt.%, respectively). This composition of laurite is similar to that described for other laurites from Loma Caribe chromitite bodies (Proenza et al. 2007). The euhedral shape of these laurites included in unaltered chromite suggests that this mineral was formed during the high-temperature magmatic stage before and contemporaneously with the crystallization of chromite.
oxygen, low analytical totals (80–90 wt.%). However, their chemical compositions in terms of Ru–Os–Ir proportions mimic the distribution of laurite-erlichmanite solid solution minerals. Therefore, it is suggested that these oxides resulted from the desulfurization of former primary laurite.

The Pt–Fe–Ir–Ni–Cu and Ir–Pt–Rh–Fe alloys, with minor contributions of Os, Ru, Ni and Cu, occur as irregular grains or anhedral aggregates of crystals with high porosity. They are located as inclusions within chromite and along fissures cross-cutting chromite grains. Their texture and location within the chromite attest to a secondary origin. They present Pt contents up to 83.93 wt.%. 

7 Concluding remarks

According to their composition, the clots in the massive chromitites are orthopyroxenites with small amounts of olivine. The low Al and Ca contents of the orthopyroxenes in the fresh clots are typical of metasomatic secondary origin. Therefore, we infer that the orthopyroxenite was the reaction product between exotic hydrated Si-rich mafic infiltrating melts and the preexisting olivine and orthopyroxene of the peridotite. The composition of the accessory chromites from the clots is the same as the chromites from the massive chromitite in terms of Cr#. This fact, together with the textures observed at the clot–chromitite contacts, indicates a replacing character of the chromitites. Therefore, massive chromitites from Loma Las Cabirmas formed from the dissolution of orthopyroxenite. The chromitite parental melt progressively assimilated the orthopyroxenite during melt infiltration, resulting in incongruent dissolution of the orthopyroxene and minor olivine in the melt to form chromite. This reaction led to the inclusion of small pyroxene grains observed in the chromites. The chromitite geochemistry, the low occurrence of base metal sulfides and the enrichment in magmatic PGM allow us to infer that the chromitite parental melt might be boninitic in composition. The remaining orthopyroxenite clots were probably preserved due to variations in the melt/rock ratio during the formation of the chromitites. Bédard and Hébert (1998) proposed a model of formation of ophiolitic chromitite based in the assimilation of pyroxenites. According to the authors, the assimilation of pyroxenites may have further supplied silica and/or chromium required to move the hydrous melt into the chromite liquidus field. Interestingly, González-Jiménez et al. (2014) reported that in podiform-like chromitites hosted in the SCLM of Ronda there is a correlation between the chromite composition and type of pyroxenite relics found in chromitites: clinopyroxene for high-Al chromitites (e.g., CDA chromitite) versus orthopyroxene for high-Cr chromitite (e.g., ARC and ARC chromitites), reflecting the Cr2O3/Al2O3 of the mafic rock being assimilated.

This research has been financially supported by the Spanish project CGL2015-65824 as well as the FPU by a PhD grant to JFdP sponsored by the “Ministerio de Economía y Competitividad” (MINECO) (Spain). JMGJ also thanks the Ramón y Cajal Fellowship RYC-2015-17596 granted by the MINECO.

References


Acknowledgements
Olivine orthopyroxenite-hosted chromitite veins in the ophiolitic mantle, Havana-Matanzas, Cuba

Núria Pujol-Solà, Joaquín A. Proenza
Departament de Mineralogia, Petrologia i Geologia Aplicada. Universitat de Barcelona.

Harlinson Torres
Fundación Universitaria del Area Andina – Sede Valledupar, Colombia.

Thomas Aiglsperger
Department of Civil Engineering and Natural Resources. Luleå University of Technology.

José María González-Jiménez, Antonio Garcia-Casco
Departamento de Mineralogía y Petrología. Universidad de Granada.

Angélica Isabel Llanes Castro
Departamento de Petrología y Mineralogía, Instituto de Geología y Paleontología, Cuba.

Abstract. The Havana-Matanzas ophiolite contains an example of chromitite veins hosted in olivine orthopyroxenites within mantle peridotites. Accessory Cr-spinel in the harzburgite and in the Ol-orthopyroxenite, and chromite in the chromitite vein show a wide range of composition (Cr# 0.39-0.75). However, the chromite in the vein and the Cr-spinel in the Ol-orthopyroxenite show similar composition with Cr#> 0.7 (Cr-rich), probably related to crystallization from boninitic-like mantle melts. The study of platinum-group minerals hosted in the chromite shows that Os-rich laurite is the main mineral phase, as it is typically observed in chromitites that formed from magmas of boninitic affinity. The Ol-orthopyroxenite bands are believed to represent melt channels that formed after replacement of peridotites by a Si-rich melt with boninitic affinity. This is supported by the Cr-spinel composition of the pyroxenites (Cr#>0.7) and the low Al, Ca and Cr content of orthopyroxene. The interaction between a Si-rich melt with harzburgite/dunite formed Ol-orthopyroxenite and a Cr-saturated melt, which also circulated through the pyroxenite channels and formed the chromitite veins.

1 Introduction

Chromitites found in the mantle section of ophiolites are usually enveloped by dunite bodies hosted in mantle harzburgites. The chemical composition of these chromitite bodies is strongly dependent on their location within the ophiolitic mantle peridotite. Typically, Al-rich chromitite bodies are located at the Moho transition zone, whereas Cr-rich chromitite bodies are found deeper in the ophiolitic sequence (e.g. Proenza et al. 1999; González-Jiménez et al. 2011).

Mantle orthopyroxenites have been described in various ophiolitic massifs, including Oman (Tamura and Arai 2006), Troodos in Cyprus (Chum 2014), and Newfoundland in Canada (Varfalvy et al. 1997). However, in general there are very few examples of chromitite bodies or veins hosted in orthopyroxenite. Bédard and Hébert (1998) reported peridotitic intrusions that assimilated and reacted with host gabbros, pyroxenites (clinopyroxene- to orthopyroxene-rich facies) and peridotites (harzburgites, dunites, lherzolites, and wehrlites) in the Bay of Islands ophiolites (Newfoundland, Canada). These peridotites include local Cr-rich chromitite layers whose Cr-spinel composition arguably depends more on the nature of the minerals that are being replaced than on the composition of the intruding magma. Moreover, Ahmed and Arai (2002) described unusual high IPGE discordant chromitite pods deep in the mantle section, which have high-Cr# (>0.7) and are related with orthopyroxenite bands within harzburgite.

Here we present an example of Cr-rich chromitite veins hosted in Ol-orthopyroxenite (Fig. 1) from the ophiolitic mantle tectonites of the Havana-Matanzas region, Cuba. The goal of this contribution is to give a detailed description of this occurrence and the interpretation of its genesis.

2 Geological setting and occurrence of chromitite veins

The studied samples belong to the Havana-Matanzas ophiolitic massif (HMO), located in the western part of central Cuba. The Havana-Matanzas massif is part of the Northern Cuban Ophiolite Belt (NCOB), the largest exposure of ophiolites in the circum-Caribbean region. These ophiolites represent slices of oceanic lithosphere obducted onto the North American continental paleo-margin in the Latest Cretaceous to Late Eocene, during the collision of the Caribbean volcanic arc with Jurassic-Cretaceous passive margins of the continental Maya block and the Bahamas platform (Iturralde-Vinent 1996; Garcia-Casco et al. 2008; Iturralde-Vinent et al. 2016).

The HMO is tectonically imbricated with Cretaceous intra-oceanic volcanic arc units and syn-tectonic sedimentary sequences as part of a tectonic mélangé that covers an area of 30 km² (Llanes et al. 2015). Although tectonically dismembered, the reconstructed HMO sequence is about 4 km thick and consists of upper mantle peridotites, a mantle-crust transition zone (MTZ),
and a crustal section composed of massive gabbros, dolerites, pillow lavas, and sedimentary rocks (Llanes et al. 2015). The mantle tectonites consist of serpentinized harzburgites showing porphyroclastic textures and containing ubiquitous pyroxenite veins. Minor dunite bodies are found as subconcordant layers in the harzburgites and as chromitite envelopes (Llanes et al. 2015). Volcanic rocks tectonically embedded in deformed serpentinites and serpentinized peridotites from the Havana-Matanzas massif have been described as IAT (Island Arc Tholeiites) and boninites (Fonseca et al. 1989; Kerr et al. 1999). Around ten Al- and Cr-rich chromitite orebodies (each approx. 0.5 m wide and 2 m long) have been described in the HMO hosted in the mantle tectonites close to the MTZ (Llanes et al. 2015).

The chromitite veins are hosted in Ol-orthopyroxenite bands within the mantle tectonites of the HMO. These chromitite veins are centimetric (Fig. 1a,b) with lateral extension of few tens of centimeters. The pyroxenite bands have a maximum width of 1.5 m and are hosted in harzburgites.

![Figure 1. a. Outcrop view of chromitite vein hosted within Ol-orthopyroxenite. b. Thin section of the chromitite vein within Ol-orthopyroxenite. c. Representative microphotograph of the Ol-orthopyroxenite under crossed nicols. Orthopyroxene (Opx) is the main mineral with interstitial olivine (Ol), both crosscut by late serpentine veins.](image_url)

### 3 Petrological background

The peridotites hosting the pair chromitite-pyroxenite are harzburgites, consisting mainly of partially serpentinized olivine (65-75%), orthopyroxene (25-35%), clinopyroxene (<2%), and accessory Cr-spinel (up to 1%). Their texture is characterized by plastic deformation of orthopyroxene porphyroblasts, which may form crystals up to 5 mm in diameter enclosed in partially serpentinized fine-grained olivine. Orthopyroxene is characterized by Mg# \(\frac{Mg}{(Mg+Fe)} \approx 0.91\), up to 2.6 wt% Al\(_2\)O\(_3\), 0.7-0.8 wt% Cr\(_2\)O\(_3\), and up to 0.04 wt% TiO\(_2\). Olivine crystals (up to 2 mm) are strongly serpentinized; however, fresh cores show typical mantle forsterite content (Fo\(_{91}\)), 0.43 wt% NiO, and up to 0.16 wt% MnO. Clinopyroxene is rare and strongly altered. Accessory Cr-spinel forms subhedral to anhedral grains of variable size (up to 1 mm) and appears partially or completely replaced by ferrian chromite, magnetite and chlorite. The composition of spinel is described below.

Pyroxenites consist mainly of orthopyroxene (80-90%), olivine (up to 18%), minor clinopyroxene (up to 3%), and accessory Cr-spinel (up to 1%), corresponding to olivine orthopyroxenite. The general texture is granoblastic (Fig. 1c) with orthopyroxene crystals up to 5 mm that are serpentinized. Orthopyroxene has Mg# = 0.9, up to 1.2 wt% Al\(_2\)O\(_3\), 0.5 wt% Cr\(_2\)O\(_3\), and 0.06 wt% TiO\(_2\). Olivine crystals, with grain sizes up to 0.5 mm are interstitial to orthopyroxene and partially serpentinized, the composition is Fo\(_{89}\), 0.43-0.50 wt% NiO, and 0.11-0.18 wt% MnO. Clinopyroxene is rare and strongly altered. Accessory Cr-spinel forms euhedral crystals up to 0.2 mm across, hosted both in the orthopyroxene and the olivine. The application of different geothermometers (Brey and Köhler 1990; Köhler and Brey 1990) to the Ol-orthopyroxenite (olivine – orthopyroxene – spinel – clinopyroxene assemblage) yields a range of equilibrium temperatures from 700 to 1100ºC.

Chromite in the veins is euhedral to subhedral with variable size (up to 0.5 mm across), unaltered and showing equilibrium textures. Orthopyroxene and olivine crystals are included within the chromitite vein, indicating that chromitite replaces a pre-existing pyroxenite host. Platinum group minerals (PGM) are found as inclusions within chromite (see below).

### 4 Mineral chemistry of Cr-spinel

Cr-spinel in peridotites, Ol-orthopyroxenites and chromitites exhibit a wide compositional range (Fig. 2) with Cr# [Cr/(Cr+Al)] between 0.39 and 0.75. The composition of accessory Cr-spinel in harzburgite is Cr# 0.39-0.50, 27-39 wt% Al\(_2\)O\(_3\), and 0.02-0.08 wt% TiO\(_2\). This composition differs significantly from the accessory Cr-spinel in the Ol-orthopyroxenite, characterized by Cr# 0.63-0.69, 14-16 wt% Al\(_2\)O\(_3\), and 0.16-0.23 wt% TiO\(_2\). On the other hand, it is similar to the composition of chromite in the chromitite vein: Cr# 0.70-0.75, 11.67-13.62 wt% Al\(_2\)O\(_3\), and 0.17-0.26 wt% TiO\(_2\). The composition of chromite in the vein is homogeneous, showing no variations near the contact with the Ol-orthopyroxenite.
5 Platinum-group element (PGE) mineralogy

A representative sample from the chromitite vein was processed by hydrosedimentation techniques in order to separate PGE phases. 17 PGM grains were identified in the obtained mineral concentrates, predominantly in the <30 µm fraction. In addition, 3 PGM grains were recognized in-situ hosted in chromite on polished sections.

The identified PGMs are euhedral to subhedral laurite with sizes up to 25 µm in the concentrates (Fig. 3) and 15 µm in-situ. Generally, laurite is inclusion-free (Fig. 3a) but occasionally may contain inclusions of Cu-Fe-S sulfides (<1 µm). Secondary minerals include chalcopyrite and Ir phases attached to the rims of laurite (Fig. 3b). The in-situ laurite grains appear together with silicates as inclusions in chromite. The laurite composition is Os-rich, between \([\text{Ru}_{0.76}\text{Os}_{0.16}\text{Ir}_{0.08}\text{Fe}_{0.02}\text{S}_{1.99}]\) and \([\text{Ru}_{0.63}\text{Os}_{0.22}\text{Ir}_{0.12}\text{Fe}_{0.02}\text{Ni}_{0.01}\text{S}_{1.99}]\) (Fig. 4).

Typically, Cr-rich chromitites are richer in PGE, especially IPGE (Ir, Os, Ru), compared to Al-rich chromitites, and the PGM association is dominated by laurite (González-Jiménez et al. 2014 and references therein). The presence of IPGE and the predominance of laurite is observed in the studied chromitite vein.

The PGE content in the chromitites depends mainly on the PGE concentration in the parental melt from which the chromitite crystallizes (Barnes et al. 1985). As indicated above, Cr-rich chromitites have been interpreted to crystallize from magmas with boninitic affinity, whereas Al-rich chromitites form from magmas with tholeiitic compositions. Boninitic magmas are sulfur-undersaturated and normally contain higher PGE contents than tholeiitic magmas (e.g. Zhou et al. 1998).

The PGMs found in the studied chromitite vein could have formed either during the migration of a very hot magma within magmatic channels pre-dating the chromite crystallization, or as mineral phases in the residual mantle formed during or after an episode of high-degree partial melting (Luguet et al. 2007; González-Jiménez et al. 2014). The second hypothesis is more consistent with the geochemical characteristics of the chromitite vein and the host Ol-orthopyroxenites.
6 Concluding remarks

There is a general consensus that orthopyroxenites in the suboceanic mantle do not crystallize from a primary magma generated by partial melting of depleted mantle. Despite, they represent Si-rich melts that migrate through mantle tectonites by porous flow (Grant et al. 2016). In this case, pyroxenite would act as melt circulation channels in the mantle (Zack and John 2007), similar to dunite circulation channels. The parental melts for pyroxenites have boninitic composition (Mg-rich anodesites). Thus, orthopyroxenites are interpreted as the “footprint” of boninitic-affinity melt circulation in the mantle, which forms dikes and lavas in the shallower levels of the ophiolitic sequence (e.g. Varfalvy et al. 1996). These boninitic lavas are generally related with the initial stages of formation of intraoceanic arcs (subduction-initiation ophiolite type). The observed composition of chromite in the studied Ol-orthopyroxenite and the chromitite vein (Cr# ≥ 0.7) is in agreement with an origin from boninitic magma.

The formation mechanism could be represented in the “forsterite – chromite – SiO2” phase diagram from Irvine (1967). In this system, a Si-rich melt (M1) reacts with the mantellic harzburgite/dunite, forming Ol-orthopyroxenite and a secondary melt saturated in Cr [M1 + harzburgite/dunite = Ol-orthopyroxenite + M2]. Chromite would then precipitate from the Cr-saturated melt (M2). Therefore, chromitite veins in the mantle levels of the HMO formed after the reaction between harzburgite/dunite and a Si-rich melt, which formed Ol-orthopyroxenite and chromitite.

Acknowledgements

This research has been financially supported by the Spanish project CGL2015-65824 as well as the FPU PhD contract to NPS sponsored by the Ministerio de Educación (Spain). JMGK thanks the Ramón y Cajal Fellowship RYC-2015-17596 granted by the Spanish “Ministerio de Economía y Competitividad (MINECO)”.

References

Chum CY (2014) Cumulate pyroxenite and pyroxenite dykes in the Troodos ophiolite, Cyprus: Hong Kong, University of Hong Kong Theses Online (HKUTO), 193 p.
Köhler TP, Brey GP (1990) Calcium exchange between olivine and clinopyroxene calibrated as a geothermobarometer for natural peridotites from 2 to 60 kb with applications. Geochim Cosmochim Ac 54:2375-2388
Luguet A, Shirey SB, Lorand JP, Horan MF, Carlson RW (2007) Residual platinum-group minerals from highly depleted harzburgites of the Lherz massif (France) and their role in HSE fractionation of the mantle. Geochim Cosmochim Ac 71(12):3082-3097
Chemistry of primary and altered Cr-spinels in chromitites and peridotites from the ophiolitic massif in SE Kosovo

Magdalena Ożóg, Jadwiga Pieczonka
AGH University of Science and Technology, Poland

Abstract. The diversity of Cr-spinels, which make up chromitites and represent accessory mineral in peridotites occurring within the ophiolitic massif in SE Kosovo, has been studied using EPMA. Grains displaying composition of magnesiochromite and chromite, as well as spinel (only in harzburgite), have been distinguished. The results indicate a supra-subduction zone setting for the studied ophiolite, corroborating with the boninitic affinity of the parental magma. The investigated Cr-spinels show resemblance with spinels from forearc peridotites. The chromite in chromitites and Cr-spinels in dunite have similar Cr# and TiO2 content (~0.80; ~0.20 wt.%), whereas the Cr-spinels in harzburgite have significantly lower Cr# and TiO2 content (0.61; 0.11 wt.%). It shows that harzburgite has been formed by high degrees of partial melting of a fertile MORB mantle source and dunite has been influenced by melt-peridotite interaction process. The primary accessory Cr-spinel is richer in Fe, Mg and Al than the primary chromite in chromitites, due to more effective subsolidus reequilibration with silicates during crystallization in peridotites. As the products of Cr-spinel alteration, ferritchromite and magnetite have been formed along cataclastic fractures and rims. Generally, the altered spinels have higher abundances of Mn, Si, Zn, Ni and Co compared to the unaltered spinels. The significant increase of MnO content (up to 1.26 wt.%), especially in dunite, indicates Mn mobilization by hydrothermal fluids and its addition to ferritchromite.

1 Introduction

Chromian spinel [solid solution with general formula (Mg, Fe2+)(Cr, Al, Fe3+):O4] is an important mineral phase both from scientific and industrial points of view. It commonly occurs in ultramafic-mafic rock sequences of various genesis, and its chemistry is useful in geological environment reconstructions (e.g. Irvine 1965; Dick and Bullen 1984; Barnes and Roeder 2001). Cr-spinels concentrate in form of chromite ores (chromititites), which can be used in ferrochrome production. Although they are highly resistant to alteration processes and metamorphism, their primary composition can be changed (e.g. González-Jiménez et al. 2009; Kapsiotis 2014). The most common secondary phases replacing chromite are ferritchromite and magnetite. Ferritchromite (or ferrian chromite) is characterized by significant to high Fe3+ content, variable Cr/Al and Mg/Fe2+ ratios, and may be slightly to highly enriched in Cr2O3 in comparison with primary Cr-spinel (e.g. Mellini et al. 2005; Merlini et al. 2009; Gervilla et al. 2011; Gervilla et al. 2012).

This paper provides the first data on the chemistry of Cr-spinels widespread within the studied ultramafic massif located in SW Kosovo. Major (Cr, Al, Fe, Mg) and minor (Ti, V, Mn, Ni, Co, Zn) metal oxide contents have been measured to distinguish features of chromite composing ores and accessory Cr-spinels in peridotites. Based on the primary chromite composition, the tectonic setting and the melt type have been identified for the studied ophiolite. The altered spinels have been investigated in order to indicate general trends in chemical changes, caused by alteration processes.

2 Geological background

The study area is located in SE Kosovo, along the border with North Macedonia, and represents a part of the Middle - Late Jurassic ultramafic massif (~80 km²), so-called the Radusha massif. It belongs to the Drenica unit, which is situated between two extensive ophiolite belts, running from N/NW to S/SE through the Balkan Peninsula: the Vardar Zone (on E) and the Mirdita Ophiolite Belt (on W). Elezaj and Kodra (2012) suggest that the origin of this ultramafic complex is related to the Mirdita-Gjakova oceanic basin closure during Late Jurassic period, and constitutes the detached and tectonically emplaced part of the W ophiolite belt.

Harzburgite is dominating in the area and hosts numerous irregularly shaped dunite bodies. Serpentinite occurs mostly along borders of the ultramafic complex. Chromitite have been documented within dunite. Massive, semi-massive and disseminated ores as well as textures specific for ophiolitic chromitites, such as breccia, schlieren, banded and vein types, have been observed in the field. The area is known from Cr deposits exploitation in Radusha, Orasje and Gorne, which started before WWI and was over in 1970’s.

3 Samples and analytical methods

In order to study the diversity of Cr-spinel composition, different types of samples have been collected in the study area. Panned-concentrates have been obtained from alluvium (containing mix of various spinel grains) and diluvium (weathering cover containing soil material) developed on dunite and harzburgite, separately. Chip samples of massive, disseminated and vein type chromite ores have been taken from the outcrops and excavations. After microscopic observation in reflected light, representative samples (5 polished grain mounts prepared for both sample types) have been selected for electron microprobe analyses.

The analyses were carried out using a JEOL SuperProbe JXA-8230 electron microprobe (EPMA) at
the Laboratory of Critical Elements at the AGH-University of Science and Technology in Krakow (Poland). The EPMA was operated in the wavelength-dispersion mode at an accelerating voltage of 15 kV, a probe current of 20 nA, focused beam with a diameter of <1 μm. The counting times on peak and on both (+) and (-) backgrounds were 20 and 10 seconds, respectively. Data were corrected to the ZAF procedure using an original software. 286 analyses have been obtained for unaltered parts of Cr-spinels and 60 within their altered parts (risms and veins). FeO and Fe₂O₃ concentrations were determined assuming ideal spinel stoichiometry (AB₂O₄; cations calculated to 4 oxygens).

4 Results

4.1 Textural observations

Cataclastic fractures within spinels occur in all studied samples. Crosscutting cracks are usually filled with secondary silicates (both in the ores and the detrital Cr-spinels) and/or magnetite (only in the detrital Cr-spinels) (Fig. 1A, B, D). In the massive ore, brittle deformation is preserved as very intense fracturing and also microbrecciation. Alteration effects within the chromitite display only in the form of brighter and porous phase formation along crystal borders and cracks, whereas the studied panned-concentrates contain unaltered (homogeneous, without pores) spinels, as well as spinels showing different patterns of changes/zoning (Fig. 1C, F, G, H). The most abundant alteration effect, observed in the detrital Cr-spinels, is magnetite veins or/and rims development (Fig. 1D). Microscopic observations have revealed also formation of magnetite-hematite or hematite rims. The replacement by ferritchromite takes place from grain boundaries or micro-cracks inwards, giving rise to zoned grains, which consist of unaltered chromite enveloped by ferritchromite rims, and sometimes also magnetite on the edges (Fig. 1E, F). Some grains have been totally replaced by porous phase or/and magnetite, other have unaltered core or contain small relics of primary spinel (Fig. 1C, G).

4.2 Primary composition of Cr-spinels

The unaltered Cr-spinels in the massive chromite ore can be classified as magnesiochromite, having average Cr#\[Cr/(Cr+Al)\] = 0.80 and Mg#\[Mg/(Mg+Fe²⁺)\] = 0.60, whereas in the disseminated and vein type ores as chromite, having average Cr# = 0.78 and Mg# = 0.48. The primary composition of Cr-spinels in dunite show wider ranges of Cr# and Mg# values than it is observed for the ores, still representing the same mineral phases (Fig. 2A). Some grains in harzburgite and from alluvium show Cr# < 0.50 and Mg# > 0.50 and can be classified as spinel (Fig. 2A). The Cr₂O₃ content in the chromite composing ores varies from 54.83 to 63.15 wt.%. The range of Cr₂O₃ content in dunite is from 36.73 to 59.72 wt.%, whereas in harzburgite from 32.87 to 60.26 wt.%. Chromite in chromitites contains significantly less FeO than the accessory chromite in peridotites (av. in wt.%; 17.24 for the ores; 19.13 for dunite; 18.46 for harzburgite). Ranges of Fe₂O₃ content are 0.74 – 4.86, 1.81 – 8.16, 0.52 – 10.09 wt.%, respectively in the ores, dunite and harzburgite. Among the analyzed spinels, the highest average contents of Al₂O₃ has been noted in harzburgite (20.70 wt.%), and the highest average MgO content in the massive ore (11.99 wt.%). The spinels in the studied chromitites and the accessory spinels in dunite characterize similar average content of Al₂O₃. The ranges of MgO content are more than two times wider for accessory spinels in the studied peridotites than in the ores.

Figure 1. Backscattered electron images of the different types of Cr-spinel grains affected by alterations (explanations: Cr – Cr-spinel, Fcr – ferritchromite, Mg – magnetite; image F is a close-up of the grain shown on the image E; for points 1 – 4 see Fig. 3)

The TiO₂ content in chromite making up the ores includes in the range characteristic for accessory Cr-spinels in dunite (Fig. 2B). The Cr-spinels in harzburgite are characterized by the lowest contents of TiO₂, which are rarely similar to those observed in the studied chromitites (Fig. 2B). The ranges of NiO content both in the ores and rocks are similar (Fig. 2D). In contrary to the other studied spinels, the spinel grains from harzburgite are Co-free (Fig. 2F). The primary Cr-spinels from peridotites show remarkably wider ranges of ZnO content than chromite in the ores (Fig. 2E). The ranges of V₂O₅ content are different for the ores and peridotites (ores:
0.06 – 0.29, dunite: 0.06 – 0.23, harzburgite: 0.10 – 0.29 wt.%) The highest MnO content in the studied unaltered Cr-spinels has been measured in dunite (Fig. 2C). PbO and CuO in almost all analyses have not been detected (or <0.1 wt.%).

4.3 Alteration effects in Cr-spinels

The Cr# for the altered chromite composing the studied ores and for the accessory Cr-spinels noticeably increased (av. 0.88 for both), whereas the Mg# value are significantly lower (av. 0.51 and 0.26, respectively) (Fig. 2). The enrichment in Cr2O3 is simultaneous with both Fe2O3 and FeO increase, and depletion of Al2O3 and MgO, indicating the ferrichromite formation during serpentinization process. This alteration effect has been observed for Cr-spinels in the ores as well as for the detrital spinels. Ferrichromite from the studied samples is characterized by following average values of major oxides contents (in wt.%): 62.82 Cr2O3, 6.07 Al2O3, 3.14 Fe2O3, 17.05 FeO, 10.05 MgO (chromitites) and 52.25 Cr2O3, 4.96 Al2O3, 12.18 Fe2O3, 24.29 FeO, 4.92 MgO (peridotites). The removal of Al2O3 and MgO from Cr-spinels during alteration has caused mass loss and porous texture development (Fig. 1C, E, F). Magnetite crystallization was possible thanks to the continuous supply of iron to the porous ferrichromite in the next stage of compositional modification, which took place under oxidizing conditions (Fig. 1F, 3). It has been observed only within detrital spinels, not within the chromitite samples so far. The studied magnetite veins and rims contain up to 1.50 wt.% of Cr2O3. They are usually slightly contaminated by SiO2 (up to 1.57 wt.%) and may be also enriched in Mn (up to 1.58 wt.%).

The alteration processes have caused generally slight variations in Ni, Co, Zn, V and Ti content. Only single analyses have shown anomalous enrichment in Ni, Co, Zn, Ti and V in accessory spinels (Fig. 2). Intriguingly, elevated abundance of Ti (up to 0.71 wt.%) has been detected. The most profound chemical change in minor elements concentration concerns the increase of Mn content (Fig. 2C). The Mn enrichment trend is prominent for accessory Cr-spinels in dunite. No enrichment in Pb or Cu in spinels has been noticed due to alteration.

The point analyses within alteration rim of magnesiochromite have revealed chemical tendencies during formation of ferrichromite and magnetite (Fig. 3). Both mineral phases display higher concentration of Ni and Mn in relation to unaltered magnesiochromite. Ferrichromite has also higher contents of Zn and Mn than both primary spinel and magnetite.

5 Discussion and conclusions

High #Cr for the studied chromitites enables to classify
them as Cr-rich chromitites, which crystallized from melts of boninitic affinity. Many authors assumed that such magmas are formed solely in arc-forearc terrains and represent the magmatic products of subduction initiation (e.g. Stern and Bloomer 1992; Reagan and Meijer 1984; Hawkins and Castillo 1998). González-Jiménez et al. (2014) indicate that in the high-Cr chromitites, chromite has identical (or higher) Cr# as accessory chromite in the host dunite, whereas this value is lower for the chromite in the enclosing harzburgite. Our results confirm such pattern of chemical behaviour, which have been also observed for other ophiolitic chromitites in the region (e.g. Troodos, Cyprus; Vourinos, Greece; Mirdita Ophiolite, Albania) (González-Jiménez et al. 2011). Based on the Cr# and Mg# ranges for the studied Cr-spinels in dunite and harzburgite, they show much resemblance with spinels from forearc peridotites. The studied accessory Cr-spinels in harzburgite have been found to contain significantly less TiO₂ than the Cr-spinels in the ores and dunite (Fig. 2B). It has been suggested that Cr# increases and Ti content rapidly decreases along with melting and thus Cr# in residual spinel is a sensitive indicator for the extent of melting of their host peridotite (e.g. Dick and Bullen 1984, Pearce et al. 2000). A part of the analyses of Cr-spinels from the studied massif (with Cr# from 0.39 to 0.60) indicates that harzburgite is consistent with its residual nature after ~20% melting (estimated based on Pearce et al. 2000) of a fertile mid-ocean ridge basalt (MORB) mantle source. The rest of analyses shows an increase of Ti content, thus these peridotites have been formed rather by melt-rock interaction process than melting alone. The accessory chromite in peridotites is significantly richer in Fe, Mg and Al than the chromite in chromitites. The subsolidus re-equilibration with silicates (olivines and pyroxenes) during cooling, which is easier and more effective for chromite crystallizing in peridotites compared to chromitites, may explain observed differences (e.g. Irvine 1967; Roeder and Campbell 1985). The same process could be responsible for slight enrichment in Zn, Mn, Ni and Co, that also has been noticed in pristine composition of the accessory spinels.

Textural and compositional changes indicate that the studied spinels have been obscured by post-magmatic processes. The formation of ferrichromite and magnetite can be explained as the result of the ions exchange process, limited to fractures and edges of primary chromite crystals. During fluid migration in peridotites, Al₂O₃ and MgO were expelled from Cr-spinel boundaries and introduced in secondary silicates, whereas Fe₂O₃ was incorporated into ferrichromite. In general, the analyzed primary spinels have lower abundances of Mn, Si, Zn, Ni, and Co compared to ferrichromite. Authors suggest that the significant enrichment in Mn is a direct indication for its mobilization by infiltrating hydrothermal fluids and incorporation into ferrichromite. However, both magmatic and hydrothermal processes have been considered as responsible for Mn enrichment in chromite (e.g. Economou-Eliopoulos 2003; Grieco and Merlina 2011). The observed anomalous TiO₂ content may be related to remobilization of Ti in spinel lattice after the magmatic stage, as it was proposed by Kapsiotis (2014) for well-studied magnesiochromite from Vourinos ophiolite.

Acknowledgements

This study was partially financed by the Hugh McKinstry Fund of Society of Economic Geologists.

References

Using chromite chemistry to correlate PGE-bearing chromitite reefs within the Bushveld Igneous Complex

Malose. M. Langa, Pedro. J. Jugo
School of Earth Sci., Laurentian University, Canada

Matthew I. Leybourne
Department of Geological Sci. and Geological Engineering, Queen’s University

Danie F. Grobler
Exploration and Geology, Ivanplats (Pty) Ltd

Abstract. The Bushveld Igneous Complex (BIC) is known for its laterally extensive PGE-bearing layers, the most famous being the Merensky Reef and the UG-2 chromitite in the Eastern and Western limbs of the BIC. In the Northern Limb, the Platreef and a thick chromitite seam below (henceforth the "UG-2 equivalent" or UG-2E) have been proposed to be the extensions of the Merensky Reef and UG-2, respectively. Using chromite as a petrogenetic tool, chromite compositions from the UG-2E are compared to a UG-2 reference suite (from the Western Limb) and literature data. The results show that UG-2E chromite have a distinct compositional field, partially overlapping the Cr# and Mg# field that characterizes UG-2 chromite. Although most UG-2E chromite grains have lower Cr# and Mg# than UG-2 samples, the differences are more pronounced in sections of the UG-2E with lower chromite modal abundance, consistent with UG-2E magmas having interacted with local footwall rocks (the Duitschland Formation). However, samples with at least 80% chromite show a match in UG-2E and UG-2 chromite composition. Thus, we conclude that for chromite modes higher than 80% the chromite composition retains enough information to allow correlations and that the UG-2E is very likely the UG-2.

1 Introduction

The Bushveld Igneous Complex (BIC) is the largest known mafic-ultramafic igneous complex on Earth. The BIC consists of four different igneous rock suites with the most studied being the Rustenburg Layered Suite (RLS), in part because it contains the largest reserves of platinum-group elements (PGE) in the world (USGS 2019). The RLS consist mainly of mafic-ultramafic cumulate rocks exposed mainly at three limbs: the Eastern, Western, and Northern limbs. These limbs host PGE mineralization in layers referred as 'reefs', namely: UG-2, Merensky Reef (MR), and Platreef. The Western and Eastern limbs host PGE ores within the UG-2 (massive chromitite) and the MR (chromite- and sulfide-bearing pyroxenite), whereas ores within the Northern Limb are associated with the Platreef (also chromite- and sulfide-bearing pyroxenites).

Although there is a general consensus that the Platreef is stratigraphically the lateral equivalent of the Upper Critical Zone in the rest of the BIC, there is no consensus on whether the Platreef mineralization correlates with the Merensky Reef (i.e. a thickened MR with the corresponding UG-2 chromitite below it) or constitutes a different rock unit (e.g. Wagner 1929; Yudovskaya et al. 2017). Deep drilling by Ivanplats intersected a chromitite seam below what has been interpreted as the Merensky Cyclic Unit (Grobler et al. 2019); based on this correlation, the chromitite seam has been interpreted as the UG-2 (Grobler et al. 2019) and labeled here as the UG-2 equivalent or UG-2E to distinguish it, provisionally, from the UG-2 in the Eastern and Western limbs.

Because chromite is an early cumulate phase, a key mineral in all the reefs, and has relatively high closure temperatures (> 800°C, Van Orman & Crispin 2010), it likely preserves information about crystallization conditions in its crystal chemistry (e.g. Junge et al. 2014). Here we document results on major and minor element chemistry in chromite samples from the UG-2E and a reference UG-2 chromitite seam and show evidence supporting the interpretation of the UG-2E as the UG-2. However, in contrast to the UG-2, parts of the UG-2E interacted and equilibrated with magmas that were affected by crustal contamination.

2 Samples and Methods

Drill core from hole UMT-366, intersected a chromitite seam 70 meters below the main mineralization in the Platreef. The complete chromitite seam is 189 cm thick, with textures varying from massive to semi-massive and few intervals having only disseminated chromite. The entire seam was sampled as quarter core (NQ type core, 4.7 cm diameter) and polished sections of the complete seam were prepared. A reference suite from a 60 cm thick UG-2 chromitite seam (the Waterval suite, Naldrett et al. 2012) was also prepared and analyzed. The samples were characterized petrographically and analysed using electron probe microanalysis (EPMA) for major and minor elements (Mg, Fe, Cr, Al, Ti, V, Zn, Mn, Ni, Co, Mn). Ferric iron content was estimated from stoichiometry of EPMA data (Droop 1987).

3 Results

Petrographically, the main similarities between the UG-2 and UG-2E are that the majority of chromite grains occur as discrete euhedral to subhedral crystals with
intercumulus pyroxene and plagioclase. The main differences are that sulfides are more abundant in the UG-2E (from roughly 1 to 5 %), whereas the reference UG-2 chromitite contained very little sulfides (up to ~ 1% in some sections). Sulfide minerals are mostly interstitial but sulfide inclusions inside chromite grains are also more abundant in the UG-2E. Modal proportions and grain size are also slightly different. The UG-2 reference suite is predominantly massive (chromite proportions generally > 90 %) and with smaller crystals (from 0.001 to ~ 0.6 mm), whereas the UG-2E is more variable (chromite proportions range from < 10 % to > 90 %) and slightly larger chromite grains (from ~ 0.04 up to 1.6 mm). In both cases the chromite grains were homogenous in composition (no zoning was identified, petrographically or chemically). Highlights of the results are summarized in Figures 1 to 4. Mg# = Mg/(Mg + Fe2+), Cr# = Cr/(Cr + Al), and Fe3+/∑Fe= Fe3+/(Fe3++Fe2+).

3.1 UG-2 chromite chemistry across the Bushveld

Figure 1 shows data from the reference UG-2 chromite (in orange) compared to previously documented data.

![Figure 1. Compilation of chromite Mg# vs Cr# data of UG-2 from the Eastern (EL) and Western (WL) limbs [EL data: Mathez & Mey (2005), grey circles; Adetunji et al. (2013), black circles. WL data: Eales & Reynolds (1986), yellow circles; Junge et al. (2014), blue circles; Veksler et al. (2015), purple circles]. Reference samples analyzed in this study (WL) are shown in orange circles.](image)

Close inspection of the data revealed that chromite with Mg# < 0.40 correspond to chromite grains at the margins of chromitite seams and disseminated chromite. Chromite from the massive sections of the UG-2 have Mg# ranging from 0.40 to 0.50, and Cr# between 0.61 and 0.67. The compositions are broadly similar but, in general, Eastern Limb samples seem to have slightly lower Cr# and Mg# compared to Western Limb samples.

3.2 UG-2E compared to UG-2

Figure 2 shows the data for the UG-2E compared to the compiled UG-2 data. There is a direct overlap for samples with Mg# > 0.40 (and Cr# from 0.58 to 0.64) especially with the Eastern Limb suite documented in Mathez & Mey (2005) but samples with Mg# < 0.40 deviate from the trend seen in BIC samples having roughly constant Cr# (at ~ 0.60). The UG-2E samples with composition that directly overlap with the UG-2 are from the base of the UG-2E.

![Figure 2. Comparison of chromite Mg# vs Cr# from UG-2E to UG-2 reference samples (as shown in Figure 1).](image)

3.3 Variations in chromite chemistry with chromite modal proportions

The UG-2 reference chromitite is predominantly massive (≥ 90 modal chromite) with the exception of two samples with 49% and 2% modal chromite proportions (a silicate parting). The UG-2E chromitite seam ranges from massive to semi-massive to disseminated chromite, with chromite modal proportions varying from 10 to 90%. Both the UG-2 and UG-2E show a decrease in Mg# with decreasing chromite modal proportions (Figure 3A), but different ‘trends’ in Cr# (Figure 3B).

![Figure 3. A) Variations in Mg# with increasing chromite modal proportions for the UG-2 and UG-2E samples. B) Variations in Cr# with increasing chromite modal proportions for the UG-2 and UG-2E.](image)

3.4 Ferric iron content

Figure 4 shows that the UG-2E chromite have a wider range of Fe3+/∑Fe (0.26 to 0.34), compared to the UG-2 (0.25 to 0.29). In general, UG-2E samples with the lowest Mg# (corresponding to lowest chromite modal proportions) have the highest Fe3+/∑Fe values. Figure 4B shows that the UG-2E has a wider range of Cr# (0.59 - 0.75).
populations, with no overlap. Clearly be distinguished as two separate chromite mineralization (e.g. Holwell et al. 2011). This is in part due to interaction with footwall sediments, although available evidence indicates that mineralization is primary and Mg chromitites) have different and distinct Mg and Al composition because of re-equilibration with interstitial liquid. However, Mössbauer analyses are needed to properly assess Fe$^{3+}$/ΣFe because of know disparities with calculated Fe$^{3+}$/ΣFe from EPMA (Adetunji et al. 2013; Evans 2017). Constant Cr# of samples with low chromite abundance likely result from an increase in the substitution of Fe$^{3+}$ into chromite, with the Cr-Al ratio represented by Cr# remaining in relatively equal proportions. The most likely scenario to explain the differences between UG-2E and UG-2 is that the Northern Limb magmas were influenced by assimilation of footwall rocks affecting the Fe content (as both Fe$^{2+}$ and Fe$^{3+}$) as well as Mg and Al content (due to assimilation of banded iron formation, dolomites, pelites, shales of the Transvaal Supergroup). The results are consistent with the UG-2E chromite being a UG-2 layer that has been disrupted and affected by magmas that have interacted with local footwall sedimentary rocks.

5 Conclusions

The Cr# and Mg# of UG-2 chromite samples from the Eastern and Western limbs of the BIC define a relatively narrow field. Chromite grains at the edge of the UG-2 have Mg# < 0.4 and show a dispersion pattern towards higher Cr# which is interpreted to reflect re-equilibration with the silicate melt during cooling (Barnes 1986). Chromite Cr# and Mg# from the UG-2E show only a
partial match with reference values from UG-2 samples but deviate from the UG-2 trend by having decreasing Mg# at roughly constant Cr#. However, UG-2E samples with more than 80% chromite modal proportion have Mg# ≥ 0.40 and match with the reference UG-2.

The similarity in Cr# and Mg# between the UG-2E and the UG-2 for samples with more than 80% chromite indicate that the UG-2E crystallized from a magma of the same composition as the UG-2, hence the UG-2E is likely the UG-2. The discrepancies between UG-2E and UG-2 composition have likely two reasons: (a) more variations in chromite modal abundance in the UG-2E, resulting in re-equilibration with variable amounts of silicate/trapped liquid; (b) re-equilibration in an open system (i.e. with a magma that assimilated metasedimentary footwall rocks). However, the fact that some compositions match indicates that the magma either crystallized chromite prior to interaction with meta-sedimentary rocks or trapped liquid effect is minimal for modal abundance > 80% chromite.

Regardless of whether the trapped-liquid shift effect has affected the samples, major element chemistry (Cr# vs. Mg#) should be a helpful correlation tool in chromite samples with more than 80% chromite. Ongoing work aims to complement major element data with trace element data obtained by LA-ICP-MS and Mössbauer spectroscopy.

Acknowledgements

We thank the Canadian Queen Elizabeth II Diamond Jubilee Scholarships (QES), the International Development Research Centre (IDRC), the Natural Sciences and Engineering Research Council of Canada (NSERC), and Ivanplats for funding. We thank Tim Dunnett, Albie Brits, Jan Mapeka, Alexandra Crossingham and the rest of the Ivanplats team in Mokopane for field and logistics support; Dave Crabtree (Ontario GeoLabs) and Dr. Yanan Liu (University of Toronto) for assistance with EPMA work.

References


Platinum-group elements in weathered Lower Group and Middle Group chromitites of the Bushveld Complex

Malte Junge
Institute of Earth and Environmental Sciences, University Freiburg, Germany

Kai Bachmann
Helmholtz-Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology, Germany

Thomas Oberthür
Federal Institute for Geosciences and Natural Resources (BGR), Germany

Abstract. All major sources of economically important platinum-group elements (PGE) are associated with sulfides and chromite in mafic-ultramafic rocks. The Bushveld Complex in South Africa is the largest PGE deposit worldwide. Chromitites of the Lower Group (LG) and Middle Group (MG) of the Bushveld Complex hold PGE contents of a few ppm. However, these chromitites are mainly mined for Cr only and extraction of PGE as a by-product is limited. Surface weathering in the area of the Bushveld Complex is up to 50 m down from surface. Attempts to recover Pt and Pd from these weathered ores lead to recoveries of <30 %, despite that Pt and Pd concentrations are similar in pristine and weathered ores. A comparison of pristine and weathered LG and MG chromitites of the Thaba Mine, in the northwestern Bushveld Complex, showed higher Pt/Pd ratios in the weathered chromitites compared to the pristine ores, as well as elevated concentrations of Pt and Pd in the hanging and footwall. Only relict platinum-group minerals exist in the weathered chromitites (mainly PGE-sulfarsenides and newly formed PGE-oxides/hydroxides). The higher Pt/Pd ratios in the weathered chromitites indicate that Pd is more mobile than Pt. Mobilization of Pd takes also place on a small scale into the hanging walls and footwalls of the chromitite seams. Primary PGM grains are largely destroyed and only relict grains occur. The newly formed PGM phases in the weathered ores are mainly associated with secondary minerals such as Fe-silicates and Fe-oxy/hydroxides. In the weathered chromitites, PGE are dissolved from PGM and very locally reprecipitated, indicated by the neoformation of PGM-oxides/hydroxides.

1 Introduction

The world’s largest layered mafic-ultramafic intrusion is the 2050 Ma old (Scoates and Friedmann 2008) Bushveld Complex in South Africa, which contains vast resources of chromite, PGE and vanadium. Currently, the Merensky Reef and the Platreef and the UG-2 chromitite seam are the major mining targets for PGE, although chromitites of the Lower Group (LG) and Middle Group (MG) may also contain concentrations up to several ppm PGE (e.g. Bachmann et al. 2019a,b). Nowadays, the chromitites of the LG and MG are predominantly mined for Cr, but extracting PGE as a by-product could significantly increase the resource efficiency of these mines. At present, only two mining companies produce PGE-concentrates from active LG- and MG-mining operations and old mine dumps: Sylvania Platinum (Junge et al. 2016; Oberthür et al. 2016) and Tharisa Mine.

In unweathered ores, the PGE are bimodally distributed, occurring both as discrete platinum-group minerals (PGM) and hosted by sulfides. Especially, pentlandite [(Fe,Ni)9S8] contains elevated concentrations of Pd and Rh (e.g. Godel et al. 2007; Junge et al. 2014). Pt/Pd ratios in the LG-6 and MG chromitites usually range from 1 to 3 (Bachmann et al. 2019a). Platinum-group minerals are usually associated with sulfides and occur either enclosed or at grain boundaries of sulfides and chromite (e.g. Bachmann et al. 2018).

The weathering zone in southern Africa reaches up to 50 m in depth, having an enormous effect on PGE recovery of near-surface PGE ores which are weathered and PGE-bearing sulfide minerals are partially to completely replaced by Fe-oxy/hydroxides (Oberthür et al. 2013; Junge et al. 2018).

In this study, the differences between pristine and weathered LG and MG chromitites of the Thaba Mine, located in the northwestern Bushveld Complex, are studied. The variations in mineralogy between near-surface weathered ores are compared to published data of pristine ores in order to unravel the effects of weathering on the PGE distribution. The results are essential for the development of novel PGE extraction methods for these ores.

2 Samples and Methods

2.1 Origin of samples

The Thaba Mine is located in the northwestern Bushveld Complex, approximately 25 km SW of Thabazimbi and 85 km NW of Rustenburg. The LG-6, -6A and several MG chromitite seams are mined for chromite by Cronimet Chrome Mining SA (Pty). Chromitite ore complemented by hanging and footwall samples were collected in the active pits and within exploration trenches (n=62). Mineral liberation analysis (MLA) was conducted on drill core intersections from near-surface ores (<30 m) of the
LG-6, MG-1, MG-2, MG-3 and MG-4 chromitite seams (n=36).

2.2 Whole-rock analysis

Whole-rock analysis was carried out by Activation Laboratories Ltd. (Actlabs), Canada. Major and trace elements were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) following a four-acid digestion (HF, HClO₄, HNO₃, HCl). Gold, Pd and Pt concentrations of all samples were determined by ICP-MS following a fire-assay procedure. Chromitite ore samples were analyzed by X-ray fluorescence (XRF) of fusion disks to determine the oxide composition.

2.3 Mineral Liberation Analysis

From the drill cores which are intersecting chromitite seams close to surface (<30 m), 36 polished thin sections were prepared. Quantitative mineralogical analysis using the MLA software was carried out using a FEI-Quanta 650 F field emission scanning electron microscope (FE-SEM) equipped with two Bruker Quantax X-Flash 5030 energy dispersive X-ray spectroscopy (EDX) detectors and FEI’s MLA suite 3.1.4 software for data acquisition at both BGR and Helmholtz-Institute Freiberg for Resource Technology (HIF). In-depth information on the MLA system and PGM identification can be found in Fandrich et al. (2007), and Osbahr et al. (2015). In the present study, the sparse phase liberation (SPL)-Lite measurement mode was applied for identification of PGM grains with high spatial resolution and accuracy (Fandrich et al. 2007). In this mode, a series of BSE images is collected and only mineral grains matching defined grey scale ranges are analyzed by EDX. Polished sections of the concentrates were analyzed in a first run, then re-ground and re-polished and analyzed again in a second run.

3 Results

3.1 Whole-rock

Platinum concentrations in weathered chromitite seams (LG-6 to MG-4) generally exceed those of Pd (Table 1,2). However, differences are observed by comparing individual chromitite seams as total PGE concentrations of weathered chromitites from the LG-6 to MG-4 in the pits range between 760 and 1300 ppb. Pt/Pd ratios increase stratigraphically upwards, while the IPGE/PPGE ratio decreases (Table 2).

Table 1. Median Pt and Pd concentrations (all in ppb) and Pt/Pd ratios of merged LG and MG-chromitites of the pits (n=6), trenches (n=30), hanging and footwall (n=15) and carbonate veins (n=11).

<table>
<thead>
<tr>
<th></th>
<th>Pt/Pd</th>
<th>Pt</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>chromitites - pits</td>
<td>4.7</td>
<td>270</td>
<td>57</td>
</tr>
<tr>
<td>chromitite - trenches</td>
<td>6.5</td>
<td>315</td>
<td>48</td>
</tr>
<tr>
<td>hanging/footwall</td>
<td>7.9</td>
<td>333</td>
<td>42</td>
</tr>
<tr>
<td>carbonate veins</td>
<td>1.5</td>
<td>77</td>
<td>49</td>
</tr>
</tbody>
</table>

Elevated concentrations of Pt and Pd are also present in hanging and footwalls of chromitite seams (median 333 ppb Pt). In the MG-1 chromitite, Pt/Pd ratios are partly lower in the hanging and footwall compared to the associated chromitite seams (Figure 1).

Figure 1. Whole-rock geochemistry of Pt and Pd from the MG-1 chromitite in trench 1, as well as hanging wall and footwall of the MG-1 chromitite.

Within the chromitite seams in the trenches, green and white carbonate veins crosscut the chromitite seams. These alteration veins were selectively sampled and have variable concentrations of up to 1900 ppb Pt and 120 ppb Pd.

Table 2. Individual whole-rock PGE concentrations (all in ppb) of chromitites from the pits analyzed by nickel sulfide fire assay and instrumental neutron activation analysis (INAA). Additionally, Pt/Pd and IPGE/PPGE ratios are given. IPGE: Os, Ir, Ru; PPGE: Rh, Pt, Pd.

<table>
<thead>
<tr>
<th></th>
<th>IPGE</th>
<th>Rh</th>
<th>Pt</th>
<th>Pd</th>
<th>Pt/Pd</th>
<th>IPGE/PPGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG-4</td>
<td>165</td>
<td>8</td>
<td>716</td>
<td>54</td>
<td>13.3</td>
<td>0.2</td>
</tr>
<tr>
<td>MG-3</td>
<td>736</td>
<td>86</td>
<td>395</td>
<td>80</td>
<td>4.9</td>
<td>1.3</td>
</tr>
<tr>
<td>MG-2</td>
<td>752</td>
<td>69</td>
<td>157</td>
<td>41</td>
<td>3.8</td>
<td>2.8</td>
</tr>
<tr>
<td>MG-1</td>
<td>567</td>
<td>46</td>
<td>109</td>
<td>42</td>
<td>2.6</td>
<td>3.0</td>
</tr>
<tr>
<td>LG-6</td>
<td>779</td>
<td>28</td>
<td>91</td>
<td>57</td>
<td>1.6</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Figure 2 shows chondrite-normalized PGE patterns of weathered MG-2 chromitite sampled from the pits and trenches, as well as from pristine drill cores. From the MG-2 chromitite in the weathered and near-surface ores Pt and Pd (n=7; green in Figure 2) were analyzed and only in one sample IPGE (blue in Figure 2). The PPGE (Rh, Pt, Pd) contents of weathered ores (blue and green in Figure 2) are generally lower than those of the pristine ores (red in Figure 2). The IPGE (Os, Ir, Ru) are very similar in both pristine and weathered ores. Particularly, Ru concentration are in the same range as the pristine ores.
Figure 2. Chondrite-normalized PGE concentrations of the MG-2 chromitite seam sampled in the mining pits of the Thaba Mine (n=1), median values of MG-2 chromitites sampled in the trenches (n=7) and pristine MG-2 chromitites from drill cores of the Thaba Mine (Cronimet). Normalized after McDonough and Sun (1995). Upper right corner shows laurite \([\text{RuS}_2]\) inclusion in chromite as an explanation for the similar Ru concentrations in weathered and pristine MG-2 chromitite.

3.2 PGE mineralogy in weathered ores

The MLA study of weathered ores identified the following major PGM groups: PGE-sulfarsenides (hollingworthite \([\text{RhAsS}]\), irarsite \([\text{IrAsS}]\), platarsite \([\text{PtAsS}]\)), laurite \([\text{RuS}_2]\), Pt-Fe alloys, and cooperite-braggite \([\text{Pt(Pd)}S]\). Laurite \([\text{RuS}_2]\) is often present as inclusions in chromite (Figure 2). Relicts of PGM at different degrees of breakdown typically show PGE halos around them (Figure 3). Furthermore, PGE-minerals stoichiometrically resembling PGE-oxides were analysed by SEM/EDX (Figure 3).

Figure 3. BSE images of weathered platinum-group minerals within secondary Fe-silicates in the near-surface ores. A: Intergrowth of laurite \([\text{RuS}_2]\), platarsite \([\text{PtAsS}]\), and stibiopalladinite \([\text{Pd}_3\text{Sb}_2]\). B: Pt-Rh-Ir mineral. C.,D.: Pt-(Fe)-oxides.

4 Discussion

4.1 Geochemical behavior of PGE during weathering

Platinum concentrations increase from LG-6 to MG-4, whereas Pd remains at near-constant levels, resulting in a strong increase of the Pt/Pd ratio from 2.2 to 15.3 (Table 1). In pristine ores, Pt and Pd concentrations increase from the LG to the UG chromitites. Bachmann et al. (2019a) presented median Pt and Pd concentrations of the LG and MG chromitite seams at Thaba Mine (LG-6: 330 ppb Pt, 60 ppb Pd; MG-1: 680 ppb Pt, 160 ppb Pd; MG-2: 1270 ppb Pt, 270 ppb Pd; MG-3: 1280 ppb Pt, 496 ppb Pd; MG-4: 1230 ppb Pt, 200 ppb Pd). Platinum, therefore largely remains within the chromitite seams and is only locally mobilized within the chromitites and their surrounding hanging and footwalls, whereas a large proportion of the Pd is leached out (Table 2). Oppermann et al. (2017) also showed for the soils at Thaba Mine, that Pt is transported in small quantities only over short distances away from chromitite horizons. Palladium is mobilized and the concentrations in the near-surface chromitites are lower than in pristine, unweathered ores and therefore the Pd concentrations do not show the same primary orthomagmatic trend as Pt (cf. Table 1, 2).

Weathering causes mobilization of Pt and Pd out of the chromitites, locally into the hanging and footwall. The general decrease (in particular of Pd) can also be observed by comparing with the average Pt/Pd ratio of pristine chromitites from the Thaba Mine (Bachmann et al. 2019a). Carbonate veins which intersected chromitite seams near surface show elevated concentrations of Pt and Pd. Therefore, Pt and Pd are to some extent locally transported along these veins and may be precipitated within the hanging and footwall due to changes in the physio-chemical conditions within the hanging and footwall.

Stratigraphically upwards, Pd probably has a similar fate as Pt. However, due to the impact of weathering and the strong mobilization of Pd, the effect cannot be shown here. The dominance of IPGE and Pt (+Pd) dominated processes evolved upwards during the primary magmatic formation of the chromitite seams. The highest concentrations are for Ru (maximum value in the LG-6 chromitite is 640 ppb) and Pt (maximum value in the MG-4 chromitite is 715 ppb), also indicated by the concomitant decrease of the IPGE/PPGE ratio from 4.4 to 0.2 from the LG-6 to the MG-4 chromitites (Table 2). The IPGE are generally less affected by weathering processes which may be explained by the fact that laurite \([\text{Ru} \text{Os}_{0.5}\text{Ir}_{0.5}]\) commonly occurs as inclusions in chromite (Figure 2), and PGM incorporated in chromite are largely unaffected by weathering processes. In addition to discrete PGM, it was shown that Ru is incorporated in the chromite lattice (Pagé and Barnes 2016), underlining that Ru (both as inclusion of laurite and within the crystal lattice) is not affected by weathering processes. Originally, Ru-rich PGM associated with sulfides, however, can be affected by weathering as only relict laurite grains are associated with silicates in the weathered ores.

4.2 Mineralogical behavior of PGE-phases during weathering

Only relict PGM grains are present in the near-surface ores and they are moderately to completely destroyed. Analysis by EPMA and LA-ICP-MS revealed good correlations between Pt, Pd with Ni and Cu in secondary
Platinum-group elements transport is local in character, oxy/hydroxides (Junge et al. 2018). Liberated metals into secondary silicates and pentlandite and chalcopyrite and incorporation of the silicates, indicating the breakdown of sulfides such as pentlandite andchalcopyrite and incorporation of the liberated metals into secondary silicates and oxy/hydroxides. These processes are also the reason for neoformation of PGM under supergene conditions and the formation of PGE-oxides as shown in Figure 3. These grains are intergrown with various types of secondary minerals (e.g. clay minerals). Palladium can be transported further away from the system, evidenced by the high Pt/Pd ratios of the most weathered ores, which is also in agreement with experimental studies on the transport of Pt and Pd in hydrothermal fluids (Barnes and Liu 2012).

5 Conclusions

The higher Pt/Pd ratios in the pervasively weathered chromitites indicate that Pd is more mobile during weathering processes than Pt. Elevated concentrations of Pt and Pd in the hanging walls and footwalls of the chromitite seams indicate that Pt and Pd redistribution occurs on a small scale. Weathering processes cause local redistribution of the Pt and Pd. The newly formed PGM phases in the weathered ores are mainly associated with secondary minerals such as Fe-silicates and Fe-oxides/hydroxides. Primary PGM grains are largely destroyed and only relict grains occur. Platinum-group elements are dissolved from these PGM and very locally reprecipitated, indicated by the neoformation of PGM-oxides/hydroxides.

Acknowledgements

This is a contribution of the German/South African R&D project AMREP—Applied Mineralogy for Resource Efficiency of Platinum-Group Metals—funded by the German Ministry of Education and Research (BMBF; grant number BMBF-033R119E). Many thanks to Cronimet Mining Group for providing access to their core data and drill core intersections from the Thaba mine, and for the contribution of additional analytical data as well as information on the local geology and beneficiation.

References

Oppermann L, Junge M, Schuth S, Holtz F, Schwarz-Schampera U, Sauthoff L (2017) Mobility and distribution of palladium and platinum in near-surface weathered soils from the Lower and Middle Group chromitites of the western Bushveld Complex, South Africa. S Afr J Geol 120:511-524
Mineral chemistry of major sulfides: application to the understanding of PGE mineralization in the Northern limb of the Bushveld Igneous Complex

Sharlotte C. Mkhonto, Pedro J. Jugo
Laurentian University

Danie Grobler
Ivanplats (Pty) Ltd

Matthew I. Leybourne
Queen’s University

Abstract. The Platreef is generally characterized by interaction of Bushveld magmas with underlying metasedimentary rocks or granitoids and it is of interest because of the PGE-Ni-Cu mineralization it contains. One puzzling aspect is the lack of correlation between PGE-Ni-Cu contents and sulfide abundance, which is relevant because of the role of sulfide saturation on ore formation. Clearly, a better understanding of how sulfide abundance relates to PGE-Ni-Cu mineralization is essential to understand ore formation and distribution. This study focuses on samples showing at least two different populations (from whole rock data): One with relatively low S/Ni values; the other with higher S/Ni (and stratigraphically associated with footwall assimilation). Mineral chemistry of major sulfides (by EPMA and LA-ICP-MS) was used to determine how the differences identified in whole rock chemistry were preserved in the sulfides. The results show that selenium contents in sulfides spatially associated with PGE-Ni-Cu mineralization is higher than in sulfide minerals associated with footwall assimilation and also that other trace elements (e.g. Co contents in pyrrhotite and pentlandite, Cd contents in chalcopyrite) are useful to distinguish between different types of sulfides. This approach could be useful to distinguish the degree of footwall assimilation elsewhere.

1 Introduction

The PGE mineralization in the Platreef is relatively in the same stratigraphic position as the Merensky Reef in the Eastern and the Western limbs of the Bushveld Igneous Complex (BIC) and is reported to contain more base metal sulfides than the latter (Kinnaird et al. 2005). Previous studies (e.g. Harris and Chaumba 2001) suggested that footwall assimilation may have been involved in the mineralization process, whereas other studies indicated that PGE mineralization is mostly magmatic and subsequently affected by footwall assimilation (e.g. Holwell and McDonald 2007; Hutchinson and McDonald 2008).

One of the reasons there has not been better constraints is because it is commonly difficult to have independent assessments of the primary vs. secondary process in the samples analyzed. Deep drilling by Ivanplats intersected sequences that allowed isotopic (S and Sr) and trace element studies that confirm that the PGE-Ni-Cu mineralization is magmatic (Mayer 2008; Mayer et al. 2018) and that the footwall assimilation zone contains S derived from metasedimentary rocks (Keir-Sage et al. 2018). The Sr and S isotopic data, combined with litho-chemostratigraphy (Grobler et al. 2019) is strong evidence to conclude that the Platreef is, in essence, the expression of the Merensky Reef in the Northern Limb of the Bushveld Igneous Complex. The goal of this study is to complement those studies by documenting systematic differences in the mineral chemistry of major sulfide minerals associated with PGE-Ni-Cu mineralization compared to those associated with the footwall assimilation zone (and with lower grades).

2 Background, samples used, and working hypothesis

Work was done on samples from drill hole UMT094 (Turfspruit locality), which was selected because it shows a relatively clear separation between PGE-Ni-Cu mineralization (with no visible evidence of assimilation) and a zone of footwall assimilation. Sulfides, mostly pyrrhotite (Po), pentlandite (Pn), and chalcopyrite (Cc) are visible through mineralization and through the footwall assimilation zone without any significant changes in mode of type. Previous work on samples from the same drill core (Sr isotopic stratigraphy, Mayer et al. 2018; sulfur isotopes and whole rock geochemistry, Keir-Sage et al. 2018) showed that although there is contribution of footwall S into the footwall assimilation zone, the PGE-Ni-Cu mineralization is mostly magmatic and not significantly affected by footwall assimilation.

Inspection of S vs. Ni contents from whole rock data (Fig. 1) show that there are at least two populations: one with relatively low S/Ni, the other with relatively high S/Ni. A third trend (labeled as ‘intermediate’) seems to branch off the low S/Ni trend. Similar trends (not shown) are observed for S vs. Cu and S vs. PGE.
The working hypothesis is that if the differences identified in figure 1 are a consequence of different geochemical processes then the composition of major sulfides is likely to keep record of such differences.

Figure 1. Whole rock S vs Ni content showing three distinct populations of sulfides: (a) high S, low Ni; (b) low S, high Ni; (c) an inferred 'intermediate population'. The lines shown are approximate ratios (S/Ni) that can be used to define each group (solid line S/Ni = 4.5; dashed line S/Ni = 3.0). The three populations converge and are difficult to distinguish when S content is less than 0.3 wt% and Ni content is less than 0.1 wt%.

Figure 2 shows that the group with low S/Ni is stratigraphically higher and includes the interval associated with PGE mineralization, whereas most of the samples in the group with high S/Ni group are lower in the stratigraphy. Core logging and previous work (Keir-Sage et al. 2018) show that most of the samples characterized by high S/Ni are associated with footwall assimilation. The intermediate group overlap the stratigraphic range of the low S/Ni group but seem restricted to what appears to be a break between the high S/Ni group (~ 1365 m) and the sharp increase in PGE content (~ 1300 m).

Figure 2. Stratigraphic variations in S, 3PGE and Ni content from whole rock geochemistry. Except for four samples with high S/Ni there is a clear separation in the depths of each group (with a significant overlap between the ‘intermediate’ and the low S/Ni groups.

3 Methods

Core logging and sampling for geochemical analysis of sulfides was done on drill core UMT094. Selected samples were sectioned and prepared as thick polished sections (~ 100 μm thick). Major sulfides were identified in the polished sections using reflected light microscopy and secondary electron microscopy (SEM) at Laurentian University. Grains of major sulfides (Po, Pn, Ccp) representative of each population were analysed for major and minor elements using a Cameca SX100 electron probe microanalyzer (EPMA) at the Ontario GeoLabs. Trace elements data were obtained by LA-ICP-MS using a Resonetics RESOlution M50 laser probe coupled to a Thermo-Fisher XSeriesII ICP-MS.

4 Results

The most significant results are summarized in figures 3 and 4. A diagram of Co content in Pn vs. Se content in Pn (Fig. 3) shows that Pn in sulfide assemblages within the mineralized interval contain higher Se but lower Co contents than Pn in sulfide assemblages that are stratigraphically lower and associated with footwall assimilation.

Figure 3. Pentlandite from the low S/Ni group have a large range in Se content (0.007<Se<0.033 wt%) whereas Pn from the high S/Ni group have Se < 0.003 wt% (with some outliers ranging to up to 0.008 wt%). The Co contents are less than 0.9 wt% in Pn from the low S/Ni group and range from 1.7 to 3.0 wt% in Pn from the high S/Ni group (but with some outliers having Co content as low as 0.3 wt%).

Figure 3 shows that in general the Se content is one of the most useful discriminants and that combined with Co content demonstrates that the differences in whole rock data correspond to differences in sulfide compositions. There is however, some overlap in Co contents and some samples with low Se have the lowest Co contents documented.

Figure 4 shows that mineral chemistry is also distinct for Po and Ccp and can be used to discriminate the different populations. It complements figure 3 because it provides evidence to consider the ‘intermediate’ population as a distinct group that can be distinguished from the other two, having Se/Co in Po > 1 and a range in Se/Cd in Ccp that spans the range of both of the other populations.
Figure 4. Se/Co in Po against Se/Cd in Ccp. This is an example of how data from two different sulfides can be used to discriminate among the different sulfide assemblages. Sulfide assemblages associated with footwall assimilation have Se/Co in Po < 1 and variable Se/Cd content in Ccp. In contrast, sulfide assemblages associated with mineralization have Se/Co in Po > 1 and restricted Se/Cd in Ccp (< 0.15).

5 Discussions and conclusions

Our understanding of the role of footwall-magma interaction on PGE mineralization in the Northern Limb has changed over time. For example, Harris and Chaumba (2001) suggested that footwall assimilation occurred prior to emplacement, inducing sulfide saturation and PGE mineralization of the Platreef. Later studies reached different conclusions. For example, Holwell and McDonald (2007) concluded that the PGE mineralization was primarily orthomagmatic and that sulfides formed in a deep staging chamber but were later affected by hydrothermal activity. Hutchinson and McDonald (2008) suggested that melting and devolatilization of the local floor rocks resulted in the introduction of S and metalloids (As, Sb, Te and Bi) and that addition of footwall-derived S diluted the PGE tenors.

Although all the assemblages contain the same minerals (Po, Pn, Ccp), the results of this work demonstrate the existence of three distinct sulfide assemblages, which can be distinguished based on trace element content. When combined with S isotope stratigraphy (Keir-Sage et al. 2018) and Sr isotopic stratigraphy (Mayer 2018; Mayer et al. 2018) it leads to the conclusion that the high S/Ni group belongs to the footwall assimilation zone and the low S/Ni group, which includes the interval with PGE-Ni-Cu mineralization, is magmatic. If mineralization in drill core from UMT094 is representative of the Platreef in general, then the results of this study provide solid evidence that Platreef PGE-Ni-Cu mineralization is essentially magmatic and that footwall assimilation likely has a detrimental effect on PGE-Ni-Cu mineralization, even if it contributes S and other valuable metals (such as Co) to the system. Ongoing work aims to apply this approach to other Platreef drill core samples in which the separation between magmatic units and footwall assimilation is not as clear as in UMT094. The approach could be useful elsewhere to evaluate the role of primary vs. secondary processes in PGE-Ni-Cu mineralization.

Acknowledgements

We thank the Canadian Queen Elizabeth II Diamond Jubilee Scholarship program (QES), the Goodman School of Mines (GSM), the Natural Sciences and Engineering Research Council of Canada (NSERC), and Ivanplats for financial and logistic support; Alexandra Crossingham, Malesela Mapeka, and the rest of the Ivanplats team in Mokopane for field and logistic support; Dave Crabtree (Ontario GeoLabs) for analytical assistance with EPMA; Joe Petrus and Michael Langa for assistance with LA-ICP-MS.

References

Hutchinson D and McDonald I (2008) Laser ablation ICP-MS study of platinum-group elements in sulphides from the Platreef at Turfspruit, northern limb of the Bushveld Complex, South Africa. Miner Deposita 43:695–711
Mayer CC (2018) Strontium Isotope Stratigraphy of the Platreef at Turfspruit, Northern Limb, Bushveld Igneous Complex. MSc thesis, Laurentian University, pp. 121
Significance of S and Sr isotopic variations across the Platreef in the Northern Limb of the Bushveld Igneous Complex

Evan Keir-Sage, Cedric C. Mayer, Pedro J. Jugo
Harquail School of Earth Sci., Laurentian University

Danie Grobler
Exploration and Geology, Ivanplats (Pty) Ltd.

Matthew I. Leybourne
Department of Geological Sci. and Geological Engineering, Queen’s University

Abstract. Previous studies in the Eastern and Western Limbs of the Bushveld Igneous Complex (BIC) have documented variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ values across the Upper Critical Zone (UCZ) that mark the stratigraphic position of PGE-Ni-Cu mineralization at the Merensky Reef, as well as $\delta^{34}\text{S}$ values that do not match mantle estimates but can be considered characteristic of BIC mineralization. Understanding mineralization in the Northern Limb has been more challenging because the UCZ was emplaced directly into a footwall of metasedimentary rocks and granitoids, creating a wide interval of magma-footwall interaction (the Platreef) containing PGE-Ni-Cu mineralization and making it difficult to separate magmatic from footwall contributions to the isotopic data. Drill core samples collected away from the outcropping Platreef show a clear separation between mineralization and footwall assimilation. Isotopic data show that $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ values across mineralization in the Northern Limb match the characteristics documented for the Eastern and Western limbs, providing strong evidence that the Platreef and the Merensky Reef were produced by the same magmas.

1 Introduction

The Bushveld Igneous Complex (BIC) is the largest known igneous intrusion on Earth and the largest repository of PGE. Historically, mineral exploration focused on the Eastern and Western Limbs but over the last two decades there has been a stronger focus on exploration for PGE mineralization in the Northern Limb. The Rustenburg Layered Suite of the BIC is roughly 8 km thick and mineralization is contained within a few hundred meters near the top of the Upper Critical Zone (UCZ) almost immediately below the base of the Main Zone (Zientek et al. 2014). In the Eastern and Western Limbs, PGE extraction is focused on two distinct layers: the Merensky Reef (a mining term used to describe the roughly 1 m thick interval that is extracted for PGE recovery; Cawthorn et al. 2002) and the UG-2 chromitite (the uppermost massive chromitite seam within the UCZ). In the Northern Limb PGE mineralization is also located stratigraphically near the top of the UCZ, right below anorthosites and gabbronorites considered to represent the base of the Main Zone. However, in the Northern Limb the PGE mineralization has been widely described as being completely different from that in the Merensky Reef and the UG-2 mostly because proximity to footwall resulted in a wide interval of complex interaction between footwall rocks and magmas. Thus, PGE mineralization in the Northern Limb has been considered by some authors to have formed due to contamination of the magma by country rocks (e.g. Von Gruenewaldt et al. 1985). Because of these differences the term Platreef was coined to describe the rocks in the Northern Limb that are below the Main Zone, have complex magma-footwall interaction and include intervals containing PGE mineralization. One of the best definitions of the Platreef was provided by Gain and Mostert (1982, p. 1396): "The Platreef is composed of a complex sequence of medium- to coarse-grained pyroxenites, melanorites, and norites, in places pegmatoidal and serpenitined, containing metasedimentary xenoliths of the floor rocks. It contains sporadic enrichments of Ni, Cu, and platinum-group element mineralization which locally make it of economic significance". Further work (e.g. McDonald et al. 2005) concluded that the Platreef was generated by a different magma and is not genetically linked to the Merensky Reef. However, compilation of $\delta^{34}\text{S}$ data (e.g. Magalhaes et al. 2018) show that the isotopic composition of the mineralization in the Platreef is undistinguishable from that in the main limbs of the BIC, a fact documented also by other workers (e.g. McDonald and Holwell 2011) who concluded that PGE mineralization in the Platreef is primarily magmatic and that external S (from country rocks) was mostly an ore-modifying process. More recently, Grobler et al. (2019) used stratigraphic, lithological and compositional evidence to conclude that the Platreef sequence (including a chromitite seam below it) correlates with the interval between the UG-2 chromitite and the top of the UCZ (the Bastard Reef) in the main limbs of the BIC.

To further elucidate the links between the Northern Limb and the Eastern and Western Limbs of the BIC, the Sr isotopic stratigraphy across the Platreef was determined by Mayer (2018) on Platreef samples where footwall assimilation was minimal (as documented by core logging and confirmed by $\delta^{34}\text{S}$). Numerous studies (e.g. Kruger and Marsh 1982; Seabrook et al. 2005) have shown a distinctive variation in $^{87}\text{Sr}/^{86}\text{Sr}$ across the upper...
part of the UCZ in the Eastern and Western Limbs from $^{87}\text{Sr}/^{86}\text{Sr} = 0.706$ to $^{87}\text{Sr}/^{86}\text{Sr} = 0.708$. Such variations are distinct enough to be useful for correlation between the Northern Limb and the Eastern and Western Limbs. Mangwegape et al. (2016) documented $^{87}\text{Sr}/^{86}\text{Sr}$ values in plagioclase in drill core samples from the Upper Zone and not across the Platreef. However, Yudovskaya et al. (2018) documented $^{87}\text{Sr}/^{86}\text{Sr}$ in three samples from uncontaminated Platreef and concluded that “plagioclase in the reef sequence at the top of the Platreef has a more radiogenic Sr isotope composition that is identical to that of the Merensky reef, and the persistence of this signature over the entire Bushveld does not allow derivation from local contamination. This similarity supports the previously interpreted correlation between the Turfspruit reef and the Merensky reef” (Yudovskaya et al. 2018; p. 203). Here we show combined $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{\delta 34}\text{S}$ data that further demonstrates a clear correlation between the PGE-Ni-Cu mineralization in the upper part of the Platreef and the Merensky sequences in the Eastern and Western Limb of the BIC.

2 Methods

Sulfur and strontium isotopic data were collected at the Queen’s Facility for Isotope Research (QFIR), Queen’s University. Sulfur isotope analyses were completed using whole rock powders and by microdrilling sulfide minerals from drillcore. Samples for S isotope analyses were weighed into tin capsules and analyzed using a Finnigan MAT 253 stable isotope ratio mass spectrometer system coupled to a Costech ECS 4010 elemental analyzer. The $^{\delta 34}\text{S}$ values were calculated by normalizing the measured $^{34}\text{S}/^{32}\text{S}$ values in the sample to that in the Vienna Canyon Diablo Troilite (VCDT). Values are reported using the delta ($\delta$) notation in permil units (‰). Sample duplicate analyses were reproducible within 0.2 ‰. The certified reference material (CRM) used was NBS-127 (calibrated back through 4 analyses to 20.2, 20.3, 20.3 and 20.4 ‰) as well as an in-house standard from QFIR (M6801).

The analytical protocol used for in-situ $^{87}\text{Sr}/^{86}\text{Sr}$ in plagioclase was based on the procedures documented in Yang et al. (2013), Mangwegape et al. (2016), and Wilson et al. (2017). Polished petrographic sections (100 µm thick) were prepared from thirty-seven samples covering the magmatic stratigraphy including the base of the Main Zone, through the Platreef and towards the footwall assimilation zone. Some samples contained slightly altered plagioclase grains but only fresh plagioclase grains were selected for analysis. Analyses were performed by laser ablation multi-collector inductively coupled plasma mass spectrometry using a 193 nm excimer laser (Elemental Scientific NWR193) coupled with a Thermo-Finnigan Neptune MC-ICP-MS. A laser beam of circular section and 150 µm diameter was used with a repetition rate of 10 Hz, a beam energy density of ~2.3 J/cm² and a duration of 120 s per analysis preceded by a 60 s blank analysis. The masses analyzed were $^{82}\text{Kr}$, $^{83}\text{Kr}$, $^{84}\text{Sr}$, $^{85}\text{Rb}$, $^{86}\text{Sr}$, $^{87}\text{Sr}$, $^{88}\text{Sr}$, $^{44}\text{CaPO}$, as well as double charged REE ($^{163}\text{Dy}^{++}$, $^{167}\text{Er}^{++}$, $^{171}\text{Yb}^{++}$, $^{173}\text{Yb}^{++}$ and $^{175}\text{Lu}^{++}$). Five to ten spot analyses (including core and rim) were completed per sample with one reference material (BHVO-2G, BIR-1G or TB-1G) analyzed after every two spot analyses on plagioclase. In total, 131 analyses of BHVO-2G, 55 analyses of BIR-1G, and 56 analyses of TB-1G were completed. The $^{87}\text{Sr}/^{86}\text{Sr}$ obtained were within error of the certified values for those standards. Additional details are described in Mayer (2018).

3 Results

The results are summarized in Fig. 1, which shows variations in $^{\delta 34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values with depth obtained on samples from drillcore UMT094.

Figure 1. Combined $^{87}\text{Sr}/^{86}\text{Sr}$ in plagioclase (red circles) and $^{\delta 34}\text{S}$ (blue rhombs) in samples from UMT094. The sharp break in $^{87}\text{Sr}/^{86}\text{Sr}$ at 1290 m coincides with what was previously defined at the base of the Merensky Cyclic Unit (MCU) based on core logging, litho- and chemostratigraphy (following the units defined in Grobler et al. 2019). The $^{\delta 34}\text{S}$ values above 1290 m are consistently below $^{\delta 34}\text{S} = +4$ ‰ and mostly within the range established for the entire BIC (Magalhaes et al. 2018). Data sources: $^{87}\text{Sr}/^{86}\text{Sr}$ from Mayer (2018), $^{\delta 34}\text{S}$ from Keir-Sage (2019).

The $^{\delta 34}\text{S}$ data (Keir-Sage 2019) show a progressive decrease up section in $^{\delta 34}\text{S}$ values from $^{\delta 34}\text{S} = +8.0$ ‰ in the footwall assimilation zone towards to $^{\delta 34}\text{S} = +4.0$ ‰ in the mineralized interval (the bulk of the PGE-Ni-Cu
mineralization is located roughly between 1240 and 1290 m). The $^{87}\text{Sr}/^{86}\text{Sr}$ values (Mayer 2018) are nearly constant at 0.706 below 1290 m and then increase up section to 0.709 and then decrease again to fluctuate between 0.707 and 0.708 on the top of the UCZ and into the Main Zone (the contact with the Main Zone is located at approximately 1210 m).

4 Discussion and Conclusions

As shown in Fig.1, the variations in $\delta^{34}\text{S}$ indicate an increasing influence of footwall assimilation with depth, which matches the observed increase in abundance of footwall xenoliths in drill core. However, at the level of PGE mineralization (where evidence of footwall assimilation is absent in drill core) the $\delta^{34}\text{S}$ values are within the $\delta^{34}\text{S}$ range that has been documented in the Eastern and Western Limbs of the BIC (e.g. Buchanan et al. 1981 and data compilation in Magalhaes et al. 2018). This is consistent with interpretations of PGE-Ni-Cu mineralization in the Platreef as being essentially magmatic, with crustal contamination being mostly an ore-modifying process (as suggested, for example, by McDonald and Holwell, 2011). In addition, the trend defined by $^{87}\text{Sr}/^{86}\text{Sr}$ values, with a sharp increase from 0.706 (below mineralization) to up to $^{87}\text{Sr}/^{86}\text{Sr} = 0.709$ (across PGE-Ni-Cu mineralization) is essentially identical to the $^{87}\text{Sr}/^{86}\text{Sr}$ patterns documented in the Eastern and Western Limbs of the BIC (e.g. Seabrook et al. 2005). We interpret the $^{87}\text{Sr}/^{86}\text{Sr}$ pattern as strong evidence that PGE-Ni-Cu mineralization in the Upper Critical Zone of the Northern Limb correlates with the Merensky Reef sequence in the Eastern and Western Limbs of the BIC as suggested, for example by Wagner (1929) and most recently by Grobler et al. (2019).

Acknowledgements

We thank the Canadian Queen Elizabeth II Diamond Jubilee Scholarships (QES), the Natural Sciences and Engineering Research Council of Canada (NSERC), and Ivanplats for funding. We thank Tim Dunnett, Albie Brits, Jan Mapeka, Alexandra Crossingham and the rest of the Ivanplats team in Mokopane for field and logistics support. Isotopic analytical work at Queen’s University could not have been completed without the help of Donald Chipley and Alexandre Voinot.

References

McDonald I, Holwell DA (2011) Geology of the northern Bushveld Complex and the setting and genesis of the Platreef Ni-Cu–PGE deposit. Rev. Econ Geol 17:297–327
Palladium and platinum seleno-tellurides and their associations

Anna Vymazalová¹, Marek Tuhý¹², František Laufek¹
¹Czech Geological Survey, Prague, Czech Republic
²Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Prague, Czech Republic

Abstract. Palladium and platinum tellurides and selenides were experimentally investigated at 400 °C. We have synthesized the binary and ternary phases in the systems Pd/Pt-Se-Te and evaluated them by means of X-ray powder-diffraction analysis, reflected light and electron microscopy. The experiments were performed using the evacuated silica-glass tube method. The phase relations were assessed in the system Pd- Se-Te at 400 °C. Miessite (Pd₁₁Te₂Se₂) forms stable associations with Pd₁₃Te₃ and keithconnite (Pd₂₀Te₇), keithconnite and palladseite (Pd₃₄Se₁₁). Miessite also coexists with Pd₄Se, Pd₆Se₂, Pd₈Se₁₁, and Pd₆Se₄. Telluropalladinite coexists with Pd₄Te₂ and palladseite. Palladseite coexists with Pd₄Te₂ and kotulskite ss. Preliminarily experimental results in the Pt-Se-Te system have shown the complete solid solution sudovikovite (PtSe₂) – moncheite (PtTe₂). A new ternary phase PtSeTe was observed in the system and is being further investigated. Assessed stable associations should be sought in assemblages with other PGM and known Pd/Pt selenides and tellurides, likely in magmatic Cu-Ni-PGE mineral deposits, associated with mafic and ultramafic igneous rocks, but also at low temperatures formations like selenide vein-type mineralization.

1 Introduction

Among palladium tellurides and selenides there are the following minerals known: merenskyite (PdTe₂), kotulskite (PdTe), palladotelluride (Pd₉Te₄), keitconnite (Pd₂₀Te₇), palladseite (Pd₃₄Se₁₁) and verbeekite (PdSe₂). Furthermore, among palladium tellurides there are additional five synthetic binary phases known, revised in Vymazalová et al. (2014) and three palladium tellurides recently re-investigated by Vymazalová et al. (2015). In the Pd-Te-Se system there is also one ternary mineral - miessite (Pd₁₁Te₂Se₂) found in a heavy minerals placer concentrate from the Miessi River in Finland (Kojonen et al. 2007). Nevertheless, the phase relations of the Pd-Te-Se system have not been studied so far.

Among platinum selenides and tellurides there are the following minerals known: sudovikovite (PtSe₂), luberoite, (Pt₅Se₆), moncheite (PtTe₂) and the recently discovered mineral mitrofanovite (Pt₃Te₄) from low-sulphide disseminated ore in the eastern Chuarvy deposit, Fedoro-Pana intrusion in Russia (Subbotin et al. in press). The ternary system itself has not been experimentally studied yet.

Selenides are formed from hydrothermal fluids at conditions of high fugacity of f_S/f_S₂ ratio and are closely associated with chalcogenides and native elements in a variety of mineral assemblages. They are known to occur in low-temperature selenide mineralization, Au-Ag epithermal deposits, unconformity-related uranium deposits, sandstone-hosted uranium deposits or in mineralized black shales. Whereas palladium-platinum tellurides are generally observed in Cu-Ni-PGE mineral deposits associated with mafic and ultramafic igneous rocks.

We have experimentally investigated platinum and palladium selenides and tellurides at 400 °C. We have studied the ternary Pt/Pd selenide-tellurides and assessed their stable assemblages in the corresponding ternary systems. The evacuated silica tube method was applied for the purpose of this study. The experimental products were examined with X-ray powder diffraction, differential thermal analyses and in polished sections by means of reflected light and electron microscopy.

2 Techniques and methods

2.1 Experimental

Experiments were performed in evacuated and sealed silica glass tubes in horizontal tube furnaces. Charges of about 200-300 mg were carefully weighed out from the native elements (palladium powder, 99.95% purity; platinum powder, 99.999% purity, selenium pebbles, 99.999% purity and tellurium ingot, 99.999% purity). The starting mixtures were first melted at 1000°C for two days. Then, the run products were ground in an agate mortar under acetone and reheated to 400°C (for 50-70 days). After heating, quenching occurred by dropping the capsules in cold water. Phases in the run products were characterized by X-ray powder diffraction, in polished sections examined in reflected light, and with electron-probe techniques (EPMA).

2.2 Electron probe microanalyses

EPMA were performed with a CAMECA SX-100 electron probe microanalyser in a wavelength-dispersion mode using an electron beam focussed to 1-2 μm. Pure elements were used as standards. Concentrations were quantified on the Pd₅L₅, Pt₅L₅, SeL₅ and TeL₅ with an accelerating voltage of 15 keV, and a beam current of 10 nA. In a sample, compositional data were collected from several grains within a polished section.
2.3 X-ray diffraction analyses

The X-ray diffraction patterns (XRD) were collected in Bragg-Brentano geometry on Bruker D8 Advance diffractometer equipped with the Lynx Eye XE detector and CuKα radiation source. The data were collected in the angular range from 10 to 140° 2Θ°.

3 Results and Discussion

3.1 Pt-Se-Te

The following binary platinum selenides and tellurides Pt5Se4, PtSe2, PtTe, Pt3Te4, Pt2Te3, PtTe2 are stable in the system at 400 ºC. The plot of minerals and phases belonging to the Pt-Se-Te system is depicted in Fig. 1.

According to the experimental results there is a new ternary phase PtTeSe in the system (Fig. 2). Preliminarily experimental results have shown that sudovikovite and moncheite form a complete solid solution.

![Figure 1](image1.png)

**Figure 1.** Plot of minerals and phases in the ternary Pt-Se-Te system.

![Figure 2](image2.png)

**Figure 2.** BSE image showing association of sudovikovite-moncheite ss (dark grey) with ternary phase (PtSeTe) (light grey) and native Pt (white). Run No7, heated four months, T = 400 ºC.

3.2 Pd-Se-Te

The following binary Pd-selenides are stable at 400 ºC: Pd4Se, Pd7Se2, Pd34Se11 (stable up to 430 ºC), Pd5Se4 (stable up to 415 ºC), Pd7Se6, Pd17Se15, PdSe, and PdSe2. The phase diagram of the Pd-Se-Te system at 400 ºC is shown in Fig. 3. Palladseite (Pd17Se15) dissolves up to 3 at. % Te. Among binary Pd-tellurides, the following phases are stable at 400 ºC: Pd13Te3, Pd20Te7, Pd7Te3, Pd5Te4, Pd3Te2, PdTe, and PdTe2. Keithconnite (Pd20Te7) dissolves up to 6 at.% Se, telluropalladinite (Pd33Te4) dissolves up to 5 at.% Se, kotulskite (Pd7Te7) dissolves up to 10 at. % Se. The part Se-PdSe2-PdTe2-Te of the ternary diagram has been studied preliminarily so far therefore the tie-lines are depicted tentatively as dash-lines in Fig.1.

![Figure 3](image3.png)

**Figure 3.** Isothermal section of the phase diagram of the ternary Pd-Se-Te system at 400 ºC.

In the system, there is only one ternary phase, an analogue of mineral miessite (Pd11Te2Se2). Miessite forms stable associations with Pd13Te3 and keithconnite (Pd20Te7), keithconnite and palladseite (Fig. 4). Also, it coexists with PdSe, Pd5Se4, Pd4Se11 and Pd-Se4. Telluropalladinite coexists with Pd7Te2 and palladseite. Palladseite coexists with Pd3Te2 and kotulskite ss. Assessed stable phase associations are depicted in Fig. 3. Such associations are expected to be observed under natural conditions.
4 Conclusions

The phase relations in the systems Pd/Pt-Se-Te have been studied at 400 °C. The synthetic analogue of mineral miessite was synthetized and stable association were assessed. Phase relations determined the mineral assemblages that can be expected to occur in nature. Such assemblages should be sought in association with other PGM and known palladium/platinum selenides and tellurides, likely in magmatic Cu-Ni-PGE mineral deposits, associated with mafic and ultramafic igneous rocks, involving Se-rich fluids, but also at low temperatures formations like selenide vein-type mineralization.

Acknowledgements

Financial support through the Project No 18-15390S from the Grant Agency of the Czech Republic (GACR) is gratefully acknowledged.

References

The state of platinum in pyrrhotite studied by X-ray absorption spectroscopy of synthetic crystals

Olga N. Filimonova, Maximilian S. Nickolsky, Elena V. Kovalchuk, Vera D. Abramova, Boris R. Tagirov
Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry Russian Academy of Sciences

Dmitry A. Chareev
Institute of Experimental Mineralogy

Alexander L. Trigub
NRC “Kurchatov Institute”

Kristina O. Kvashnina
European Synchrotron Radiation Facility

Abstract. Pyrrhotite (Fe\textsubscript{1-x}S) is a typical mineral carrier of Pt in many types of deposits, including ores of magmatic, metamorphic, hydrothermal, and supergene origin. In order to reveal the likely state of Pt disseminated in natural minerals we synthesized Pt-bearing pyrrhotite via salt flux technique at 650°C and 720°C (temperature of crystals growth). EPMA and LA-ICP-MS examination of the crystals showed that pyrrhotite can contain up to 0.5 wt% of homogeneously distributed Pt. The state of Pt was determined using X-ray absorption spectroscopy (XAS). In all samples the “formal” oxidation state of Pt is close to +4. Pt is coordinated by ~6 S atoms at 2.36-2.39Å.

1 Introduction

In ore deposits of magmatic origin Pt occurs commonly as a discrete Pt accessory minerals (e.g., compounds with other PGE, base metals, or metalloids collectively known as platinum-group minerals (PGM)), micro/nanoscale inclusions or isomorphous solid solution in sulfide mineral associations, which almost ubiquitously consist of chalcopyrite CuFeS\textsubscript{2}, pentlandite (Fe,Ni)\textsubscript{9}S\textsubscript{8}, pyrite FeS\textsubscript{2}, and pyrrhotite Fe\textsubscript{1-x}S. LA-ICP-MS studies report the relatively high concentrations of PGE in pyrrhotite (e.g., Barnes et al. 2006). In order to reveal the state of Pt (the oxidation state and parameters of the local atomic environment) in pyrrhotite, we studied synthesized Pt-bearing pyrrhotite crystals by means of X-ray absorption spectroscopy.

2 Synthesis of pyrrhotite in Fe-Pt-S system

A salt flux technique was employed to synthesize pyrrhotite in Pt-saturated system. Starting chemicals were: ~0.5 g of FeS\textsubscript{2}+S, or Fe\textsubscript{0.9}S+S, or Fe\textsubscript{0.8}S+FeS\textsubscript{2}. These reagents were loaded into silica glass ampoules together with a Pt wire, which controlled the activity of Pt in the experimental system, and CsCl/NaCl/KCl, or NaCl/KCl, or RbCl/NaBr/KI eutectic salt mixtures. The composition of every mixture was chosen in accordance with Chareev (2016). The ampoules were evacuated, sealed with an oxygen gas torch and placed into horizontal tube furnaces. The temperatures were 710°C hot end/ 650°C cold end (samples Nos. 5590, 5592, 5601), and 795°C hot end/ 720°C cold end (sample No. 5602), the duration of the experiment was about 2 weeks. At the end of the experiment the ampoules were extracted from the furnaces and quenched in cold water.

3 Analytical methods

The morphology of the obtained synthetic phases was checked by means of scanning electron microscopy (SEM/ EDS) using the JSM-5610LV microscope equipped with INCA-450 energy dispersive spectrometer. Chemical composition was determined via electron probe microanalysis (EPMA), and laser ablation inductively coupled mass spectrometry (LA-ICP-MS). EPMA analyses were performed using JEOL JXA-8200 WD/ED combined electron probe microanalyzer equipped with 5 wavelength dispersive X-ray spectrometers. LA-ICP-MS analysis was performed using the New Wave 213 laser coupled with the Thermo X Series2 quadrupole ICP-MS to determine the concentration of \textsuperscript{195}Pt. MASS-1 and UQAC-FeS-1 sulfide reference materials were employed as the external standards, the \textsuperscript{57}Fe isotope was used as internal standard.

X-ray absorption experiment was performed at the Rossendorf Beamline BM20 of the ESRF (Grenoble, France). The Pt \textsubscript{L\textsubscript{3}-edge X-ray absorption spectra were recorded in total fluorescence yield (TFY) mode using 13-element high-throughput Ge-detector. The fits were performed using IFEFFIT software package (Ravel and Newville 2005).

4 Results

According to EPMA and LA-ICP-MS analyses the pyrrhotite samples contained up to 0.5 wt% of Pt. The observed absence of zoning within pyrrhotite grains on the SEM images, combined with the smooth character of LA-ICP-MS time-resolved spectra, proved the homogenous distribution of Pt within the pyrrhotite crystals (Fig. 1).

Fe\textsubscript{1-x}S (0.11<x<0.13) was found to be in equilibrium with other Pt-bearing phases: FeS\textsubscript{2}+Fe\textsubscript{1-x}S (Nos. 5590, 5592, 5601). The state of Pt was determined using X-ray absorption spectroscopy (XAS). In all samples the “formal” oxidation state of Pt is close to +4. Pt is coordinated by ~6 S atoms at 2.36-2.39Å.

1 Introduction

In ore deposits of magmatic origin Pt occurs commonly as a discrete Pt accessory minerals (e.g., compounds with other PGE, base metals, or metalloids collectively known as platinum-group minerals (PGM)), micro/nanoscale inclusions or isomorphous solid solution in sulfide mineral associations, which almost ubiquitously consist of chalcopyrite CuFeS\textsubscript{2}, pentlandite (Fe,Ni)\textsubscript{9}S\textsubscript{8}, pyrite FeS\textsubscript{2}, and pyrrhotite Fe\textsubscript{1-x}S. LA-ICP-MS studies report the relatively high concentrations of PGE in pyrrhotite (e.g., Barnes et al. 2006). In order to reveal the state of Pt (the oxidation state and parameters of the local atomic environment) in pyrrhotite, we studied synthesized Pt-bearing pyrrhotite crystals by means of X-ray absorption spectroscopy.

2 Synthesis of pyrrhotite in Fe-Pt-S system

A salt flux technique was employed to synthesize pyrrhotite in Pt-saturated system. Starting chemicals were: ~0.5 g of FeS\textsubscript{2}+S, or Fe\textsubscript{0.9}S+S, or Fe\textsubscript{0.8}S+FeS\textsubscript{2}. These reagents were loaded into silica glass ampoules together with a Pt wire, which controlled the activity of Pt in the experimental system, and CsCl/NaCl/KCl, or NaCl/KCl, or RbCl/NaBr/KI eutectic salt mixtures. The composition of every mixture was chosen in accordance with Chareev (2016). The ampoules were evacuated, sealed with an oxygen gas torch and placed into horizontal tube furnaces. The temperatures were 710°C hot end/ 650°C cold end (samples Nos. 5590, 5592, 5601), and 795°C hot end/ 720°C cold end (sample No. 5602), the duration of the experiment was about 2 weeks. At the end of the experiment the ampoules were extracted from the furnaces and quenched in cold water.

3 Analytical methods

The morphology of the obtained synthetic phases was checked by means of scanning electron microscopy (SEM/ EDS) using the JSM-5610LV microscope equipped with INCA-450 energy dispersive spectrometer. Chemical composition was determined via electron probe microanalysis (EPMA), and laser ablation inductively coupled mass spectrometry (LA-ICP-MS). EPMA analyses were performed using JEOL JXA-8200 WD/ED combined electron probe microanalyzer equipped with 5 wavelength dispersive X-ray spectrometers. LA-ICP-MS analysis was performed using the New Wave 213 laser coupled with the Thermo X Series2 quadrupole ICP-MS to determine the concentration of \textsuperscript{195}Pt. MASS-1 and UQAC-FeS-1 sulfide reference materials were employed as the external standards, the \textsuperscript{57}Fe isotope was used as internal standard.

X-ray absorption experiment was performed at the Rossendorf Beamline BM20 of the ESRF (Grenoble, France). The Pt \textsubscript{L\textsubscript{3}-edge X-ray absorption spectra were recorded in total fluorescence yield (TFY) mode using 13-element high-throughput Ge-detector. The fits were performed using IFEFFIT software package (Ravel and Newville 2005).

4 Results

According to EPMA and LA-ICP-MS analyses the pyrrhotite samples contained up to 0.5 wt% of Pt. The observed absence of zoning within pyrrhotite grains on the SEM images, combined with the smooth character of LA-ICP-MS time-resolved spectra, proved the homogenous distribution of Pt within the pyrrhotite crystals (Fig. 1).

Fe\textsubscript{1-x}S (0.11<x<0.13) was found to be in equilibrium with other Pt-bearing phases: FeS\textsubscript{2}+Fe\textsubscript{1-x}S (Nos. 5590, 5592, 5601). The state of Pt was determined using X-ray absorption spectroscopy (XAS). In all samples the “formal” oxidation state of Pt is close to +4. Pt is coordinated by ~6 S atoms at 2.36-2.39Å.
5592, 5601) or Fe_{1-x}S+PtS_{2} (No. 5602). Despite the absence of PtS(cr) in equilibrium with Fe_{1-x}S, the calculated values of sulfur fugacity fell within the PtS stability field.

Figure 1. a. Backscattered electron image of grain of synthetic Pt-bearing pyrrhotite sample No. 5592. b. LA-ICP-MS spectra of ^{57}Fe and ^{195}Pt. Note the similarity in the shape of the spectra of the signal of Fe (major element) and Pt (dopant element).

X-ray absorption spectroscopy (XAS) was applied in order to determine the local atomic environment and oxidation state of Pt in the synthesized samples.

According to Pt L-edge XANES spectra treatment the "formal" oxidation state of Pt is close to +4 (Fig. 2). The edge jump (e.j.) and the most intense feature (white line (WL)) positions, and intensities of the spectral features of Pt in pyrrhotite are significantly different from those of Pt(cr) and PtS(cr), indicating the increase in number of unoccupied 5d states on the Pt atoms in pyrrhotite structure. At the same time the position of the e.j. and the WL of Pt-bearing pyrrhotites and PtS_{2}(cr) are similar within the measurement error of ±0.5 eV.

Figure 2. Normalised Pt L-edge XANES spectra of model substances (Pt, PtS, PtS_{2}) and Pt-bearing pyrrhotites. Vertical solid lines indicate position of white lines (WLS).

Preliminary fits of the EXAFS spectra were performed with calculation of the coordination numbers of atoms and interatomic distances only for the 1st coordination shell, which consists of ~4.7-6.2 S atoms. Considering the large ionic radius of Pt in comparison with Fe (0.625 Å of Pt^{4+} vs. 0.61 Å of Fe^{2+}, Shannon 1976), we could expect the increase of Me-S distance when Pt substitutes for Fe in pyrrhotite lattice. However, the distance R_{Pt-S} ~ 2.36-2.39 Å (Fig. 3) in the first coordination shell decreased by ~0.07 Å relative to the Fe-S distance in pyrrhotite (pure Fe_{1-x}S: R_{Fe-S} ~ 2.43 Å, N_{S} ~ 6). This fact can take place due to the presence of nano/microinclusions of PtS or PtS_{2} (PtS: R_{Pt-S} ~ 2.31 Å, N_{S} = 4; PtS_{2}: R_{Pt-S} ~ 2.39 Å, N_{S} = 6). Besides, the nonstoichiometry of pyrrhotite composition could result in the reduction of number of S atoms in the 1st coordination shell of Pt.

We did not observe any contribution from the heavy Pt atom at the distance of 2.77 Å, which corresponds to Pt-Pt interatomic distance in pure Pt(cr). The Fourier transforms of EXAFS spectra in the region of distant coordination shells (R>3 Å) are different from those of pure PtS and PtS_{2}. We suppose that the distant coordination shells of Pt are of disordered character due to the nonstoichiometry of pyrrhotite structure, or due to the mix of the signals from more than one forms of Pt in Fe_{1-x}S (e.g., Pt-bearing nanoincclusions and Pt incorporated in the pyrrhotite lattice).

Results of our study provide an insight into the important role of pyrrhotite as a potential carrier of Pt. Further EXAFS spectra fitting will provide the information about the 2nd coordination shell and help to explain whether Pt substitutes for Fe and/ or disseminated in pyrrhotite lattice in form of micro/nanoincclusions.
Figure 3. Results of Pt $L_3$-edge EXAFS spectra fitting performed by means of ARTEMIS program. Fourier transforms (FT) of the $k^2$-weighted background-subtracted EXAFS spectra (not corrected for phase shift). Dotted black lines – model substances, thin black lines – experiment, dotted red lines – fit results. Vertical lines indicate individual contributions of the 1st coordination shells to FTs of model substances.

Acknowledgements

This study was supported by the Russian Science Foundation grant No. 17-17-01220. The authors thank the ESRF for the beamtime allocation under the proposal No. 20-01-782 (ROBL).

References


Morphological and compositional features of native platinum from the Yaman-Sandra river placer deposit (Altai, Russia)

Mikhail Brysin, Irina Tretiakova, Natalia Pozdnyakova
Central Research Institute of Geological Prospecting for Base and Precious Metals, Moscow, Russia

Sergei Shabalin
Sobolev Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia

Abstract. The Yaman-Sadra gold placer also contains native platinum with grains size of up to few millimeters. The Malyi Atalyk mafic-ultramafic layered intrusion is considered as the only possible source of the platinum due to its proximity to the placer and absence of other mafic-ultramafic rocks within the region. However, morphology and composition of the platinum grains suggest a complex history of their formation, evolution and relocation from the source to the placer. The present study provides results of a first investigation of the typomorphic features of native platinum from the Yaman-Sandra river alluvial placer.

1 Introduction

The study focuses on the platinum mineralization found in the gold-placer deposit of the Yaman-Sandra river. The Yaman-Sandra river headwaters are in the northern slope of the Malyi Atalyk mafic-ultramafic intrusion and flowing into the Sadra river in the Lebed basin in the northern part of the Altai Republic (Fig. 1).

Fig. 1 Geological scheme of the Yaman-Sadra river area (modified from the map of gold mineralization of the Altai Republic, Bedarev et al. 2005)
The Malyi Atalyk mafic-ultramafic intrusion is a slightly elongated (5.5 x 2 km) body striking towards northeast. This is a steeply dipping plate-like intrusive, with its base composed of dunite and similar rocks mostly altered to serpentine. Dunite is overlain by wehlrite and olivine-pyroxenite, and locally by magnetite-bearing dunite and olivine-gabbro. These rocks form a rhythmically layered series with gradual transitions. The Malyi Atalyk intrusion is hosted by Early-Cambrian volcanic-sedimentary mafic rocks (basaltic lavas and associated tuffs) bordering the Sadrynsky granite intrusion (Bognibov and Polyakov, 1995). Variously altered and mineralized gabbro, as well as felsic and serpentinized ultramafic rocks are exposed in the Yaman-Sadra river valley. The only known outcrop with anomalous platinum content (0.02-0.7 ppm) is located within clinopyroxenite, gabbro and microgabbro at the Maliy Atalyk mafic-ultramafic intrusion.

The studied samples were collected from heavy mineral concentrate obtained by LTE "Altaigeoresourse" from the gold placer in the upper stream of the Yaman-Sadra river.

2 Study methods

Platinum-group minerals were studied by various techniques. Optical research of PGM grains and polished sections and IR spectroscopy (Nicolet 380 IR spectrometer with Centaurus microscope from THERMO Scientific) were carried out at TsNIGRI (Moscow). The composition of grains was investigated by electron probe microanalysis using JEOL JXA-8100 with energy-dispersive spectrometer Link Pentafet at FSBI "VIMS" (Moscow). In addition, scanning electron microscopy (JSM-6510LV (Jeol Ltd) with AZTEC Energy XMax-80 microanalysis system) was carried out at IGM SB RAS (Novosibirsk).

3 Main results

Grains of platinum are characterized by dull light-grey color, small size from 0.25 to 0.5 mm (53%), occasionally up to 1 mm (31%). The majority of these grains occurs in the electromagnetic fraction, whereas insignificant amounts are found in the magnetic fraction. The shape of the platinum grains is mostly isometric or plate-like crystals and their aggregates are of irregular, elongated or rounded shape. Crystal faces are often clearly visible on grains (Fig. 2a, 2c).

There are two different types of aggregates. The first type consists of massive aggregates of isometric particles, occasionally showing traces of growth textures (striae, rungs). Their surface is smooth, sporadically lumpy, with rare imprints of other minerals (Fig. 2d). The second type of aggregates is found only in the electromagnetic fraction. These are complex aggregates of crystals of various sizes, often with rounded crystal heads (Fig. 2a). Surface of these aggregates is pitted, rarely porous, sometimes smooth.

![Morphology of platinum grains. Rounded crystals and their aggregates with smooth surface (a, c, d); irregular platinum aggregates(b).](image-url)
Platinum grains of irregular shape with single clear ledges (Fig. 2 d) are present in small amounts. Also, there are single grains of rounded plate-like morphology.

The composition of analyzed platinum grains is represented by isoferroplatinum-tetraferroplatinum series. Within a single grain the composition is not homogeneous: tetraferroplatinum and tulaminite form rims around isoferroplatinum (Fig. 3f, 3g, 3h) and native osmium (Fig. 3g). Isoferroplatinum contains inclusions of ferroarsenite (Fig. 3a) and native gold (Fig. 3c). A few grains host multiple inclusions, the composition of which was determined by EMPA (Table 3) as (Pd,Rh)(Sb,As) (Fig. 3i).

Table 1. Calculated composition of PGE minerals (based on SEM quantitate data)

<table>
<thead>
<tr>
<th>№</th>
<th>Point</th>
<th>Total</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Pt</th>
<th>Pd</th>
<th>Os</th>
<th>Ru</th>
<th>Ir</th>
<th>Rh</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>98,44</td>
<td>13,5</td>
<td>1,2</td>
<td>7,98</td>
<td>75,77</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>101,17</td>
<td>0,62</td>
<td>-</td>
<td>10,31</td>
<td>31,34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29,1</td>
<td>4,21</td>
<td>25,58</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>97,75</td>
<td>12,81</td>
<td>0,79</td>
<td>8,12</td>
<td>76,03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>96,3</td>
<td>8,77</td>
<td>-</td>
<td>-</td>
<td>86,01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1,52</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>96,19</td>
<td>13,77</td>
<td>1,29</td>
<td>6,08</td>
<td>75,05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>95,59</td>
<td>8,85</td>
<td>-</td>
<td>-</td>
<td>86,74</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Table 1. continuation

<table>
<thead>
<tr>
<th>№</th>
<th>Point</th>
<th>Total</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Pt</th>
<th>Pd</th>
<th>Os</th>
<th>Ru</th>
<th>Ir</th>
<th>Rh</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>1</td>
<td>96,07</td>
<td>11,83</td>
<td>-</td>
<td>9,7</td>
<td>73,85</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0,68</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>95,69</td>
<td>8,85</td>
<td>-</td>
<td>-</td>
<td>86,39</td>
<td>0,44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>97,04</td>
<td>13,19</td>
<td>0,89</td>
<td>7,43</td>
<td>74,94</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0,59</td>
</tr>
<tr>
<td>c</td>
<td>1</td>
<td>96,49</td>
<td>8,34</td>
<td>-</td>
<td>-</td>
<td>88,15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>95,22</td>
<td>12,32</td>
<td>-</td>
<td>9,54</td>
<td>73,36</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>e</td>
<td>1</td>
<td>94,2</td>
<td>8,14</td>
<td>-</td>
<td>0,44</td>
<td>85,11</td>
<td>0,51</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>f</td>
<td>1</td>
<td>98,48</td>
<td>8,87</td>
<td>0,28</td>
<td>-</td>
<td>87,33</td>
<td>1,34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0,66</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>100,49</td>
<td>15,25</td>
<td>5</td>
<td>1,4</td>
<td>78,2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0,63</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>95,57</td>
<td>14,7</td>
<td>4,88</td>
<td>0,87</td>
<td>73,82</td>
<td>0,45</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0,86</td>
</tr>
<tr>
<td>g</td>
<td>1</td>
<td>102,15</td>
<td>8,88</td>
<td>-</td>
<td>0,63</td>
<td>89,44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1,78</td>
<td>1,42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>100,52</td>
<td>13,53</td>
<td>2,34</td>
<td>6,47</td>
<td>75,35</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1,63</td>
<td>1,2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>100,8</td>
<td>-</td>
<td>-</td>
<td>2,16</td>
<td>-</td>
<td>82,11</td>
<td>14,2</td>
<td>2,38</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>h</td>
<td>1</td>
<td>99,11</td>
<td>8,9</td>
<td>-</td>
<td>-</td>
<td>89,32</td>
<td>0,88</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>100,62</td>
<td>15,91</td>
<td>0,54</td>
<td>5,69</td>
<td>76,96</td>
<td>0,52</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1,01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>99,22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45,97</td>
<td>20,1</td>
<td>3,01</td>
<td>30,14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>i</td>
<td>1</td>
<td>100,00</td>
<td>9,53</td>
<td>0,20</td>
<td>0,34</td>
<td>87,99</td>
<td>0,77</td>
<td>0,10</td>
<td>-</td>
<td>-</td>
<td>0,54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>100,00</td>
<td>9,58</td>
<td>0,11</td>
<td>0,60</td>
<td>87,58</td>
<td>0,07</td>
<td>0,82</td>
<td>-</td>
<td>-</td>
<td>0,73</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

4 Discussion

The complex structure and composition of platinum grains may imply that the primary set of PGMs and Pt-bearing sulfides have been destroyed and/or dissolved with the extraction of PGE and their redistribution during later metasomatic-hydrothermal processes (Bowles et al., 2018, Mochalov 2013). Moreover, the known state of metasomatic alteration of the Malyi Ataluk mafic-ultramafic layered intrusion is in agreement with a proposed model of hydrothermal overprinting of the primary PGM mineralization. The presence of rims on platinum grains and their state of development, clearly indicates not only the role of hydrothermal overprinting in their formation but also the proximity of the placer to its source (Zhmodik et al., 2016). In addition, crystal faces clearly visible on many nuggets imply that the grains were not transported far from their parental rocks.

5 Conclusions

Thus, the data herein presented suggest a multistage history of formation, evolution and relocation of PGMs in the Yaman-Sadra placer. The rocks of Malyi Atalik intrusion are prospective for PGE mineralization, which may be the source of the placer deposit. However, these complex platinum grains should be studied in more detail in order to obtain information about their origin and ore-bearing potential of the Malyi Atalik intrusion.

References


LA-ICP-MS study of sulfide blebs from a gabbroid intrusion in North-Western Mongolia

Maria Cherdantseva
Novosibirsk State University, Ltd “Norilskgeologia”, Russia
Andrey Vishnevskiy
Novosibirsk State University, Sobolev’s Institute of Geology and Mineralogy, Russia
Pedro Jugo
Laurentian University, Canada

Abstract. The Devonian Rudniy intrusion located on the Tsagaan-Shuvuut ridge (NW Mongolia) is the only one of the numerous small gabbroid intrusions surrounding the Tuva depression known to contain magmatic sulfide Ni-Cu-PGE mineralization. The sulfide mineralization is confined to a prolonged narrow ultramafic horizon as disseminated blebs, which are zoned and composed of pyrrhotite, pentlandite, chalcopyrite and cubanite. The intrusion is of interest because it is a small body that solidified quickly and therefore the sulfide blebs are interpreted to keep a record of the geochemical behaviour of chalcophile elements from the crystallization of a sulfide melt in a closed system. Using LA-ICP-MS and ICP-MS analyses the concentrations of chalcophile and platinum group elements in the base metal sulfides (BMS) were measured. This allowed us to calculate partition coefficients and mass balances of PGEs in base metal sulfides.

1 Introduction

The Devonian Rudniy ultramafic-mafic intrusion is located in the Tsagaan-Shuvuut Range, NW Mongolia. Ni-Cu-PGE mineralization is represented by disseminated sulfide blebs, ranging from 3 mm to 30 mm in size. Sulfide blebs are settled in a narrow horizon at the base of a melanogabbro unit in the Rudniy ultramafic-mafic intrusion. These blebs are suitable to investigate the behaviour of PGE during the crystallization of a sulfide melt because the system can be considered as relatively closed. Firstly, the presence of rounded or ellipsoid sulfide droplets can be considered as an evidence of quick crystallization because otherwise disseminated interstitial or massive sulfides would have formed. In addition, there are several petrographic evidences of rapid crystallization of the silicate matrix: a) dendritic crystals of olivine, Cr-spinel, and plagioclase, b) metasomatic rims (1-2 mm thick) around sulfide blebs characterized by absence of olivine, decrease in the An-content of plagioclase, and the presence of volatile-rich minerals (biotite, chlorite, apatite, magnesian hornblende, potassic chlorohastingsite). These rims are also interpreted as segregation vesicles (Barnes et al. 2019). There are no changes in the paragenesis of the melanocratic olivine gabbro outside of these silicate caps. All these features indicate that the crystallization of the sulfide melt occurred in an almost closed system and that hydrous fluids associated with the sulfide melt affected only the silicates immediately surrounding the blebs. We aimed to reveal how platinum group elements behave during the crystallization of natural sulfide melts (i.e. which sulfide phase is preferred for each particular element) and through the comparison of obtained data with data from giant intrusions and experimental data, construct a distribution model, which can be applied for every deposit of the same type.

2 Materials and Method

In total 17 polished epoxy pucks containing 80 sulfide blebs were prepared. Firstly, all polished sections were studied using reflected-light microscopy, PGM and silicate mineral compositions were examined by Tescan Mira 3 scanning electron microscope with an Oxford X-Max 80 high-resolution energy-dispersive X-Ray spectrometer (EDS) at the Sobolev’s Institute of Geology and Mineralogy, Russian Academy of Sciences. The analyses were carried out with an accelerating voltage of 20 kV, beam current of 1 nA, counting time of 25 sec. The EDS spectra were optimized for quantification using INCA Energy software.

Three samples with different types of blebs were crushed and pulverized in a mill in order to examine whole rock compositions. Analyses were carried out in the Intertek Genalysis Lab (Australia). PGE contents were analyzed using Ni fire assay with ICP-MS, other elements were analyzed by XRF except sulfur, which was analyzed by IR spectroscopy.

Polished sections of three relatively large blebs were chosen to examine the distribution of PGE and other chalcophile elements in detail. The concentrations of 25Mg, 33S, 47Ti, 55Mn, 57Fe (used as internal standard), 58Co, 60Ni, 61Ni, 63Cu, 65Cu, 66Zn, 75As, 77Se, 99Ru, 103Rh, 105Pd, 106Pd, 107Ag, 111Cd, 118Sn, 121Sb, 130Te, 185Re, 189Os, 193Ir, 195Pt, 197Au, 208Pb and 209Bi were determined by laser ablation inductively coupled plasma mass spectrometry at Laurentian University (Sudbury, Canada). The analyses were carried out using Resonetics, RESOlution M50 ArF excimer 193 nm laser coupled to a Thermo-Fisher XSeriesII ICP-MS with beam diameter set at 66 µm, ablation time of 40 s, and blank time of 30 s, laser frequency of 8 Hz. Dwell time was 15 ms on Fe, PGE and metalloid, 5ms on other elements.
The carrier gas consists of mixture of 0.65 l/min helium and 1.06 l/min argon. Po725 sulfide (from Memorial University) was the standard reference material used for 99Ru, 101Ru, 103Rh, 189Os, 193Ir, 195Pt, whereas NIST610 glass was used for all other elements. Iolite software was used for signal quantification using 57Fe as internal standard with Fe content determined by probe microanalysis. Element concentration in sulfides, metalloid-rich parts of the spectra were integrated, as described in Cafagna and Jugo (2016). Moreover, three distribution maps were conducted using the method described in Ulrich et al. (2009). The dimension of the mapped area is ca. 2 mm × 1.2 mm.

3 Ore horizon

3.1 Sulfide blebs

The construction of ore horizon was described in Vishnevskiy and Cherdantseva (2016) and will be briefly summarized here. The abundance of sulfides is about 10 %-15 %. Three types of sulfide globules, which differ in size, shape, PGM mineralization and host rock, were distinguished. The first outcrop (‘1’ in Fig. 1) has two different layers: the Lower Layer (LL) is a melanocratic olivine gabbro with spherical and slightly vertically elongated blebs (MSB-medium size blebs: average 4-10 mm); and the Upper Layer (UL) is a melanocratic gabbro with large (7-30 mm) horizontally elongated sulfide globules (LB – large blebs). The Lower Layer is characterized by abundance of dendritic olivine crystals of different orientation, which sometimes are assembled in groups with parallel direction, as those described in O’Driscoll et al. (2006). Similar skeletal olivine crystals were described in the Kharaerlakh intrusion in the Norilsk region (Barnes et al. 2019). Down the slope there is a second outcrop (‘2’ in Fig. 1) with small (1-4 mm) spherical and ellipsoidal blebs (SSB – small size blebs) hosted by leucocratic gabbro with skeletal plagioclase (“chicken-feet” structure, Fig. 1). We suggest that the second outcrop is a continuation of the same ore horizon, and the difference with the first outcrop can be explained by lateral variability.

All types of sulfide blebs are clearly vertically differentiated and consist of chalcopyrite and cubanite in the top, coarse-grained pentlandite in the center and pyrrhotite in the bottom (the predominant phase). The structure of the droplets is complicated by second-order structures. Cubanite forms thin or wide lamellae that intersect at an angle of 120 degrees in chalcopyrite (but are almost absent in SSB-type blebs). Pentlandite is present as a coarse-grained, fine-grained veins and flame-like lamellae. Chalcopyrite forms similar exsolution lamellae as pentlandite. They are mostly confined to the cleavage, and surround inclusions of other minerals (e.g. apatite) as well as forming small rounded inclusions surrounded by pyrrhotite with flame exsolutions of pentlandite. In some cases, small individual grains of pyrrhotite are enclosed in chalcopyrite or around them. Moreover, relatively large areas of complex fine-grained sulfides occur in many sulfide blebs. Those zones are represented by small-size randomly mixed chalcopyrite, pyrrhotite, pentlandite and cubanite intergrowth. Oxide mineralization is represented by ilmenite and titanomagnetite. The ilmenite usually forms elongated dendritic crystals, up to 10 × 0.3 mm, piercing or partially surrounding blebs. Large titanomagnetite crystals located on the bleb margin have a reticulated texture formed by the preserved lamellae of ilmenite and partially replaced by pyrrhotite and chalcopyrite.

Figure 1. The outcrop of the Rudniy intrusion. The dotted line shows the position of the ore horizon with outcrops of the two segments with sulfide mineralization. Pictures of three polished sections represents the three types of sulfide blebs: LB – large blebs, MSB – medium size blebs, SSB – small size blebs.

3.2 PGE Mineralization

Platinum-group minerals (PGM) occur in all BMS but are only rarely found outside the sulfide blebs (only close to the sulfide bleb margin). A total of 240 grains of PGMs in three types of blebs were investigated. Among them 190 representative analyses were selected. The size of each PGM grain was measured to evaluate which phases are predominant in each BMS and to estimate the allocation of PGM between different sulfide bleb types. The results of estimations are depicted on pie diagrams (Fig. 2). Summarizing all analyzed grains from the ore horizon in the Rudniy intrusion the main host minerals for PGM are pentlandite (51%) and chalcopyrite-cubanite intergrowth (37%); only 9% of PGM were found in pyrrhotite, 2% in complex fine-grained sulfide intergrowths and 1% in silicates on the border with sulfide blebs. It can be noticed that the similar tendency of PGM distribution persist in all types of blebs, with one small exception of horizon with small blebs, where chalcopyrite is the main host for PGMs.

Regarding the mineralogy of PGM, the dominant phases are Ni-Pt-Pd bismuthotellurides (moncheite PdTe2 - merenskyite PtTe2 - melonite NiTe2), which are characterized by wide variations in composition due to isomorphic substitution. Together, those three minerals compose 77 area percentage of the studied PGM grains. These phases are common in all three types of sulfide blebs, with the exception of melonite, which was not
found in the horizon with small sulfide blebs. Sperrylite (1.2%) was only identified in blebs from LL. Several Ag-bearing phases are present including hessite Ag₂Te (13.3%), sopcheite Ag₄Pd₃Te₉ (3.7%), electrum (Au,Ag) (3.4%), empressite AgTe (0.6%), telargpalite (Pd,Ag)₃(Fe,Bi) (0.03%), as well as Sn-bearing phases such as stannopalladinite (Pd, Cu)₃Sn₂ (0.09%), taimyrite (Pd,Cu,Pt)Sn (0.02%), paolovite Pd₂Sn (0.2%) and an unknown phase A, which formula was calculated as Pt₃SnTe₄ (0.6%) were found solely in the Upper Layer. The predominant host mineral for bismuthotellurides and arsenides of Pt, Pd or Ni is pentlandite, followed by chalcopyrite with only a small percentage in pyrrhotite, sulfide intergrowths and in silicates. The Ag-bearing phases are hosted in almost equivalent quantity in chalcopyrite and pentlandite, whereas Sn-bearing phases were found solely in chalcopyrite.

4 ICP-MS and LA-ICP-MS study

The combination of ICP-MS and LA-ICP-MS data allowed calculation of mass balance using the equations documented in Godel et al. (2007) and Chen et al. (2015) and recalculating the partition coefficients between the monosulfide solid solution (mss) and the residual liquid using the equation of Barnes et al. (2006). Mass balance recalculation data showed that only about 55% of all cobalt is concentrated in the base metal sulfides. Small blebs concentrate a much larger amount of Os, whereas in medium globules, about 40% of Os probably forms discrete PGE minerals. Also in medium size globules (LL), the percentage of Ir, Pt, Pd and Au is lower, most likely for the same reason. Conversely, the proportions of Ag, Ru, Sn and Zn are higher in medium-size sulfide globules than in small sulfide globules. This may be explained by different proportions of each sulfide type in different types of globules. Most likely, in the medium-size sulfide blebs, the volume of the residual sulfide liquid was larger. In addition, the lower concentrations of Ag in small sulfide globules may be explained by the lack of cubanite lamellae, which, in our observations, is the main silver host. In general, the recalculation of the mass balance also makes it possible to estimate the distribution of elements between BMS. For example, the difference in the distribution of Os between pyrrhotite and pentlandite in medium-size and small sulfide blebs is more noticeable. In medium sulfide globules, a greater percentage of Os is concentrated in pyrrhotite, which corresponds to normal understanding of the distribution of this element, and in small sulfide globules a larger percentage of Os concentrates in pentlandite (Fig. 3).

5 Conclusions

Based on the obtained data - distribution maps, concentration of PGE minerals, and concentrations of precious elements in BMS, mass-balance calculation and recalculated partition coefficients the distribution scheme for trace elements was refined (Fig. 4), using as a basis the scheme constructed by Holwell and McDonald (2010).

The results of the study show that Ni and Co, are compatible with the monosulfide solid solution and, as expected are concentrated in pyrrhotite and pentlandite. The opposite distribution is characteristic for Cu, Cd, Zn, and Sn, which are concentrated in intermediate solid.
solution (eventually in chalcopyrite and cubanite). The patterns of PGE distribution are more complicated. Pt, Ir and to a lesser extent Pd tend to form small individual grains in association with Bi and Te. These Pt-bearing nuggets are mostly concentrated in chalcopyrite. Chalcopyrite also contains small amounts of Os, Ir, Ru and Au. Concentrations of the platinum-group and chalcophile elements in the base metal sulfides (BMS) from the Rudniy intrusion and mass balance calculations reveal that pentlandite hosts a large proportion of Co, Ni, Pd, Os, Ir and Au. High concentrations of Pd in pentlandite confirm the idea that it was formed via peritectic reaction between MSS and the fractionated sulfide liquid (Mansur et al. 2019). Pyrrhotite accommodates significant proportions of Os, Ru and Rh. At relatively high temperatures, silver accumulates in pentlandite, and when the temperature decreases it concentrates in residual sulfide liquid. When the intermediate solid solution exsolves, Ag has low solubility in chalcopyrite and concentrates in cubanite. Gold at low initial concentrations is redistributed to pentlandite.

Figure 4. Distribution scheme for trace elements during cooling of a sulfide melt, refined from the scheme constructed by Holwell and McDonald (2010).

It also can be concluded that the rate of crystallization of small sulfide globules was higher than the rate of crystallization of medium sulfide globules, since the dissolved form of their sulfides contained higher concentrations of Os, Ir, Pt and Au, which did not manage to form their own PGE phases due to the high crystallization rate. As a confirmation, only 5% of all PGMs were found in small sulfide globules. In addition, lower concentrations of Ag and Pd in chalcopyrite indicate that no prolonged accumulation of residual Ag and Pd occurred in the residual sulfide liquid.

Acknowledgements

The project was supported by the Ministry of Science and Higher Education of the Russian Federation (Projects no. 5.1688.2017.4.6 and 14.Y26.31.0018) and the Russian Foundation for Basic Research (Project 17-05-00825).

References


Rathbun Lake revisited: a magmatic-hydrothermal Pd-Pt-Cu occurrence possibly related to the Sudbury impact

Alexander Kawohl and Hartwig E. Frimmel
University of Würzburg, Germany

Wesley Whymark
Inventus Mining Corp., Toronto

Andrejs Bite
Bite Geological Ltd., Sudbury

Abstract. Quartz diorite dykes resulting from impact melts, locally referred to as Offset Dykes, occur concentrically and radially around the 1.85 Ga Sudbury Igneous Complex (SIC), and are a principal host to world class Ni-Cu-PGE-sulfide deposits. Here we report on a new discovery of such an Offset Dyke at Rathbun Lake, 15 km east of the SIC, at a location known for its high grade Pd-Pt-Cu mineralization at the intrusive contact between gabbro of the 2.2 Ga Nipissing Suite and wacke. Amphibole-quartz diorite occurs in direct vicinity to the mineralization and contains abundant mafic inclusions of locally derived country rock, the latter being a diagnostic feature of mineralized Offset Dykes. Preliminary bulk geochemical analyses support its correlation to the SIC. PGM-, sulfide- and silicate assemblages, ore textures and Pd/Ir of >50,000 are consistent with a hydrothermal modification and re-mobilization of magmatic sulfate. This massive and high-grade (>30 ppm PGE) sulfate concentration is unique within the large area over which Nipissing Suite diabase is exposed and, therefore, genetically presumably not related to this suite. The local presence of inclusion-bearing quartz diorite rather points to an impact origin of the Rathbun Lake Pd-Pt-Cu occurrence, analogous to known Offset Dyke-hosted deposits in the SIC.

1 Introduction

The 1.85 Ga Sudbury Igneous Complex (SIC) around Greater Sudbury, Ontario (Fig. 1), the deformed and eroded core of the second largest preserved impact structure on Earth, is one of the richest known ore provinces as it hosts numerous world-class Ni-Cu-PGE-sulfide deposits. Consensus exists on a genetic link between mineralization and impact-induced crustal melts through separation of sulfidic melt droplets and gravitational accumulation thereof at the base of sloping sides of the impact crater (see review by Lightfoot 2016). As much as 50% of the total metal resources of the Sudbury mining district are, however, not hosted by the central igneous complex, but by surrounding impact-melt dykes. The so called “Offset Dykes”, 17 of which are known to date, are narrow (10s to 100s metres wide) igneous bodies of quartz (monzo-)dioritic composition that disect the footwall rocks either radially to, or concentrically around, the SIC and can be traced for several kilometers along strike (Grant and Bite 1984; Lightfoot 2016). Formed at an early stage of the impact cratering process (e.g. Ostermann et al. 1996), maybe during crater collapse, they are thought to preserve the undifferentiated composition of the impact melt, although their exact mode of emplacement is not yet fully understood.

Figure 1. Geological sketch map of the Sudbury Igneous Complex and surrounding dykes related to impact melts.

The recognition of similar, yet unmineralized, Offset Dykes as much as 50 km east of the SIC (Kawohl et al. 2019) has prompted exploration activities which also include re-mapping and re-visiting of known intrusive rocks and ore occurrences in the area. One such prospect is the frequently cited Rathbun Lake showing (Fig. 1), where anomalously high Pd (up to 53 ppm) and Pt concentrations (up to 33 ppm) have been reported for massive Cu-Fe-sulfide within a hydrothermally altered diabase of the regional 2.2 Ga Nipissing Suite (Rowell and Edgar 1986; Lightfoot et al. 1993). Here, we report on a hitherto unrecognized lithology in the direct vicinity of the mineralization and provide first evidence of this quartz diorite being related to the Sudbury impact event, likely another impact melt-related dyke, with some implications for future exploration regarding the Nipissing


Suite, distal Offset Dykes and the eastern periphery of the SIC.

2 Geological background

2.1 Nipissing Diabase

The 2.2 Ga Nipissing Diabase is a voluminous suite of mafic intrusive rocks in the Southern Province, Ontario, extending over an area of 250 km, covering ~25% of the Huronian Basin and having an estimated volume of 10⁵ km³ (Lightfoot et al. 1993). The gabbroic melts intruded the 2.45-2.31 Ga siliciclastic Huronian Supergroup as undulating sills with thicknesses ranging from a few hundred to >1000 m. Predominant rock type is a tholeiitic orthopyroxene gabbro, but calc-alkaline granophyric, granodioritic and aplite varieties are typically found in the upper parts of the intrusive bodies. All of the geochemical and lithological variations are explicable by in-situ differentiation and assimilation of Huronian country rock (Lightfoot and Naldrett 1996). Least differentiated rocks, i.e. the chilled margins, have a remarkably uniform composition. The parental magma had elevated SiO₂ contents (50-51.5 wt%) and was low in Ni (80-160 ppm) and MgO (8-9 wt%). All chills show geochemical features indicating an enriched, maybe subduction-modified or subcontinental lithospheric mantle source (Lightfoot et al. 1993; Lightfoot and Naldrett 1996). The Nipissing Diabase is considered as the root of an eroded flood-basalt province and might have been part of a larger radiating dyke swarm linked to an ancient mantle plume (Ernst 2014).

Using the Rathbun Lake showing as an argument, some workers have tried to emphasize the economic potential of the Nipissing Suite for Cu-Ni-PGE, but over the past decades only one deposit was discovered throughout the Nipissing magmatic province (Sproule et al. 2007; Lightfoot 2016). If at all, disseminated sulfide (<5 vol%) is typically found in the center of a Nipissing intrusive body, several hundred meters above the basal contact. Assimilation did not seem to have played an important role in the sulfide saturation of the magma, nor did the addition of external sulfur as the most intensely contaminated Nipissing bodies are generally unmineralized (Lightfoot and Naldrett 1996), and no S-rich evaporates or shales are known in the Huronian Supergroup. Only one case is documented where Nipissing magma might have assimilated uraninite-pyrite-bearing conglomerates (Sproule et al. 2007; Dasti 2014). Instead, Lightfoot and Naldrett (1996) proposed sulfide saturation was commonly achieved upon crystallization.

2.2 Rathbun Lake showing

The Rathbun Lake showing is located at the intrusive contact of an ordinary Nipissing Diabase body, referred to as the Wanapitei intrusion, and laminated wacke of the Gowganda Formation, both of which experienced greenschist-facies metamorphic overprint (see Dressler 1982). Except for a higher modal proportion of hypersthene, the Wanapitei intrusion does not differ significantly from other unmineralized Nipissing complexes in terms of size, shape, level of emplacement, footwall rocks, geochemistry, degree of assimilation and alteration, parental magma composition or PGE- and base metal enrichment/depletion (Lightfoot et al. 1993; Lightfoot and Naldrett 1996). It is, however, the only known example of massive sulfide at the base of a Nipissing intrusive body. Much of the original ore had been excavated during sinking of an exploration shaft in the 1920s, and previous studies indicate that the massive sulfide (55% chalcopyrite and 40% pyrite ± millerite, violarite, arsenopyrite, magnetite, pyrrhotite, covellite, molybdenite) was a vein-like body, 12 m long and up to 0.6 m wide, which did not follow the diabase-sediment contact but stroke perpendicular to it (Dressler 1982; Edgar 1986). The transition from massive to disseminated sulfide has been described as gradational over several meters, with all sulfide confined to the “diabase” (Dressler 1982). According to Dressler (1982) and Rowell and Edgar (1986) the mineralization is associated with footwall irregularities, shear zones and, most remarkably, an alteration zone, where the original mafic host was altered to biotite, chlorite, sericite, epidote and quartz. Several authors have reported anomalously high values of Pd (up to 53 ppm, on average 21 ppm) and Pt (up to 33 ppm, average 10 ppm) as well as ~3 ppm Au for the massive sulfide (up to 20 wt% Cu and 0.5 wt% Ni), whereas all other PGE concentrations are far below 20 ppb (Rowell and Edgar 1986; Lightfoot et al. 1993). PGM are sperrylite (PtAs₂), bismuthian merenskyite (PdTe₂), subordinate kotulskite (PdTe) and temagamite (Pd₃Hg₃Te₃), all of which are associated with hydrous silicates, chalcopyrite, or entirely enclosed in pyrite (Rowell and Edgar 1986). Most of the Wanapitei intrusion is unaltered and contains only disseminated (<1 vol%) magmatic sulfide.

3 A Sudbury Offset Dyke at Rathbun Lake?

Poor outcrop conditions and previous excavation limit in-situ investigations to the cliffs at the southern shoreline of Rathbun Lake. The Offset Dyke, obscured by a gossan, is exposed at the entrance of the old exploration shaft, located at the contact between wacke and diabase (46°45’51”E / 80°39’21”N) and it is easily overlooked in outcrop. Additional material was found on a nearby stockpile. Even on freshly broken and wet surfaces, the rock can be easily confused with diabase, but polished slabs (Fig. 2) reveal the presence of abundant dark-grey aphanitic inclusions embedded in a light-grey phaneritic matrix. The inclusions are spherical, between a few mm and 10 cm in diameter, and exhibit sharp but undulating contacts with the matrix. This groundmass consists of ~45 vol% altered plagioclase, ~35 vol% quartz, ~20 vol% amphibole. Plagioclase is up to 0.8 mm large, compositionally zoned, and arranged in an interlocking manner. Alteration to epidote/sericite is omnipresent, leaving only rims of albite behind. Quartz occurs as up to 3 mm-large, undeformed, anhedral poikilitic grains enclosing plagioclase. Amphibole, up to 1.5 mm in length, is green in thin section and has a needle-like habit.
Accessory minerals are ilmenite/magnetite, chlorite after biotite, and sericite maybe after K-feldspar. There are two types of inclusions, minor arkosic wacke and predominantly mafic inclusions. The latter have a spherulitic to doleritic texture of, in places radiating, plagioclase/epidote, clinopyroxene and minor (~10 vol%) tremolite replacing hypersthene, and contain less than 1 vol% quartz. One sample of the mafic inclusion-bearing quartz diorite contains disseminated chalcopyrite (5 vol%).

![Figure 2. Polished slab of the mafic inclusion-bearing quartz diorite at Rathbun Lake.](image)

The petrography of the quartz diorite at Rathbun Lake is different to the adjacent Nipissing Diabase, Gowganda wacke and to any other Proterozoic rock in the area, but remarkably similar to the 1.85 Ga quartz dioritic Offset Dykes. Its major element concentrations are with 55 wt% SiO$_2$, 3.5-4.5 wt% Na$_2$O+$K_2$O, 5 wt% MgO, 8-10 wt% Fe$_2$O$_3$, 0.1 wt% P$_2$O$_5$, and 0.6 wt% TiO$_2$, typical of a calc-alkaline diorite and similar to those in known Offset Dykes (e.g. Grant and Bite 1984; Lightfoot 2016). Minor discrepancies are likely due to incomplete separation of mafic inclusions or their assimilation. The mafic inclusions are classified as tholeiitic gabbro and have geochemical features (e.g. 51.5 wt% SiO$_2$, 8 wt% MgO) that match the chilled Nipissing Diabase nearby, in agreement with their quench textures. Their shape and dark reaction rims suggest they were incorporated into the diorite, and have likely undergone partial melting. Only a superheated melt, as it is discussed for the impact melt dykes (>1700°C, Ostermann et al. 1996), would be capable of this.

![Figure 3. Microphotographs of ore textures at Rathbun Lake. a) Chalcopyrite (ccp) replacing chlorite (chl) along cleavage planes; b) chalcopyrite and epidote (ep) replacing diabase; c) decimeter-long vein of pyrite (py; white) and interstitial chalcopyrite (yellow) cutting through altered wacke (reflected light).](image)

Although we are not aware of any other diorite of similar age, petrography and geochemistry around the SIC, unequivocal evidence for the diorite having formed during the 1.85 Ga Sudbury impact event would require radiometric age dating. However, this will be a challenge, partly because of regional metamorphism and hydrothermal alteration. Suitable mineral grains for U-Pb dating will be rare, small, and in the case of zircon, most of them are likely to be inherited grains older than 1.85 Ga (e.g. Ostermann et al. 1996). Alternatively, trace element patterns combined with whole-rock Nd-Sr-Pb isotopes proved to be a useful tool for discriminating SIC impact melt rocks from other “normal” magmatic rocks in the wider area (Kawohl et al. 2019), and this will be done in next step of the project. Field work will show whether the quartz diorite at Rathbun Lake is a single isolated occurrence or part of a larger dyke.

### 4 Metallogenetic considerations

PGE-, sulfide- and silicate mineralogy and textural relationships (Fig. 3) as well as extreme Pd/Ir ratios of >50,000 (Pd being the most fluid-mobile PGE, Ir the least mobile one) are consistent with a hydrothermal origin, modification or re-mobilization of magmatic sulfide (e.g. Wood 2002; Holwell et al. 2017). This could have taken place during Proterozoic orogenies and faulting, the 1850 Ma Sudbury impact itself, or the ~1700 Ma metasomatic event documented by Schandl et al. (1994), but as unclear as the timing of the sulfide formation remains the ultimate source of the metals.

Lightfoot and Naldrett (1996) found disseminated (<1 vol%) globules of sulfide within the Wanapitei and other intrusions, which show an internal segmentation into lower pyrrhotite+pentlandite and upper chalcopyrite (see Lightfoot 2016 p. 91), as it is expected for closed-system fractional crystallization of a sulfide liquid. Consequently they related the massive sulfide at Rathbun Lake to gravitational settling of dense sulfide melt droplets and their accumulation at the base of the intrusion. This hypothesis fails, however, to explain (i) why settling occurred only there and in no other Nipissing intrusion or...
at any other position of the Wanapitei intrusion; (ii) a lack of evidence of base metal depletion in the silicate rocks overlying the massive sulfide; (iii) a lack of enrichment of the parental magma in PGE (Edgar 1986; Lightfoot and Naldrett 1996); (iv) the close spatial relation between ore and hydrothermal alteration; and (v) – assuming that hydrothermal alteration/re-mobilization of proto-ores from the Nipissing Diabase did occur – the remaining of the Ni-rich counterparts of the original (magmatic) pyrrhotite-chalcopyrite-pentlandite assemblage.

We propose an alternative explanation for the Pd-Pt-Cu mineralization that does not invoke the Nipissing Diabase as the source of the metals. The mere presence of a Sudbury impact-related lithology right next to the mineralized zone already suggests a genetic relationship. The ores at Rathbun Lake could have formed by similar processes as the SIC footwall deposits, that is, either residual highly fractionated Cu-rich sulfide liquid percolated into the brecciated footwall rocks underlying the impact melt, and/or metal redistribution by high-T hypersaline fluids (exsolved from the crystallizing impact/sulfide melt, released by the partially molten footwall, or just heated groundwater) (see Pénět et al. 2008 for a discussion). Cu-PGE-Au vein-type deposits can occur as far as 1500 m away from the Ni-dominated PGE-poor “contact” ore, i.e. the former MSS (monosulfide solid solution) cumulates on the crater floor. Rathbun Lake, for which we notice striking similarities to the Broken Hammer deposit (cf. Pénět et al. 2008), could represent the distal part of such afootwall system, with the overlying Ni-rich contact ore having been eroded.

Besides, Rathbun Lake strongly resembles the Vermilion Deposit in terms of metal ratios, ore and gangue mineralogy and textures, and geological setting (Szentpéteri et al. 2003): There, located between amphibolite and Huronian sedimentary rocks, isolated pods of xenolith-rich quartz diorite of the Vermilion Offset Dyke (south of the SIC) host small veins and lenses of sulfide with average grades of 21 ppm Pt and 54 ppm Pd. Highest grades are associated with gabbroic inclusions in the diorite. Like at Rathbun Lake, PGM are bismuthotelluridurides and sparrylite, intergrown with hydrous silicates; sulfide assemblages are essentially the same, but with more Ni arsenides, and with a further advanced alteration stage (Holwell et al. 2017) marked by bornite replacing some chalcopyrite. Szentpéteri et al. (2003) referred to this as a hydrothermally modified Offset Dyke deposit and proposed a complex multistage magmatic-metamorphic-hydrothermal origin of the ores, with involvement of saline (NaCl-CaCl₂-H₂O±CO₂) fluids at temperatures between 480°C and 150°C. Previous descriptions together with our own new findings imply an analogous origin for the Rathbun Lake Pd-Pt-Cu occurrence.

Acknowledgements

We gratefully acknowledge the logistic and financial support by Inventus Mining Corp. and Stefan Spears, respectively. Uli Schüssler (Univ. Würzburg) is thanked for the assistance with the XRF analyses.

References

Dasti IR (2014) The geochemistry and petrogenesis of the Ni-Cu-PGE Shakespeare deposit, Ontario, Canada. Unpubl MSc thesis, Lakehead University, Thunder Bay Ontario, 121 pp
Ernst RE (2014) Large Igneous Provinces. Cambridge University Press
Szentpéteri K, Molnár F, Watkinson DH, Jones PC (2003) Geology and high grade hydrothermal PGE mineralization of the Vermilion quartz diorite offset dike, Sudbury, Canada. Proc 7th SGA Meeting, Athens, Greece
The nature and distribution of magmatic Ni-Cu-PGE sulfide occurrences in the Labrador Trough, Northern Québec

W.D. Smith, W.D. Maier
School of Earth & Ocean Science, Cardiff University, Cardiff, CF10 3AT

J.Ø. Anderson
Camborne School of Mines, University of Exeter, Penryn, TR10 9EZ

I. Bliss
Northern Shield Resources, Ottawa, Ontario, Canada, K1P 6L5

Abstract. Mafic-ultramafic rocks of the Montagnais Sill Complex (MSC) are actively being explored for magmatic Ni-Cu-PGE sulfide deposits. The MSC possesses several attributes that are key for the formation of orthomagmatic deposits, but exploration remains in its infancy due to a lack in understanding of the metallotects operating in this region. The Huckleberry Cu-Ni-PGE Prospect (157 samples average 1.0% Cu, 0.2% Ni and 0.74 g/t PGE+Au) hosts multiple sulfide-rich intrusives, making it an ideal location to study the prospectivity of sills that comprise the MSC. Using a series of numerical models contrasted against measured whole-rock and mineral compositions, we constrain the petrogenesis of the mafic-ultramafic rocks, highlighting its influence on the nature of sulfide ore.

1 Introduction

The MSC in the Labrador Trough (Northern Québec) is actively being explored as one potential host for the next world-class magmatic sulfide deposit. The Paleoproterozoic Labrador Trough represents an 800 km long fold-and-thrust belt that encompasses the eastern margin of the Archean Superior Craton (Fig. 1a; Skulski et al. 1993). The MSC is emplaced along the extent of the Labrador Trough, contemporaneously with those that host the Raglan and Thompson Ni-Cu-(PGE) deposits in the Circum-Superior Belt (Ciborowski et al. 2017). Occurrences of magmatic sulfide mineralization are observed in gabbroic and gabbronoritic sills of the MSC, most commonly when adjacent to sulfidic country rocks

The Huckleberry Cu-Ni-PGE Prospect hosts multiple episodes of sulfide-laden mafic-ultramafic magmas, that have been emplaced into sulfidic country rock (Fig. 1b). Recent exploration has yielded average grades of 1.0% Cu, 0.2% Ni, and 0.74 g/t PGE+Au (n = 157) across four host rock types. In addition, > 5,000 m of diamond drilling has delineated four horizons enriched in chalcophile metals. In this paper, we explore the petrogenesis of the composite MSC and provide new geological perspectives on its prospectivity regarding magmatic sulfide deposits.

2 The Huckleberry Cu-PGE Prospect

2.1 Regional geology

Many authors define the stratigraphy of the Labrador Trough through a cyclic division, where two cycles of passive margin sedimentation are topped by a third cycle of flysch deposits (Clark and Wares 2005, and references therein). The MSC intrudes cycles 1 and 2, manifesting as (i) porphyritic gabbro suite (PGS), (ii) ophitic gabbronoritic sills, locally with basal ultramafic cumulates, referred to as the Layered Norite Suite (LNS) at Huckleberry, and (iii) late-stage, thin mafic sills (Clark and Wares 2005). The former two are most prospective for magmatic sulfide ores. Atop cycle 2, the Hellancourt/Willbob basalts are considered to be co-magmatic with the MSC due to their compositional and isotopic similarities (Skulski et al. 1993). All mafic-ultramafic rocks of the MSC are proposed as originating from a transitional-MORB source, generated during extensional rifting at ~1.88 Ga (Skulski et al. 1993).

The mafic-ultramafic rocks at Huckleberry were emplaced northwards within the sulfidic Menihek Formation (cycle 2). Each sill strikes parallel with regional-scale faults (NNW-SSE) where a thick PGS sill is intruded, and assimilated by, a less evolved LNS sill that hosts a basal orthocumulate referred to as the basal peridotite. Within the PGS footwall are numerous discrete harzburgitic sills known as the lower peridotites.

2.2 Nature and distribution of sulfide

Four chalcophile-rich horizons have been delineated at Huckleberry, and are listed in order of economic importance (Fig. 2a):

Lower Peridotite: This unit can host up to 10 vol.% net-textured-disseminated sulfide, that occurs interstitially to cumulate olivine. Sulfide mineralogy is characteristic of those hosted in serpentinitized peridotites, with pyrrhotite (po), pentlandite (pn), and chalcopyrite (ccp), together with accessory marcasite, mackinawite, bornite (brn), chalcocite (cc) and Fe-Ti oxides.
Figure 1. **a.** Lithotectonic division of the Labrador Trough (Clark and Wares 2005), highlighting the occurrence of Huckleberry. **b.** The geology of Huckleberry together with borehole collars (referred to in the text with a prefix of ‘16HK-’, or ‘17HK-’) and attitudes.

(i) **Footwall PGS:** Porphyritic gabbros that directly underlie the peridotitic units can host up to 7 vol.% net-textured-disseminated sulfide. The assemblage is dominated by ccp, with lesser po, pn together with trace brn and pyrite. Sulfide is typically bound by an amphibolitized margin and often observed molded around plagioclase glomerocrysts.

(ii) **Basal Peridotite:** At the base of the aphyric sill is a coarsening-up cumulate assemblage of olivine and plagioclase, with interstitial net-textured-disseminated sulfide, that can comprise up to 1 vol.%. The sulfide mineralogy mimics that of the lower peridotite.

(iii) **Basal PGS:** The porphyritic chilled margin at the base of the PGS hosts sparsely-distributed compartmentalized sulfide globules up to 2 cm in diameter. They comprise a lower po-pn margin, an upper ccp margin, and an amphibolitized cap.

3 Results

3.1 Whole-rock and mineral compositions

Mafic-ultramafic rocks of the LNS form a geochemical continuum from high-MgO (< 28 wt.%) cumulate rocks, that are largely devoid of HFSEs (< 20 ppm Zr, < 5 ppm Hf) through to granophyric titanomagnetite gabbros at the top (Fig. 2b). This sequence is bound by the more evolved PGS (3-5 wt.% MgO), within which, Ni varies over an order of magnitude (400 to 4,000 ppm), peaking in the intervals directly underlying the LNS.

Within the LNS, inter-cumulus pyroxene and plagioclase become more evolved with stratigraphic height (decreasing Mg#, Cr#px, Cr#px-opx, and An#plg; Fig. 2b). Cumulus plagioclase in the lower half of the LNS, display normal zoning and a coarsening-up regime.

3.2 Distribution of chalcophile elements

Sulfur displays a positive correlation with chalcophile metals across all sulfide-bearing rocks. Primitive mantle-normalized PGE profiles display the same fractionated trend of low Ir, Os, and Ru (< 1x), high Rh and Pt (~10 x) and enriched Pd (~100x), indicative of a similar origin. The high Pd/Pt values (~ 3) and (Pd+Pt)/(IPGE) values of > 10 are characteristic of derivation from a basaltic magma. However, Cu/Pd values exceed that of mantle rock (>10,000), which suggests that pre-emplacement sulfide saturation may have detrimentally affected the subsequent ore tenors. Local hydrothermal remobilization is evident from Pd/Ir values exceeding 10,000 for Cu-rich ores.

In borehole 17HK-12, chalcophile metals peak in the basal and lower peridotitic units, underlain by downward-decreasing tails into the footwall PGS. These trends are concomitant with downward increasing S and Cu/Pd. It is therefore proposed that progressively fractionating sulfide liquid has percolated form the LNS into the PGS footwall.
3.3 Segregation and fractionation of sulfide liquid

To investigate the timing of sulfur saturation in the MSC, we model sulfur content at sulfide saturation (SCSS) in the co-magmatic Hellancourt basalts (Ciborowski et al. 2017; n = 14). Using COMAGMAT-5 (Ariskin et al. 2012), we estimate SCSS at different initial sulfur concentrations to investigate whether exogenous sulfur was responsible for achieving SCSS in the MSC.

Firstly, we start with 600 ppm S in the extracted partial melt, which is consistent with 30% partial melting of the upper mantle. At this initial concentration, SCSS would be achieved after ~65% low-pressure fractional crystallization, which is inconsistent with the observed distribution of sulfides in the LNS. Secondly, we begin with 1,200 ppm S, where under the same conditions as the first model, SCSS would be attained after ~20% fractional crystallization. The texture exhibited by the sulfides favors downward percolation in a porous cumulate pile. With a starting composition of 1,200 ppm S, SCSS would follow the crystallization inter-cumulus pyroxene on the liquid line of descent, which would prevent the degree of observed percolation. Thirdly, we start with 1,590 ppm sulfur, which is the average S composition of the Chukotat basalts of the Raglan deposit (Barnes and Picard 1993). We consider this a combination of mantle and sulfur. From this, immiscible sulfide would segregate coevally with olivine fractionation. This model is most consistent with measured and calculated Ni compositions of cumulus olivine and the bulk sulfide assemblage.

The degree of interaction between a silicate magma and a sulfide liquid is monitored by the mass ratio of silicate:sulfide, known as the $R$ factor (Campbell and Naldrett 1979). $R$ factors at the Raglan and Thompson Ni-(Cu-PGE) deposit are estimated to be in the region of 1000 and 300, respectively. $R$ factors were estimated using the averaged chalcophile concentration of the Hellancourt basalts (146 ppm Ni, 46 ppm Co, and 113 ppm Cu) and $D$ values of Barnes and Lightfoot (2005). We constrain the $R$ factors to be within 500 and 1,600, similar to that proposed at Raglan. However, sulfide tenors at Huckleberry are lower than those at Raglan, due to an under-representation of mss caused by early onset sulfide saturation. Nickel-in-olivine far exceeds what would be expected if originally fractionated from a magma such as the Hellancourt basalts (>2,500 ppm). Thus, fractionation must have instigated in a more primitive melt. Using a picritic starting composition (498 ppm Ni; Barnes and Lightfoot 2005), sulfide-bearing rocks plot within $R$ factors of 100 to 2,000, subjected to up to 75% sulfide fractionation prior to emplacement. Sulfide-bearing units...
Figure 3. Schematic illustration of the genesis of the Huckleberry Prospect (see text for explanation).

at the Raglan and Thompson deposits yield $R$ factors stated above, with greater mss representation, consistent with the nature and tenor of ores observed.

4 Genesis of the Huckleberry Prospect

The Huckleberry Cu-Ni-PGE Prospect records multiple injections of mafic-ultramafic magma of the MSC and provides insight into the formation and distribution of sulfide ore. Its formation can be ascribed to two events:

1. Emplacement of the PGS: The PGS is periodically emplaced as plagioclase-rich slurries where sulfide globules were entrained along the base of the initial sill. The size and compartmentalization of the globules suggest entrainment from a nearby sulfide pool followed by in situ fractionation in an up-right stratigraphy.

2. Emplacement of the LNS: The LNS intrudes the PGS, entraining a crystal cargo of olivine, plagioclase, and fractionated sulfide liquid. The silicate assemblage is sorted into a coarsening-up regime due to thermal convection, augmented by residual heat from the PGS (Holness et al. 2017). Sulfide ultimately percolates through the cumulate pile and continues into the footwall rock. The turbulent emplacement causes bulk assimilation of the footwall rock, which may instigate pot-holing at the base of the LNS. Dense sulfide and cumulus olivine concentrate in these thermo-mechanical traps and propagate into the footwall rock as harzburgitic intrusions rich in sulfide. This model is analogous to that proposed by Latypov et al. (2015) to explain sulfide-rich harzburgitic undercuttings in the Merensky Reef, Bushveld Complex.

In situ crustal contamination does not trigger sulfide saturation in the MSC, where assimilation of lower continental crust during extraction is a favorable mechanism for raising the S concentration of the parental magma. Thick sills (> 100 m) with basal cumulate assemblages become prospective when cooling rates are sufficiently slowed for the efficient accumulation of sulfide liquid at the floor of the intrusion. Thermo-mechanical traps may represent a fruitful new endeavor for magmatic sulfides in the Labrador Trough.

Acknowledgements

This work is funded through the NERC GW4+ dtp (NE/L002434/1). Northern Shield Resources, Duncan Muir, and Anthony Oldroyd are thanked for access to data, fieldwork, sampling and analytical assistance.

References


Tracking the origin of the magmatic magnetite-(apatite) deposits of the Coastal Cordillera of the Andes with Sr-Nd isotopes

Fernando Tornos
Instituto de Geociencias (IGEO, CSIC-UCM), Madrid, Spain. f.tornos@csic.es

John M. Hanchar
Memorial University of Newfoundland, Saint John’s, Canada

Rodrigo Munizaga
CAP Minería, La Serena, Chile

Francisco Velasco
Universidad del Pais Vasco, Bilbao, Spain

Abstract. In the Coastal Cordillera of the Andes, magnetite-(apatite) (MtAp) mineralization forms a distinct group of ore deposits having late Jurassic to early Cretaceous ages and that are geologically different from the sometimes proximal IOCG mineralization. The MtAp mineralization commonly infills open spaces in tensional structures within the Atacama Fault System (AFS) and are characterized by the presence of a massive core of magnetite, apatite and/or actinolite. These deposits extend for more than 10 km in vertical extent, crosscutting different types of plutonic and volcanic rocks. The individual MtAp deposits occur as large dyke-like lenses having a well-marked zonation with a lower zone of apatite-poor massive magnetite capped or enclosed in a halo of magnetite-actinolite-apatite pegmatite and an overlying zone of massive fluor-apatite with minor actinolite, ilmenite and hematite, occurring either as veins or as magmatic-hydrothermal breccias. Melt inclusion, Sr-Nd isotopes, and stable isotope data show that these MtAp systems are derived from the crystallization of unusual iron-rich melts which were likely generated in the mantle wedge due to the influence of aqueous fluids separating from the subducting slab. They have Sr-Nd signatures markedly different than the associated calc-alkaline igneous host rocks, tracing different sources and magmatic evolution.

1 Magnetite-(apatite) deposits of the Andean Coast

The MtAp deposits of the Coastal Cordillera of Chile and Peru host the largest iron resources (>10 Gt of iron ore) of the whole American Cordillera (Naslund et al. 2002; Sillitoe 2003). They extend for more than 1500 km in a narrow belt strictly controlled by the large and trans-crustal AFS and its northern prolongation. The mineralization is hosted by late Jurassic to early Cretaceous mafic to intermediate juvenile volcanic and plutonic rocks belonging to the first and westernmost magmatic arc formed in relationship with the Andean subduction, synchronously with major crustal extension and transpression. Locally they can in some locations be traced into the underlying basement.

A comparison between individual deposits shows that they form sub-vertical lens-shaped bodies occurring from mid-crustal to sub-aerial environments in a vertical extent in excess of 10 km.

Figure 1. Pegmatite-like mineralization capping massive magnetite at Carmen de Fierro mine. Large crystals of apatite with associated actinolite and with interstitial magnetite are interpreted as formed from an evolved iron-rich melt coeval with the separation of an immiscible water-rich fluid. Width photo: 40 cm

MtAp deposits formed in mesozonal to epizonal environments are always discordant to the host rocks, infill open spaces and are enclosed in a zone of alkali-calcic alteration. Individual orebodies, up to 100 m thick and up to 1.5 km long, show a marked vertical zonation with a lower zone dominated by massive, poorly vesicular, magnetite with only small amounts of fluorapatite and actinolite, which occur in irregular pods or large crystals. They are usually enclosed by a halo of coarse grained actinolite – magnetite – fluor-apatite ± scapolite ± anhydrite showing irregular contacts with the massive magnetite but sharp contacts with the hydrothermally altered host rock. This rock is texturally identical to pegmatites in in felsic systems and likely
reflects crystallization from a melt with fluctuating exsolution of an aqueous phase. At Carmen de Fierro, over only some tens of metres, massive magnetite grades upwards into another pegmatite characterized by the predominance of fluor-apatite (Fig. 1) and, above that, at the California Mine, for example, into bodies of massive fluoro-apatite with variable amounts of actinolite and traces of ilmenite and hematite occurring as veins or large breccia bodies, with the apatite supporting large fragments of the host rocks (Fig. 2). Only a few of these systems reach the surface and here the magnetite occurs as subaerial and submarine vesicle-rich lava flows and pyroclastic vents similar to those described at El Laco by Tornos et al. (2017a; 2017b). The amount of sulphides is very scarce and when they occur they replace the massive magnetite.

Figure 2. Discordant vein of actinolite-apatite with only small amounts of magnetite (California Mine) capping the large massive magnetite-(apatite) mineralization of Pleito-Melón. Width of the vein: 20 cm.

Hydrothermal alteration enveloping the mineralization includes the pervasive replacement of the host rocks by actinolite, K feldspar (adularia) or albite, magnetite, scapolite, anhydrite and small amounts of apatite; locally there are some zones of skarn-like alteration with granodiorite and diopside. These zones can host large bodies of barren massive magnetite or hematite which are sometimes the traps for later copper mineralization.

2 Geochemistry of the parental iron-rich melts

Discordant dikes of microgabbro host large blebs of magnetite that are interpreted as evidence of the existence of an immiscible iron-rich melt (Aguirre 2001; Tornos et al. submitted). Furthermore, the fluoro-apatite has abundant melt inclusions which coexist with fluid inclusions, confirming that these minerals crystallized from a melt coexisting with an exsolving fluid (Velasco and Tornos 2009). Further evidence supporting that these rocks are the product of the crystallization of iron-rich melts similar to those that form nelsonite but injected high into the crust include the geologic features (Naslund et al. 2002; Tornos et al. 2017b), abundant experimental work (Hou et al. 2018) and the presence of melt inclusions (Kamenetsky et al. 2013) showing unequivocal evidences of melt separation with one endmember having a composition identical to that observed in the MtAp systems.

Sr-Nd geochemistry of the ores shows that they have a geochemistry different to that of the broadly coeval calc-alkaline igneous host rocks. The andesite and diorite of the Coastal Cordillera have signatures consistent with that of a variably depleted mantle with εNd values between 0 and +7 and 87Sr/86Sr values of 0.7030-0.7050. Whereas the MtAp rocks have a characteristic signature with higher εNd values (+4 to +9) but a wide range of 87Sr/86Sr initial values from 0.7035 to 0.7097, suggesting an input of radiogenic Sr that is not observed in the host rocks (Fig. 3).

3 Discussion and Conclusions

Geology and geochemistry supports that the MtAp deposits of the Coastal Cordillera of Chile are the product of the crystallization of iron-rich melts that separated from a parental silicate melt and that during crystallization formed magmatic-hydrothermal systems equivalent to those in several other ore-forming environments.

The Sr-Nd isotope geochemistry shows that the MtAp rocks have a different origin to that of the associated calc-alkaline igneous host rocks, something incompatible with models proposing that the formation of these rocks is related with fluids exsolving from a crystallizing andesite (Sillitoe and Burrows 2002; Simon et al. 2018).

These data suggests that the MtAp deposits reflect mixing between two sources, one represented by the most primitive mantle beneath the arc, represented by some of the plutonic rocks such as the Copiapó, Illapel or Las Tazas intrusive complexes (Parada et al. 1999; Wilson and Grocott 1999; Marschik et al. 2003). The other endmember has even more depleted εNd values and is significantly enriched in radiogenic Sr. This enrichment could be attributed to the input of seawater that would disturb the original Sr isotope values due to its high mobility. However, the fact that these deposits occur in a subaeriel magmatic arc, that the most 87Sr-rich rocks
are the deepest ones and that the rocks having the most intense sodic alteration do not show an enrichment in $^{87}\text{Sr}/^{86}\text{Sr}$ suggest that the input of external fluids was not the ultimate cause of such an enrichment, which is also seen in submarine volcanic rocks of the area (Rossel et al. 2013). Our interpretation is that this signature is inherited from the dewatering of the subducted slab beneath the mantle wedge during prograde metamorphism. There is abundant evidence that the subducted slab has, on average, $\varepsilon_{Nd}$ values with MORB-like compositions but Sr isotope ratios inherited from the interaction with seawater (Staudigel et al. 1995; Debret and Sverjensky 2017). This origin would also explain the highly oxidized nature of these melts and their high content in fluxing elements such as P and F.

Interaction of deep fluids with the mantle wedge would promote melting (see Richards et al. 2017) due to the drop in the solidus and separation and ascent of the oxidized iron-rich melts along transcrustal structures similar to the AFS. The strike slip component of this structure promoted the shallow emplacement of these high density, but low viscosity iron-rich melts not by buoyancy but by lateral compression with the preferential pathways being small extensional structures such as pull-apart or bending zones. Gradual crystallization of magnetite would promote an increase of the other components present in the iron-rich melts (see Kamenetsky et al. 2013) until attaining saturation in actinolite and apatite. The final proportion of these minerals in the overall system would be controlled by the $D_{\text{FeO}}$ and $D_{\text{PO}_4}$ between the silicate and iron-rich melts and their contents of the parental source.

Upflow and gradual crystallization of the iron-rich melt would produce a magnetite mush and, at some stage, the gradual separation of an aqueous fluid due to primary and secondary boiling saturation (Burnham 1979). Even at very low original H$_2$O contents, these processes always lead to fluid saturation and separation.

At fluid pressures above ca. 0.2 GPa the exsolved fluid would be of an intermediate salinity but when cutting the L-V surface it will separate as two immiscible, high and low density, fluids with the proportion of the brine and the solubility of iron dramatically decreasing towards the surface. In a subaerial environment, where except at temperatures above ca. 800°C and below 100°C, the fluid phase would be composed of vapor – transporting only negligible amounts of Fe as chloride complexes – and solid chlorides (Tornos et al. 2016).

Reaction of the exsolved fluids with the host rocks would produce a zone of alkali-calcic alteration and related stratabound magnetite bodies, these late ones clearly crystallized from high temperature magmatic-hydrothermal brines. However, we have not found any evidence that the assemblage within the mineralized structures have been formed by direct hydrothermal precipitation despite the fact that there is abundant for the replacement of fluorapatite to chloro- and hydroxylapatite (Treloar and Colley 1996; Velasco and Tornos 2009) and of magnetite to hematite.

Acknowledgements

This study has been funded by a NSERC Discovery (Canada) grant and the Spanish SEIDI projects CGL2014-55949R and RTI2018-099157-A-100. We acknowledge CAP Minería, especially M. Rojo, C. Astudillo, M. Lagos and W. Riquelme, for their help in accessing and sampling mines as well as other colleagues for their help during field work, including M. Arrieta, V. Herrera, and J.L. Jara. Thanks are extended to the CAI Geocronología y Geoquímica Isotópica (Universidad Complutense de Madrid).

References


Staudigel H, Davies GR, Hart SR, Marchant KM, Smith BM (1995) Large scale isotopic Sr, Nd and O isotopic anatomy of

Tornos F, Hanchar JM, Munizaga R, Galindo C, Velasco F (submitted) Control of the subducted slab and melt crystallization in the formation of magnetite-(apatite) systems, Coastal Cordillera of Chile


Reef-type PGE-enrichment in the 2.44 Ga mafic-ultramafic Näränkävaara layered intrusion, Northern Finland

Ville Järvinen, Tapio Halkoaho, Jussi S. Heinonen, Jukka Konnunaho, O. Tapani Rämö
1) University of Helsinki
2) Geological Survey of Finland

Abstract. Several mafic-ultramafic layered intrusions were emplaced in the Fennoscandian shield during a widespread magmatic event at 2.5–2.4 Ga. The intrusions host several orthomagmatic Ni-Cu-PGE and Cr-V-Ti-Fe deposits. We update the magmatic stratigraphy of the 2.44 Ga Näränkävaara mafic-ultramafic body based on new drilling by Geological Survey of Finland and Outokumpu Oy. The body consists of a basal dunite (1700 m), and a layered series comprising an ultramafic (600 m) and a mafic zone (700 m). Two reversals are found in the layered series, one in the ultramafic and one in the mafic zone. The composition of the layered series parental magma was approximated using a previously unidentified marginal series gabbroidorite. The Cu/Pd ratio below primitive mantle suggests that the parental magma was PGE-fertile. Location of the marginal series indicates that the basal dunite represents an older wall-rock for the layered intrusion. A 25 m thick reef-type PGE-enriched zone with 150–250 ppb Pt+Pd+Au is found in the border between the ultramafic and mafic zones. The PGE reef-forming process may have been interrupted by influx of magma related to the first reversal. PGE-depleted metal ratios suggest that this replenishing magma had already undergone a sulfide saturation event.

1 Introduction

Approximately twenty Paleoproterozoic mafic-ultramafic layered intrusions have been found in the NW region of the Fennoscandian shield. The intrusions were emplaced during widespread mantle-driven igneous activity at 2.53–2.39 Ga (Bayanova et al. 2009). The mafic-ultramafic Näränkävaara layered intrusion, northern Finland, is the easternmost member of the Tornio-Näränkävaara belt (TNB) comprising six mafic-ultramafic layered intrusions dated at 2440 Ma (Iljina & Hanski 2005).

The intrusions of the TNB are typical mafic layered intrusions with marginal and layered magmatic series. They have been shown to host reef-, contact- and offset-type PGE(±Ni-Cu) deposits and Cr-Fe-Ti-V deposits (Iljina et al. 2015). However, the mineral potential of the Näränkävaara intrusion remains relatively poorly known. The discovery of a ~2 km thick dunitic unit along the southern contact of the Näränkävaara layered intrusion has already undergone a sulfide saturation event.

Figure 1. Geological map of the Näränkävaara mafic-ultramafic body. Four drill core intersecting the reef-type PGE-enriched zone (SL reef) marked with white circles. Drilling cross-section that the magmatic stratigraphy in Fig. 2 is based on marked with A-A'. Marginal series melagabbronorite intersected in drill hole R1.

2 Geological setting

The Näränkävaara mafic-ultramafic body is about 30 km long and 5 km wide and extends to a depth of 5–10 km. The body has been interpreted to represent a 2436±5 Ma mafic-ultramafic layered series, composed of a peridotitic-pyroxenitic ultramafic zone, and a gabbronoritic mafic zone (Fig. 1) (Alapieti 1982). Later studies have shown that the Näränkävaara body includes two other distinct ultramafic cumulate units. Firstly, an extensive, up to 2 km thick basal dunitic body borders the layered series along its southern contact (Lahtinen 2005). Secondly, a series of isolated poikilitic harzburgitic intrusions crosscut the basement complex along the northern contact of the layered series. The petrogenetic relationship between these two units and
the layered series remains to be determined.

The strike of the igneous layering in the pyroxenites of the Näränkävaara layered series is generally parallel to the long axis of the intrusion. A large SW-NE fault separates the intrusion into two main blocks, with the NW block dipping about 25° to the NE, and the SE block dipping 5–15° to the SW (Alapieti 1982). The Näränkävaara body is surrounded on all sides by Neoarchean granite-gneiss basement complex.

3 Samples and analytical techniques

This study is based on historical data compilation (Lahtinen 2005) and new drilling, comprising 23 drill holes in total (KSM/MUV-1–22; M4523–67R2, –72R5, –96R304; S5322017R1). Whole-rock compositions were determined by XRF from pressed powder pellets at Labtium Oy laboratories, and at the University of Oulu, Finland. Precious metal analyses were made with GFAAS and ICP-OES following Pb-fire assay fusion at Labtium Oy. Some PGE analyses were made by ICP-MS following NiS-fire assay fusion at Labtium Oy, and at Intertek Laboratories in Australia.

3 Magmatic stratigraphy

A cross section (A–A’ in Fig.1) was constructed based on compilation and interpretation of previously unpublished drill core logs, new thin section studies, and whole rock geochemical correlations. The basal dunite includes stratigraphic gaps due to lack of drill holes, but the layered series is intersected completely, except for the northern contact. A new magmatic stratigraphic column based on this cross section is presented in Fig. 2.

The basal dunite is about 1700 m thick. It is composed of strongly serpentinized olivine ad- and mesocumulate with pseudomorphs after olivine and pyroxene usually found. The layered series is mostly undeformed and unaltered. It consists of a 600 m thick peridotitic-pyroxenitic ultramafic zone, and a 700 m thick gabbronoritic-dioritic mafic zone, marked by appearance of cumulus plagioclase. Two reversals to more primitive lherzolitic compositions are found, one in the ultramafic and one in the mafic zone (units PER-2 and PER-3 in Fig. 2). In the SE block of the Näränkävaara body, a 10 m thick melagabbronoritic marginal series is intersected in the contact of the basal dunite and the layered series, on the side of the layered series (R1 in Fig. 1).

3.1 Whole-rock geochemical variations

Geochemical variation along stratigraphy is presented in Fig. 2. Variations in whole-rock compositions correlate well with mineral abundances determined by thin section petrography.

Composition of the marginal series melagabbronorite is characterized by high SiO$_2$ (54–55 wt%) relative to MgO (14–15 wt%), and low CaO (6.5–7.5 wt%) and TiO$_2$ (0.4 wt%). Mg# is 77 (FeO=FeOtot*0.9). The metal content includes 1.8 ppb Au, 6.1 ppb Pd, 8.2 ppb Pt, 50 ppm Cu, 505 ppm Ni, and 1750 ppm Cr.
4 Reef-type PGE-enriched zone

Four drill holes intersect a PGE-enriched zone (KSM/MUV-6, -16, -19, -22) along the border zone between the ultramafic and the mafic units, at a stratigraphic height of about 2350–2400 m (Fig. 2), with a strike of at least 5 km (Fig. 1). The four intersections have continuous anomalous Au+Pd+Pt concentrations in the 200–300 ppb range with an average thickness of 25 m (maximum 85 m) (Fig. 3). We will refer to the PGE-enriched zone as the Salmilammit reef (SL reef).

4.1 PGE and chalcophile geochemistry

In intersections through the SL reef there is a 10 m thick Pd-peak (highest 423 ppb), with Pd values tailing off to background values above and below. The PGE-enrichment is Pd-dominated, with Pd/Pt ratio varying between 0.5–8 (average 2.9). The highest Pt content is 200 ppb, whereas Au concentrations are low (average 15 ppb). Highest Cu and S concentrations are typically offset above the Pd-peak (Fig. 3). The SL reef is S poor with 480 ppm S on average (highest 1870 ppm). Average Cu is 105 ppm (highest 262 ppm) and average Ni is 370 ppm (highest 573 ppm); Ni/Cu is between 2–13 (average 3.2).

The PM-normalized metal pattern is bell-shaped as is typical for PGE reefs (not pictured), with Ru, Ir, and Os slightly below PM, and enrichment in Pd, Pt, and Rh, with a distinct Pd-peak. Pd/Ir ratios range between 20–160 (average 99). Cu/Pd ratios are 5000–8000 in the ultramafic zone, between 100–500 in the SL reef, and increase to 10 000–100 000 immediately above the reef.

5 Discussion and conclusions

5.1 Implications of the marginal series

The whole-rock composition of the marginal series melagabbronorite was found to be very similar to the calculated weighted average composition of the layered series (Järvinen et al. submitted). In addition, a fractional crystallization model was performed using the marginal series composition, resulting in the same crystallization sequence as observed in the layered series (Ol–Opx–Cpx–Pl). This suggests that the marginal series represents a reasonable approximation of the parental magma composition of the Näränkävaara layered series. Location of the marginal series against the basal dunite indicates that basal dunite is older than the layered series.

5.2 Reef-type PGE-enriched zone (SL reef)

The SL reef is found at the border of mafic and ultramafic zones about 5–20 m below the first appearance of cumulus plagioclase, and shares similar lithology with PGE reefs found in the Great Dyke (Wilson 1996) and the Munni Munni complex (Hoatson & Keays 1989). No PGE reefs in similar stratigraphic position are found in the other intrusions of the TNB (Iljina et al. 2015 and references therein).

The SL reef is associated with a major change in Cu/Pd (Fig. 2). The sulfides exhibit textures typical for primary magmatic sulfides formed through cooling and fractionation of sulfide solid solutions. No petrographic evidence of xenoliths or addition of external S has been identified. No evidence of significant remobilization of PGEs has been found. The mineralization seems to represent an offset-type PGE reef probably formed through passive sulfide saturation caused by fractional crystallization of mafic magma (Mungall 2002).
The history of sulfide saturation has been estimated using metal ratios. Cu/Pd vs. Pd values from the SL reef imply high R-factors between 10,000 to 100,000 similar to other reefs of the TNB (Fig. 4); the low availability of immiscible sulfides at the time of reef forming may have been a limiting factor for the formation of a high grade PGE reef (Barnes & Lightfoot 2005).

The Cu/Pd ratios of the marginal series (~8000) and the weighted average of the layered series (~5000) are below PM, implying a PGE-fertile parental magma (Barnes & Lightfoot 2005). Evidence suggests that the magma associated with the PER-2 reversal was relatively PGE-depleted at the time of its emplacement in the layered series. Excluding samples with >20 ppb Pd, peridotites and pyroxenites below PER-2 have an average Cu/Pd of ~5000, whereas from PER-2 upwards peridotitic and pyroxenitic samples have an average of ~10,000 (Fig. 4). In addition, all sulfide-bearing samples associated with unit PER-2 (~0.1–1 vol% sulfides) plot along the PGM and sulfide extraction vectors in the Ni/Pd vs. Cu/Ir diagram in Fig. 5. These evidence suggest that the magma associated with the PER-2 reversal had already undergone one sulfur-saturation event (resulting in PGE-depletion) before emplacement in the Näränkävaara layered series.

Three PGE-enriched samples analyzed from unit PX-1B (Fig. 2) share similar petrography and geochemistry as the SL reef samples, meaning that the PGE-enrichment may have begun to develop already before the PER-2 reversal. It is possible that influx of the PGE-depleted PER-2 magma halted the PGE reef forming process and, once resumed, resulted in dilution of the PGE grades for rest of the mineralization found in unit PX-2.

References
Hoatson DM, Keays RR (1989) Formation of platiniferous sulfide horizons by crystal fractionation and magma mixing in the Murni Murni layered intrusion, west Pilbara Block, Western Australia. Econ Geol 84(7):1775–1804
Petrography of the hydrothermally altered ultramafic rocks of the Kemi layered intrusion

Fabian M. Botello, Sheng-Hong Yang
University of Oulu

Timo Huhtelin
Outokumpu Chrome Oy

Sari Grönholm
Geological Survey of Finland

Abstract. The Kemi chromite deposit is located nearby the towns of Kemi and Tornio (northern Finland). The mineralization is hosted within the mafic-ultramafic Kemi intrusion (~2.4 Ga) that is part of the Tornio – Näränkävaara belt. The main chromite units are located in the basal part of the intrusion and are enveloped by peridotites and bronzites. Hydrothermal alteration has pervasively affected the ultramafic sequence mainly in the lower and upper segments, leaving the middle partly unaltered. These lithologies can still be identified due to the preservation of their primary textures. The altered ultramafic lithologies had been previously catalogued as cumulate, chlorite, amphibole, serpentine and pyroxene peridotites, amphibole and talc pyroxenites, and serpentinites (Grönholm 1994). Further petrographic observations suggest that the ultramafic rocks experienced at least six events of hydrothermal alteration that lead to the replacement of primary minerals by assemblages of serpentine, chlorite, amphibole, carbonate and talc.

1 Introduction

The 2.44 to 2.5 Ga mafic layered intrusions in the Tornio-Näränkävaara belt are located at the contact between the Archean basement rocks and the Proterozoic volcano-sedimentary, supracrustal schist belts (Peräpohja and Kuusamo belts). The origin of these magmatic intrusions is assigned to a mantle plume flare up in a failed continental rifting environment (Iljina and Hanski 2005). The footwall and hanging wall of the Kemi Intrusion are the Pudasjärvi Complex (3.5 to 2.7 Ga; Lauri et al. 2011; Muttanen and Huhma 2003; Vaasjoki et al. 2005) and the Peräpohja Schist Belt (~2.3 Ga; Laajoki 2005; Perttunen and Vaasjoki 2001; Lauri et al. 2011), respectively. Initially the layered intrusion was tilted from its primary position. Further deformation led to the metamorphism (greenschist to amphibolite facies) and hydrothermal alteration (Alapieti and Huhtelin 2005; Iljina and Hanski 2005).

The 550 m thick layer of peridotite cumulate rests on the top of the main chromitite layer. This layer is characterized by olivine- chromite ± bronzite cumulates with interlayers of chromitites. This layer is overlain by the main chromitite unit (chromite-olivine cumulates with intercumulate poikilitic bronzite ± augite) which has an average thickness of around 40 m in the mining area (Alapieti et al. 1989; Alapieti and Huhtelin 2005). A 550 m thick layer of peridotite cumulate rests on the top of the main chromitite layer. This layer is characterized by olivine – chromite ± bronzite as the cumulate minerals. 1000 m above the basal contact, plagioclase becomes the main cumulate mineral with minor bronzite and augite. This layer extends for about 800 m until the contact with the hanging wall. (Alapieti et al. 1989; Alapieti and Huhtelin 2005).

The lower and upper parts of the Kemi intrusion have magmatic processes responsible for the mineralization and genesis of the intrusion (Alapieti et al. 1989; Yang et al. 2016; Vasilopanagos 2016). However, a substantial portion of the host rocks are altered to serpentinites, chlorite-rich peridotites, amphibole-rich pyroxenites and talc (carbonate) rocks, indicating substantial hydrothermal alteration. Detailed petrographical descriptions of the alteration sequences remain unconstrained. Therefore, this study aims to present data to address the afore-mentioned alteration events.

2 Regional geology

The Tornio – Näränkävaara belt is distributed from the west to the east into the Tornio-Kemi-Penikat, Portimo and Koillismaa Complexes (Iljina and Hanski 2005). The footwall and hanging wall of the Kemi Intrusion are the Pudasjärvi Complex (3.5 to 2.7 Ga; Lauri et al. 2011; Muttanen and Huhma 2003; Vaasjoki et al. 2005) and the Peräpohja Schist Belt (~2.3 Ga; Laajoki 2005; Perttunen and Vaasjoki 2001; Lauri et al. 2011), respectively. Initially the layered intrusion was tilted from its primary position. Further deformation led to the metamorphism (greenschist to amphibolite facies) and hydrothermal alteration (Alapieti and Huhtelin 2005; Iljina and Hanski 2005).

The Kemi layered intrusion is formed from bottom to top by a 10 to 40 m basal sequence of mylonitic talc-chlorite-carbonate schist, followed by a layer of about 40 – 100 m of altered rocks (bronzite – chromite and olivine – chromite ± bronzite cumulates with interlayers of chromitites). This layer is overlain by the main chromitite unit (chromite-olivine cumulates with intercumulate poikilitic bronzite ± augite) which has an average thickness of around 40 m in the mining area (Alapieti et al. 1989; Alapieti and Huhtelin, 2005).

Previous research on the Kemi intrusion and the chromitite deposit has focused on questions related to the origin and evolution of the intrusion, the mineralogy of the chromitite deposit, the contact aureole, and the geodynamic setting. However, the work presented here is the first detailed petrographic study of the hydrothermally altered ultramafic rocks in the Kemi intrusion.
been affected by extensive alterations being stronger in the silicate phases (Alapieti et al. 1989; Alapieti and Huhtelin 2005). Alteration of chromite has affected the edges and cracks of the grains. Some of those grains also show the development of magnetite rims and corrosion produced by serpentinization.

3 Petrography

The petrographic description was done in 49 thin section samples from Grönholm (1994), belonging to the surrounding areas of the mineralization. The majority of the studied samples are either cumulate peridotites or pyroxenites of the orthocumulate type (in the sense of Wager et al. 1960). In peridotites, olivine is enveloped by anhedral orthopyroxene and clinopyroxene. In pyroxenites, orthopyroxene is the cumulate mineral (with occasional presence of olivine) and is surrounded by clinopyroxene.

For the present work, Grönholm (1994) classification was used since it takes into special consideration the host rocks of the ore of Kemi mine. Criteria of classification for the studied lithologies can be found in table 1. Peridotites are grouped in cumulate peridotites and altered peridotites (chlorite, amphibole, serpentinite and pyroxene peridotites). Pyroxenites in Kemi intrusion are bronzites, websterites and diallagites (Alapieti et al. 1989). Pyroxenite thin sections in this study only include altered bronzites – olivine bronzites (amphibole pyroxenites and talc pyroxenites). Only two thin sections of chromitites and five thin sections of serpentinites were described in this work.

Table 1. Lithologies and criteria for their classification. Modified from Grönholm (1994).

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Subgroup</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metapendotites</td>
<td>Cumulate peridotites</td>
<td>Load altered peridotites, easily recognized primary textures and abundant relics.</td>
</tr>
<tr>
<td></td>
<td>Chlorite peridotites</td>
<td>Abundance of chloride altered intercumulus from 14.9% to 22.9%</td>
</tr>
<tr>
<td></td>
<td>Serpentine peridotites</td>
<td>Most altered peridotites, containing from 59% to 98% serpentine.</td>
</tr>
<tr>
<td></td>
<td>Amphibole peridotites</td>
<td>Similar to chlorite peridotite but with higher abundance of amphibole (14.8 - 26.4%)</td>
</tr>
<tr>
<td></td>
<td>Pyroxene peridotites</td>
<td>Abundance of alteration products of pyroxene varying from 18% to 40%</td>
</tr>
<tr>
<td>Pyroxenites</td>
<td>Amphibole pyroxenites</td>
<td>Pyroxenites with a marked abundance of amphibole (29.4% - 76.6%)</td>
</tr>
<tr>
<td></td>
<td>Talc pyroxenites</td>
<td>Pyroxenites with plentiful talc alteration (13.3% - 19.8%).</td>
</tr>
<tr>
<td>Serpentinites</td>
<td>Derived from peridotite</td>
<td>Orthocumulus texture.</td>
</tr>
<tr>
<td>(71.3% serpentine)</td>
<td>Derived from dunite</td>
<td>Adcumulus texture. Formed by altered olivine.</td>
</tr>
</tbody>
</table>

3.1 Cumulate peridotites

These rocks have extensive hydrothermal alteration, although relict primary minerals and textures are easily recognized, unlike in the other peridotites. Chromite is only affected by minor fracturing and recrystallization at the grain margins. Phlogopite is recognized in the cumulate peridotites as an intercumulus mineral, slightly altered to magnetite and chlorite. Olivine relics are altered and intensely fractured, displaying the development of mesh – ribbon textures (in the sense of Wicks and Whittaker 1977; Wicks and O’Hanley 1988). Olivine grains are frequently rimmed by amphibole and serpentine flakes.

Most of the intercumulate pyroxene has been pervasively altered leaving few relict occurrences. Recognized orthopyroxenes are partially altered to bastite. Veins of fine-grained amphibole are observed in orthopyroxenes. Some clinopyroxene relics remain almost unaltered, crosscut by fractures and seldom, amphibole veins.

Pervasively altered intercumulate occurs in two types; either as chloride-altered intercumulate or the "alteration products (px)" (Grönholm 1994). The chloride-altered intercumulate is colorless to bluish-greenish in plane polarized light and gray, greenish-bluish (abnormal colors) to isotropic in crossed polarized light. It is formed by fine grained disseminated flakes of chlorite with minor presence of serpentine.

The alteration products (px) are characterized by very fine grained aggregates of different minerals in varying proportions, hard to distinguish by use of the optical microscope only. Therefore the specific minerals were not taken into account for volumetric percentages but counted as a whole group. "Alteration products (px)" in the cumulate peridotites is scarce compared to other peridotites, it is observed mostly as aggregates of flaky amphibole and serpentinite.

Later serpentine veins are observed crosscutting the samples.

3.2 Altered peridotites

Relict minerals are rarely observed in altered peridotites, as these lithologies are pervasively altered to almost 100%. Identification of primary cumulate texture is possible since the alteration minerals usually preserve the primary shape of the grains.

Phlogopite and chromite are observed in a similar fashion as in the cumulate peridotites. Relict pyroxene is scarce, only a few clinopyroxene crystals were identified. Apatite is identified as a cumulate accessory mineral, being only recognized in one sample as an elongated euhedral prismatic crystal.

Olivine relics are only recognized in a few samples. In altered peridotites olivine is almost entirely replaced by different types of serpentine. Unlike cumulative peridotites, flaky and fibrous aggregates (in interpenetrating textures) are the dominant types of serpentine. Frequently, serpentine-altered olivine crystals are rimmed by flaky and acicular amphibole (Fig. 1A). Flakes of amphibole are also observed masking the serpentine-recrystallized mesh centers. Amphibole flakes are sporadically overprinted by talc alteration, showing higher order interference colors.

Amphibole alteration is also common in pyroxenes. Alteration occurs either as mantling of pyroxenes or as aggregates of parallel to unoriented subhedral elongated amphibole flakes with a matrix of serpentine (varying amounts) and as intergrowths of bastite (replacement along cleavage) with amphibole.

Serpentine alteration over pyroxene is observed in different proportions (~2% to 100%), either as bastite
(patchy, pervasive or along cleavage; featureless or fibrous) or serpentine flakes.

Although “Alteration products (px)” and chlorite – altered intercumulate (Fig. 1A) are more abundant in the altered peridotites, their description is closely similar to the one in the cumulate peridotites. Most common alteration minerals of the “alteration products (px)” in the altered peridotites are amphibole (Fig. 1A), magnetite and serpentine, followed by carbonate, talc and chlorite.

Pyroxene is also altered by magnetite, occurring in different proportions. It’s observed usually as speckles all over the pyroxene crystal, forming along cleavage, fractures and masking the crystals.

Carbonate is observed as rims surrounding former olivine and pyroxene crystals, usually as a second rim with an inner rim of amphibole and filling spaces along the former serpentine ribbons (Fig. 1A). Carbonate is also found as disseminated aggregates within serpentine-altered olivine and the chlorite-altered intercumulate, and as a replacement mineral in the “alteration products (px)”.

### 3.3 Pyroxenites

Apparent cumulate crystals are mainly altered to amphibole of different textures. Amphibole is observed as parallel – subhedral elongated prismatic needles (Fig. 1B), perpendicular needles to crosscutting fractures, subparallel to randomly oriented amphibole in flame texture and as aggregates of amphibole and bastite in a “chessboard” appearance. Amphibole aggregates are often rimmed by finer – grained amphibole and/or contained in a matrix of serpentine (Fig. 1B), opaques, talc, carbonate and finer – grained amphibole flakes in different proportions.

Scarcely subrounded, serpentine – altered olivine grains are also observed. Further alteration over these grains is observed as the mantling of serpentine flakes by amphibole. Observed phlogopite and chlorite – altered intercumulate (Fig. 1B) share similar features with their counterparts in peridotites. Carbonate is recognized as very fine-grained aggregates, occurring randomly, either at crystal borders, matrix, or altering the core of amphibole-rimmed grains.

Talc pyroxenites are fairly similar to amphibole pyroxenites, suggesting a similar alteration process. Differences lie in a marked higher abundance of very fine-grained aggregates, smaller sized amphibole flakes and more plentiful matrix (mainly formed by talc).

### 3.4 Serpentinites

A common feature in all of the serpentinites is the abundant corrosion of chromite grains as well as recrystallization along their margins. Peridotite-derived serpentinite still preserve features of the orthocumulate structures, relatively easy to recognize thanks to magnetite alteration (disseminations in the intercumulate minerals or along former olivine cracks and margins) and differences in grain size of the alteration products of cumulate and intercumulate minerals.

Serpentine is the most common mineral in the serpentinites, followed by chromite, magnetite, carbonate and talc. Serpentine is usually observed as fibrous and flaky aggregates, occasionally preserving former textures (e.g. mesh – rim texture in the altered adcumulate dunite). Banded serpentine veins are also observed.

### 3.5 Chromitite

Orthocumulate texture is observed in the samples with disseminated euhedral chromite (~240 μm) as the cumulate grains. Intercumulate grains are altered up to 100%. Percentage of the mineral volumetric composition was not calculated due to the fine grained nature of the matrix (~10 μm). The matrix is formed by different proportions of talc, serpentine (flakes), phlogopite, amphibole and carbonate.

Figure 1. a. Photomicrograph in crossed Nicols of a pyroxene peridotite sample (altered peridotites). Serpentine altered olivine grain with recrystallized mesh texture. The same grain has amphibole rims and carbonates along fractures. The grain is in contact with chromite, chlorite intercumulate and “alteration products (px)” (mainly amphibole). b. Photomicrograph in crossed Nicols of an amphibole pyroxenite sample (pyroxenites). Altered pyroxene grain formed by an aggregate of amphibole needles and serpentine, surrounded by chlorite intercumulate. Alt px = alteration products (px). Amp = amphibole, Chl = chlorite, Chr = chromite, Srp = serpentine. Width of the photo = 1.6 mm.

### 4 Discussion

All of the studied samples show strong signs hydrothermal activity. Even though alteration is observed with different intensities, the same alteration minerals are recognized throughout almost all of the lithologies. The dominant alteration minerals are serpentine for the peridotites and amphibole and talc for the pyroxenites. Both lithologies share similar percentages of chlorite. Silicate phases in chromitites are altered in a similar...
fashion to pyroxenites, while chromite grains are less altered in chromitites than in peridotites.

An alteration sequence is defined for the Kemi deposit host rocks based on the petrographic observations. A main stage of serpentinization is proposed as the first alteration event, where pseudomorphic textures of serpentine were developed. This was followed by a second stage of serpentinization that produced non-pseudomorphic textures of serpentine (flake and fibrous aggregates). Consequently, serpentine was overprinted by chlorite alteration, seen in the mantling of pseudomorphic textures and by the occurrences of chlorite aggregates in the "chlorite intercumulate" resembling serpentine interpenetrating and interfingering textures (presumably chlorite masking serpentine). Chlorite alteration is followed by amphibole alteration. Amphibole is recognized as serpentine flakes in olivine and pyroxene, replacing pyroxene and recrystallized bastite, and is found disseminated in the chlorite intercumulate. Chlorite alteration over amphibole was not recognized in any of the samples, therefore a later timing for amphibole alteration is proposed. A third episode of serpentinization could be related to later, unaltered crosscutting veins of serpentine (with interpenetrating and banded textures).

Carbonate veins show a later crosscutting relation with amphibole and serpentine veins. Furthermore, carbonate is commonly accompanied by Talc. A relation between talc and carbonate can also be recognized in Elijarvi’s main chromitite layer (Alapieti 1989). Hence, carbonate and talc alteration presumably postdate both amphibole alteration and the later episode of serpentinization.

No timing relation for magneteite was defined. Nonetheless, magnetite is a common product during serpentine alteration (Wicks and Whittaker 1977; Paulick et al. 2006).

5 Conclusions

Six alteration events were identified in the studied samples consisting of: serpentine alteration (development of pseudomorphous textures), a second episode of serpentine alteration (development of non-pseudomorphous textures), chlorite alteration, amphibole alteration, a third episode of serpentine alteration and at last, an episode of talc-carbonate alteration. This sequence could indicate the evolution of a fluid towards more silica rich compositions.

Acknowledgements

This project was funded by K. H. Renlund foundation, Finland. Holger Paulick, Sari Grönholm and Timo Huhtelin are acknowledged for providing material and information which were crucial for the development of this work. This project was also greatly benefited from the unconditional support and critics from friends and colleagues at the University of Oulu. To Simon and Aisha

References


The Maracás vanadiferous district, Bahia-Brazil—geology, mineral resources, descriptive and genetic models

Reinaldo Santana Correia de Brito
Universidade Federal da Bahia-Brazil

Rodrigo C. Lordão,
Largo Resources

Joadson A. Carvalho
Largo Resources

Matheus P. Feitosa
Largo Resources

Abstract. The Rio Jacare Sill (RJS) is a 70km long, 1km thick, layered intrusion within the Contendas-Mirante Complex. This Complex occurs between two Archean tectonic blocks, named Jequié and Gavião, in the Northeastern part the São Francisco Craton, Bahia, Brazil. The sill is divided into two zones. The first is a Lower Zone made up of massive medium-grained gabbro. The second is the Upper Zone which consists of modally graded medium grained magnetite gabbro, magnetite pyroxenite and magnetitite and anorthosite. Fractionation indexes such as SI and #Fm and mineral chemistry data of cumulate phases denote cryptic variations. LREE/HREE ratios of different zones are strongly controlled by the modal proportion of cumulate phases. Nd and Sr isotopic ratios indicate the RJS magma was extracted from a slightly depleted chondritic mantle source. Magma mixing combined with a low degree of crustal assimilation and fractionation are ascribed to explain differentiation and the observed metallic mineralization.

1 Geological Framework

The Maracás Vanadiferous District is located in the southwestern part of the state of Bahia, Brazil and is part of a 70 km long, 2 km wide metallogenic corridor., This corridor sits in the southern segment the Contendas-Jacobina Fold Belt, that occurs between Archean Jequié and Gavião Blocks of the São Francisco Craton. This district coincides with the area of occurrence of the Rio Jacaré Sill (RJS), which is a Neoarchean (2.64 Ga) layered mafic-ultramafic intrusion emplaced in metavolcosedimentary rocks of the Mirante Complex.

2 Vanadium Resources

The RJS intrusion hosts orthomagmatic Fe-Ti-V-Ni-Cu-P and PGE mineralization. The vanadium deposits were discovered in the 1980s by CBPM-Companhia Baiana de Pesquisa Mineral, followed by significant additional exploration made by Largo Resources which has greatly increased the original resources. So far vanadium is the unique commodity being economically produced from the Menchen Mine operated by Vanádio de Maracás S/A.

The mine site is focused on the Guçari A vanadiferous magnetite deposit, that carries measured + inferred reserves of 19.81 million metric tonnes of ore @ 1.20% V₂O₅, and 7% TiO₂. The district has other seven satellite deposits named: Guçari A Norte, Guçari B e B Sul, São José, São José Oeste, Novo Amparo and Novo Amparo Norte that together present resources as large as 21.82 million metric tonnes of vanadiferous magnetic iron ores @ 0.83% V₂O₅.

3 The Rio Jacare Sill

The RJS is divided in two broad zones according to the presence of cumulus titanomagnetite and ilmenite phase layering. Using this criteria it is recognized a Lower Zone, or magnetite out zone and Upper Zone, or magnetite in zone, (Brito 2.000).

3.1 Lower Zone

The Lower Zone is an up to 200 m thick sequence of titanium biotite leucogabbro that displays plagioclase modal layering that ends up as a 6 meter thick mottled anorthosite layer showing orthopyroxene oikocrysts poikilitically enclosing cumulus plagioclase.

3.2 Upper Zone

The Upper Zone lies in sharp contact with the Lower Zone and mottled anorthosite and depicts up to six modally layered magnetite-bearing cyclic units characterized by modal and cryptically layered magnetite with decreasing V contents towards the top of the sequence. The Upper Zone has entry points that corresponds to three distincts sections: Guçari, Novo Amparo and Novo Amparo north, each one separated by a 4 km interval along a north-south trend of 8 km of extension. The magnetite ore zones exhibit good lateral extent, which is sometimes interrupted by inverse faults and later normal faults.
3.3 Cyclicity

The Upper Zone deposits correspond to six cumulus magnetite-ilmenite enriched cyclic units composed of an average of 30% Fe-Ti-V oxides, semi-massive magnetite gabbro layers and 10cm to 10m thick micro and macro magnetitite layers: 1) Cyclic unit M1 & M2, up to 30 m thick, massive magnetite layers associated to magnetite olivine clinopyroxenites, which corresponds to the main ores @ 2.0-3.0 % V₂O₅; 2) M3 and M4 cyclic unities which consists of a package of rhythmically layered magnetitites and metapyroxenites, macro and micro layers @ 2%-1.0% V₂O₅; and 3) M5 & M6 cyclic unities that are made up with magnetite pyroxenite layers, semi-massive magnetite disseminated magnetite leucogabbro, coarse grained magnetite anorthosite @ 0.6%-1.5% V₂O₅. The top of M6 ends up with the occurrence of apatite-bearing melangogabbro and apatite gabbro carrying up to 20% modal cumulus apatite fayalitic olivine and vanadium-poor cumulus magnetite. The mineralized package is overlain by an up to 100 thick very coarse anorthosite layer which is considered the very top of the intrusion.

4 Genetic Model

The orthomagmatic mineralization is considered as formed by fractional crystallization, mainly of magnetite, ilmenite, plagioclase and to a lesser extent pyroxene and olivine from at least 3 main magma pulses.

Acknowledgements

The authors wish to thank Largo Resources to finance this research work and publication of the project scientific results.

References

Gold from Orogenesis to Alluvial  627

The structural setting of the Barsele Au deposit, Sweden

Tobias E Bauer
Luleå University of Technology, Sweden

Marcello Imaña, Kåre Höglund
Agnico Eagle Sweden AB

Helen Thomas
Luleå University of Technology, Sweden

Abstract. The Barsele Au deposit is hosted in Paleoproterozoic rocks that were subject to multiple deformation events during the Svecofennian orogeny 1.9–1.8 Ga ago. Rocks have been subjected to an approx. N-S-directed extensional event (1.89 Ga) potentially responsible for the formation of VMS deposits. The crustal extension was followed by a compressional event under ductile conditions and related basin inversion (D2; 1.87 Ga) and overprinted by a brittle event at 1.8 Ga (D3). The distribution of alteration minerals and veins suggests multiple phases of fluid flow and remobilisation. The latest phase of enrichment appears to be coupled to low-angle thrusting from ESE and brittle reactivation of earlier structures with emplacement of quartz veins along fault planes and tensile structures in an oblique Riedel system.

1 Introduction

The Barsele prospect is located in the Storuman area and forms part of the so-called Gold Line, a NW-SE trending belt of anomalous gold mineralization that occur c. 50 km southwest of the Skellefte district. In addition to Barsele the deposits in the belt include Knaften, Fäboliden, Svartliden, Stortjärnshobben and Blaiken (Bark & Weihed 2007). The Storuman area is tentatively suggested as the westward continuation of the Skellefte district and hosts both volcanic-hosted massive sulphide (VMS) deposits as the Norra VMS deposit and orogenic gold mineralizations.

This ongoing project is based on field work, mainly mapping an exploration trench at Barsele Central but also regional structural geological mapping. Additionally, structural framework modelling was performed from oriented drill core data using the MOVE software package (Midland Valley Exploration). The aim is to constrain structural controls on Au mineralizations in the area.

2 Regional geological framework

The Barsele prospect is located within Palaeoproterozoic supracrustal and associated intrusive rocks (Fig. 1). Bedrock in the area consists of 1.9–1.8 Ga supracrustal and associated intrusive rocks that were deformed and metamorphosed during the Svecokarelian orogeny (Lundström et al. 1997; Mellqvist et al. 1999; Kathol & Weihed 2005). The Storuman area is tentatively suggested as the westward continuation of the Skellefte district and hosts both volcanic-hosted massive sulphide (VMS) deposits as the Norra VMS deposit and orogenic gold mineralizations.

The lowest stratigraphic unit in the area consists of metasedimentary rocks of the Bothnian Basin occur.
Vargfors Group (Allen et al. 1996). Recent studies suggest that the local stratigraphy is comparable to volcanic evolution of the Skellefte district.

The oldest intrusive rocks in the district are early orogenic, 1.89-1.88 Ga granitoids, diorites and gabbros, including a quartz-monzodiorite in Barsele that has been dated at 1880±4 Ma (Eliasson et al. 2001). These early orogenic rocks are suggested to be co-magmatic with the volcanic rocks of the Skellefte Group. Younger phases of intrusives are assigned to the Perthite-Monzonite suite (Witschard 1984), which formed between 1.88 and 1.86 Ga (c.f. Bejgarn et al. 2012) and post-date the deposition of the volcanic rocks. In the south, west and in-between the Skellefte district and the Storuman area, the Skellefte, Vargfors and Bothnian Groups are all truncated by large intrusions of 1.82-1.78 Ga, late- to post-Svecofennian GSDG-type (also referred to as Revsund-type) intrusive rocks of the Transscandinavian Igneous Belt (Kathol & Weihed 2005).

The main compressional deformation event (D2) took place at 1.88-1.87 Ga and resulted in folding, reactivation of the syn-extensional faults and related transposition of VMS deposits (Bauer et al. 2011). The latest major deformation event at 1.82-1.80 Ga (D3; Weihed et al. 2002) is inferred to have resulted from east-west crustal shortening causing reactivation of major syn-extensional high-strain zones with reverse kinematics (Bergman Weihed et al. 1996; Bauer et al., 2011; Skyttä et al., 2012). Gold deposits south of the Stensele area are classified as orogenic gold deposits and are related to the E-W crustal shortening event at 1.80 Ga (D3; Bark & Weihed 2007).

3 Structures and related hydrothermal alteration

3.1 Ductile structures

The main mineralization at Barsele (Central) is hosted by an early orogenic metagranodiorite that intruded prior to metamorphism. Multiple generations of structures occur in Barsele and can be observed in a trench above the central deposit, in oriented drill-core and regional outcrops. The earliest observable structures are represented by a penetrative foliation (S2) and can be correlated to the regional foliation that formed as a response to D2 crustal shortening around 1.87 Ga (c.f. Bauer et al. 2011; Skyttä et al. 2012). Foliation intensity is varying from unfoliated to strong with the formation of a mylonitic fabric. The deposit is located within a series of WNW-ESE-trending shear zones (D2). These high strain zone are characterized by strong strain partitioning and the formation of a strong mylonitic fabric. The cores of the high strain zones are tectonically brecciated and segmented into low strain blocks surrounded by strong foliation wrapping around the blocks.

3.2 Brittle structures

The ductile D2-structures are overprinted by a set of semi-brittle structures (D3). They appear as small-scale faults with discrete tourmaline-coating on the fault surfaces. Typically, D3-foliation is deflected into the D3 zones in their vicinity. Distinct slickenside-lineations that developed on the fault planes show the fault kinematics. Brittle high strain zones are characterized by strong cataclastic fabrics with fault gauges and the development of a spaced cleavage. The cataclastic zones inherit a strong strain partitioning with the formation of low strain blocks within the cataclastic fabric. There are several orientations of brittle structures whereas the most dominating ones are gently ESE-dipping fault zones. The slickenside foliations on the fault planes are near to down dip showing a mainly reverse sense of movement with east block up kinematics, hence low-angle thrusting. Also, a lower order set of interlinking relays developed in-between the thrust planes but show steeper orientations than the high order thrusts. Additionally, to the fault-set a network of conjugate joints developed without significant movements. Furthermore, two sets of open fissures formed. One set developed at right angle in-between the low angle thrusts hence representing a tensile opening. Another set forms an en-echelon pattern in the vicinity of reactivated shear zones as a response on sinistral reactivation.

3.3 Hydrothermal alteration associations related to structures

Hydrothermal alteration varies in style and intensity within Barsele Central. In the following sections we only provide a macroscopic description of veins related to structures. Related to the brittle faulting a series of quartz, quartz-calcite, quartz-tourmaline-bearing veins and polymetallic quartz veins were emplaced subparallel with the S3-fabric (Fig. 2). Quartz vein filling varies from anhedral, massive quartz to euhedral shapes crystallized in open fissures. Mineralogy of veins varies a lot and is not subject to this study. Both S3-foliated and unfoliated and deflected and undeformed veins are observed. This shows that the majority of veins were emplaced syn-tectonic with D3-deformation. In the vicinity of D3 high strain zones, especially associated with these veins, pyrrhotite can be found as selective pervasive alteration in form of disseminated crystals and locally also in small veinlets. Sizes vary from barely macroscopically observable up to 2mm. It is often associated with a more or less intense red staining of the surrounding rocks. Pyrrhotite is in the D3 high strain zones often accompanied by chalcopyrite. Chalcopyrite can be found both disseminated and as small veinlets. Minor occurrences of sericite, chlorite and calcite alterations were observed together with pyrrhotite within the D3 high strain zone.
4 Discussion

The Storuman area was affected by poly-phase deformation events during the Svecofennian orogeny (Fig. 3). Comparing the Norra VMS deposit with other VMS deposits in the Skellefte district we suggest that the Norra VMS formed along a syn-extensional normal fault that was later re-activated during basin inversion (c.f. Bauer et al. 2011). This together with the occurrence of alteration minerals around the ductile D2 shear zones suggest that the ore forming fluids utilized the normal faults as fluid. Nevertheless, later fault re-activation might have resulted in a certain amount of remobilization and potentially further enrichment. The timing of the brittle structures is inferred from the interpretation of the paleo stress direction, the style of deformation and regional-scale relation to late orogenic intrusions and suggested to relate to the regional-scale E-W-compression event (D3; c.f. Bergman Weihed et al. 1996).

Results suggest a strong structural control on the Au mineralization in Barsele. A combination of kinematic indicators from fault sets indicates that the entire D3-thrusting was mainly ESE-WNW-directed with a minor sinistral component.

The formation of relays in an oblique, sinistral thrust system can be explained to form in a transpressive Riedel-system where the oblique relays represent synthetic Riedel-shears (R) with also sinistral kinematics. The interpretation as a transpressive Riedel-system goes in line with the occurrence of steep faults that form a part of an imbricate system within the thrust zone (Fig. 4). The host rock to the main gold mineralization is a reologically competent granodiorite; hence, an enhanced competency difference between the supracrustal and intrusive rocks might have favoured the formation of brittle structures within the latter.

When comparing the local and semi-regional geological features of the Barsele Central prospect with the regional geological architecture of the Skellefte district and Storuman area, a close spatial relationship to major approximately N-S-trending high strain zones becomes obvious (Fig. 1). The higher order structure immediate east of the Barsele prospect might represent a major crustal scale, 1st order structure that is interpreted to have the same origin as the known and well-studied Deppis-Näsliden and Vidsel-Röjnorret shear zones in the Skellefte district. Hence, it can be concluded that the 1st order structure east of the Barsele has the same syn-extensional and syn-volcanic origin, forming clearly before or during 1.90 Ga. Additionally, there is an important spatial relationship between the major N-S-trending high strain zones and Au-deposits in the area. All economically important deposits in the area, as Björkdal, Kankberg and Boliden, are located in conjunction to the same style of structures. The orogenic Au-deposits Svarliden, and Fäboliden and the Sjölden prospect (Bark & Weihed 2007) are related to the same higher order structures as the Barsele prospect showing the high economic importance of this zone.
Acknowledgements

Agnico Eagle Sweden AB is thanked for support, access and discussions. Iain Pitcairn and Glenn Bark are acknowledged for contributions and discussions. This work was partly carried out in the EraMin project “Gold insight”. MOVE was used as part of the Academic software initiative by Midland Valley Exploration Ltd.

References


The structural control on the gold mineralization at the Galat Sufar South deposit (Block 14, NE Sudan)

Julien Perret1,2, Julien Feneyrol1, Rémi Bosc1, Aurélien Eglinger2, Anne-Sylvie André-Mayer2, Craig Hartshorne3, Emmanuel Abanyin3
1Arethuse Geology SARL, France
2GeoRessources, Université de Lorraine-CNRS, France
3Orca Gold Inc., Canada

Abstract: The Galat Sufar South (GSS) gold deposit is an example of the Neoproterozoic gold potential of the Nubian Shield, especially along major sutures and shear zones such as the Keraf shear zone and the Atmur-Delgo suture. This study represents the first published work on the deposit and controls on mineralisation despite its strong gold endowment.

This petro-structural study leads to consider a polyphase deformation history at the GSS gold deposit, from the cryptic D1GSS and the principal D2GSS (early development of the Keraf shear zone at the regional scale) ductile deformation events to the late, post-Keraf shear zone D4GSS brecciation episode. The GSS gold mineralization is critically related to deformation. Indeed, the main D2GSS deformation episode is expressed by both folding and shearing controlling the geometry of the main gold-bearing ore features, from disseminated pyrite to boudinaged quartz and sulphide-dominated veinlets. Later, the D4GSS brecciation is responsible for the formation of a polymetallic ore, potentially resulting from the remobilization of the early mineralization. Therefore, the GSS gold deposit should be ultimately classified as a structurally controlled deposit.

1 Geological setting

The Galat Sufar South (GSS) gold deposit is located within the western Nubian part of the Neoproterozoic Arabian-Nubian Shield (ANS; Fig. 1a), formed during the 850-550 Ma “Supercontinent Cycle” (Stern and Johnson 2010; Johnson et al. 2011). The ANS is one of the world’s promising Neoproterozoic regions for orogenic Au and polymetallic volcanogenic massive sulphide deposit exploration (Pyley et al. 2009; Trench and Groves 2015; Barrie et al. 2016) and contributes to the world resource of Neoproterozoic Au (Johnson et al. 2017; Goldfarb et al. 2017) as attested by probable reserves of 79.9 Mt @ 1.11g/t Au for a total of 2.853 Mozt across both the GSS and Wadi Doum deposits within the Block 14 project area (Orca Gold Inc. 2019).

The GSS gold deposit is located within the northern part of the Keraf shear zone (KSZ), at the junction with the Atmur-Delgo suture (ADS) (Fig. 1a). The N-trending KSZ, surimposed to an arc-continent suture, is interpreted to have formed during the ca. 620-580 Ma final assembly of the ANS by four-phased sinistral transpressive tectonics (Almond and Ahmed 1987; Stern 1994; Abdelsalam et al. 1995, 1998; Abdelsalam and Stern 1996; Ahmed Sulliman 2000) while the ADS possibly documents an aulacogenic oceanic re-entrant that used to separate the Halfa and Bayuda terranes (Schandelmeier et al. 1994).
Figure 2. Deformation features related to the successive deformation events that occurred at the GSS gold deposit. 

(a and b) Cross-polarized, transmitted light) $D_{GSS}$-related $F_1$ folds affecting early carbonate-(quartz) veinlets are transposed along the $S_2$ main fabric and re-folded by the $F_2$ fold system. c) $C_2$ shearing is developed along the $S_2$ penetrative fabric and affects an early quartz veinlet that is partially transposed along $S_2$. d) (Cross-polarized, transmitted light) The $D_{GSS}$-related $C_2$ shearing and $S_2$ development are responsible for early carbonate-dominated veinlet boudinage and asymmetrical dismembering along $S_2$. e) (Cross-polarized, transmitted light) $S_{ser}$-rich, asymmetrical strain fringes are developed around disseminated $Py_2$ grains displaying the non-coaxial $D_2$ shearing sense. f) Rare $D_{GSS}$-related $C_3a$ shear bands affect the $S_2$-dominated gangue. g) Multiple generations of quartz-albite-carbonate $V_{3b}$ tension gash veinlets highlight the apparent, finite $ε_{3b}$ orientation. h) The $D_{GSS}$ event occurs as quartz-carbonate hydraulic breccia mostly affecting silicified intervals and containing a variable pyrite-sphalerite-chalcopyrite-galena-fahlore amount.
At the shield scale complex interference folding has been identified from satellite imagery within the Keraf meta-sedimentary rocks at the junction between the two regional major structures, the ADS and the KSZ (Abdelsalam et al. 1995, 1998; Abdelsalam and Stern 1996). Within this domain, an andesite dominated antiformal dome complex, host to the GSS deposit, is exposed (Fig. 1b).

At the deposit scale, the GSS gold deposit is hosted by a strongly deformed, interleaved metavolcanosedimentary horizon, enclosed within a thick andesitic volcanic sequence. The deposit is thought to be “lithologically controlled” as the mineralization is limited to this unit (Davies 2016). Northwards, its extension is limited by a marine carbonate platform (Fig. 1b; Orca Gold Inc. 2017). The host unit has been altered multiple times by the variable addition of albite, sericite, silica and carbonate (Fig. 1b and 2; Orca Gold Inc. 2017). The GSS gold deposit structural framework displays a weakly preserved ENE-trending bedding orientation highlighted by the metavolcanosedimentary horizon (Fig. 1b). The mostly NNW-trending, dominant, penetrative fabric is parallel to the axial plane of upright tight folds affecting primarily the mineralized unit (Fig. 1b; Orca Gold Inc. 2017).

2 Sampling and methodology

Samples have been collected along several diamond drill cores (Fig. 1b) to provide the most representative dataset about lithology, alteration, deformation and mineralization at the GSS gold deposit. The $S_2$ penetrative fabric orientation has been systematically measured along the studied drill cores using a “rocket launcher”. Oriented thin sections have been prepared when possible.

A detailed petrographic and structural description has been carried out at the macro- and micro-scale to identify (i) the successive deformation stages and (ii) the related paragenetic sequence that occurred at the GSS gold deposit.

3 Results

The main deformation features observed at the GSS gold deposit are illustrated in Fig. 2. Index for mineral generations refers to deformation events in agreement with the paragenetic sequence that is considered.

3.1 Cryptic, ductile D1GSS deformation event

The ductile D1GSS event is weakly expressed at the GSS gold deposit because of strong overprinting by subsequent deformation. Nevertheless, evidence for an early F1 folding stage has been observed. It occurs as early, up to decimetric, boudinaged to dismembered, carbonate (Cb)-rich veinlets displaying F1 hinges that are affected by a subsequent F2 folding episode (Fig. 2a, b). Limbs of these twice-folded veinlets are transposed along the $S_2$ penetrative fabric that represents the axial plane cleavage related to this fold system (Fig. 2a, b). Rare evidence of a $S_1$ schistosity is preserved and characterized by sericite flakes folded by the F2 isoclinal folds with a $S_2$ schistosity in an axial planar position characterized by the assemblage of sericite-chlorite (Fig. 2b).

3.2 Major, ductile D2GSS deformation event

The D2GSS-related structural features control the global structural framework at the GSS gold deposit. At the deposit scale, the variable, mostly N140°- to N160°-trending $S_2$ penetrative fabric orientation is controlled by the predominant $L_2$ stretching lineation steeply dipping northwards (Fig. 3). D2GSS-related folds are observed at both macro- and microscopic scales (Fig. 2a, b) and $S_2$, mostly expressed by the Ser2-rich gangue in the metavolcanosedimentary horizon, can be interpreted as $F_2$ axial plane cleavage (Fig. 2b).

Figure 3. $S_2$ and $L_2$ distribution at the GSS gold deposit. Data are plotted in an equal area stereonet, lower hemisphere projection. C2 shearing planes are developed along the $S_2$ penetrative fabric and earlier veinlets are partially to completely transposed along them (Fig. 2c). Besides, the shape of early, pluri-millimetric to centimetric carbonate-quartz-pyrite-chalcopyrite-sphalerite-fahlore veinlets, boudinaged and dismembered along $S_2$, illustrates the C2 kinematics (Fig. 2d). The upright top-to-the-WSW $C_2$ shear sense is even better highlighted by asymmetrical strain fringes composed of variable amount of quartz, chlorite and sericite developed around disseminated, D2GSS-related pyrite grains (Fig.2e). D2GSS-related sulphide income forms the economic mineralization displayed at the GSS gold deposit.
3.3 Weak, ductile/brittle \(D_{3\text{GSS}}\) deformation event

A minor, ductile/brittle \(D_{3\text{GSS}}\) event occurred at the GSS gold deposit as pluri-centimetric \(C_{3a}\) kink bands postponing the \(S_2\) main fabric (Fig. 2f). The latter are crosscut by pluri-millimetric to pluri-centimetric Qz-albite (Ab) \(V_{3b}\) tension gash veinlets (Fig. 2g; the crosscutting relationship between \(C_{3a}\) kink bands and \(V_{3b}\) tension gash veinlets has been observed on the thin section prepared for the sample visible in Fig. 2g). Therefore, the non-coaxial \(D_{3\text{GSS}}\) event recorded the syn-albitization ductile/brittle transition at the GSS gold deposit.

3.4 Late, brittle \(D_{4\text{GSS}}\) deformation event

Finally, a late, brittle \(D_{4\text{GSS}}\) event predominantly affected the silicified zones within the meta-volcanosedimentary horizon at the GSS gold deposit. The \(D_{4\text{GSS}}\)-related quartz-carbonate breccia could be interpreted as a hydraulic breccia due to the angular shape and rather constant size of the pluri-centimetric host rock clasts (Fig. 2h). A variable polymetallic sulphide mineralization composed by a pyrite-sphalerite-chalcopyrite-galena-fahlore(electrum) is associated with these breccia occurrences (Fig. 2h).

4 Discussion

The GSS gold deposit has recorded a complex deformation history from ductile to brittle deformation. The main mineralization event, expressed by disseminated pyrite and quartz and sulphide-dominated veinlets transposed along \(S_2\) is synchronous to the ductile \(D_{3\text{GSS}}\) event controlling the deposit structural framework. The \(D_{3\text{GSS}}\) event is also expressing evidence for simple shearing illustrated by asymmetrical strain fringes and dismembered veinlets (Fig. 2d, e) transposed along the main fabric, contrary to the pure shear model considered to date (Mason 2017). The GSS structural framework is dominated by subvertical, steeply NW-dipping \(L_2\) responsible for \(S_2\) variable orientation at the deposit scale. At the regional scale, the \(D_{2\text{GSS}}\) event could be related to the early KSZ development, i.e. the early emplacement of the ANS over the Saharan metacraton (Abdelsalam et al. 1995; Abdelsalam and Stern 1996; Ahmed Suliman ETB 2000), which is expressed by large-scale emplacement of the ANS over the Saharan metacraton, i.e. related to the early KSZ development, Sinistral Transgression Along the Eastern Margin of West Gondwana. J Geol 106:133–148


Acknowledgements

The authors are grateful to the Orca Gold Inc. team for their welcome on GSS camp and their substantial logistical support. This work is part of Julien Perret’s PhD project which benefited of a CIFRE funding, reference CIFRE N°2017/17371, attributed by the French National Research and Technology Agency.

References


The invincible deposit: an example of pre-orogenic gold mineralization in the eastern Goldfields, western Australia

Sarah Jones
Gold Fields Limited

Abstract. The Invincible Deposit, located in the St Ives camp in the Eastern Goldfields, Western Australia, displays two distinct styles of gold mineralization. Type 1 mineralization comprises steep bedding-parallel quartz breccia veins and these are consistently overprinted by flat-lying to gently dipping Type 2 extension (or dilational) veins. Type 1 veins are strongly folded and boudinaged whereas the gently dipping Type 2 veins are undeformed.

Type 1 mineralized veins are truncated by unaltered conglomerate of the overlying c. 2665 Ma Merougil Formation. In contrast, the undeformed flat-lying extension veins extend into the overlying conglomerate. The Type 1 mineralizing event occurred prior to erosion and deposition of the Merougil Formation and prior to strong east-west horizontal compression and development of the flat-lying Type 2 extension veins.

1 Introduction

Most gold deposits in the Eastern Goldfields Superterrane (EGT) in Western Australia are described as orogenic gold deposits associated with structures formed during horizontal east-west compression (c.f., Groves et al., 1998).

Geochronological studies of mineralized assemblages across the EGT show gold deposition occurred over a period from ~2680 to 2620 Ma which broadly coincides with the timing of D1-4 deformation events (c.f., Czarnota et al., 2010). This indicates that at least some gold deposition occurred during the c. 2672-2660 Ma D1 event.

D1 structures comprise early recumbent folds and an axial planar layer-parallel S1 foliation that is variably developed throughout the EGT (Swager, 1997; Jones, 2014; Jones et al., 2019). D1 structures differ markedly from D2-4 structures as these formed during horizontal east-west compression and comprise upright north-trending folds, a steep axial planar S2 foliation, and D3-4 shears. Some of the larger gold deposits in the EGT display evidence for protracted mineralization during the D1 to D4 events (e.g., Golden Mile, Bateman et al., 2001; Waroonga, Jones et al., 2019).

In the St Ives camp, about 50 km south of Kalgoorlie, most gold deposits are associated with structures that developed during horizontal east-west compression (Figure 1). The Invincible deposit displays structural features that differ markedly from the other deposits in the camp and may be related to the early D1 event.

Figure 1. a) Location of St Ives Camp, Eastern Goldfields, Western Australia; b) Geology and structure of the St Ives camp.
2 Regional geological setting

The Invincible deposit, located in the St Ives camp, is in the southern part of the Kalgoorlie Terrane which forms part of the Eastern Goldfields Superterrane (Cassidy et al., 2006). The stratigraphy of the Kalgoorlie-Kambalda area can be broadly grouped into three sequences, with the dominantly mafic and ultramafic flows and interflow sedimentary units of the 2705-2690 Ma Kambalda sequence; the intermediate to felsic volcaniclastic units of the 2690-2670 Ma Black Flag Group; and the siliciclastic units of the c. 2665 Merougil Formation (Barley et al., 2008; Connors et al., 2002; Squire et al., 2010). The Merougil Formation is one of the ‘late basins’ that lie unconformably on the older sequences throughout the EGT (Figure 1).

Regional deformation events in the EGT comprise: early extension and basin development with deposition of the mafic-ultramafic and later volcaniclastic sequences (D0); layer-parallel S1 foliation and recumbent folds (D1); upright north-trending folds and a steep axial planar S2 foliation produced during horizontal east-west compression (D2); continued east-west compression and development of shears along the F2 fold limbs (D3); and northeast-southwest directed compression that reactivates earlier structures (D4).

3 Invincible deposit geology

The Invincible deposit is predominantly hosted by a mudstone unit (upper Black Flag Group) at the eastern edge of the c. 2665 Ma Merougil Basin (Figure 1). The Merougil Formation is tightly folded into a regional north-northwest trending D2 syncline. The north-northeast trending Alpha Island Fault extends through the center of the deposit and is a large dextral D4 structure but may also represent an early basin controlling structure (Connors et al., 2002).

Mining of the deposit commenced in 2015 and the current resource is 9.2 Mt at 4.5 g/t yielding 1.3 Moz gold. Two distinct styles of mineralization are observed at Invincible, with early steep bedding-parallel Type 1 quartz breccia veins and flat-lying Type 2 extension veins. Type 2 extension veins consistently overprint the steeper Type 1 mineralization.

Type 1 veins are strongly folded and boudinaged and are surrounded by a well-developed sodic alteration halo. Type 2 extension veins are undeformed and are associated with weak sodic and hematite alteration. Type 1 mineralization is best developed in the mudstone, whereas the Type 2 extension veins are best developed in a footwall sandstone unit (upper Black Flag Group). However, the Type 2 veins also overprint the Type 1 mineralization and extend up into the overlying Merougil Formation.

Steep Type 1 ore lenses are consistently truncated by unaltered Merougil Formation conglomerate (Figure 2). The contact is not sheared and there is a 10-20° difference between bedding in the mineralized mudstone and the contact with the overlying conglomerate. In addition, multi-element data such as Sb shows a dramatic change between the altered mudstone and the conglomerate unit (Figure 3).

In weakly mineralized zones, sub-vertical Type 1 extension veins cut across beds that dip 70° to the southwest. In strongly mineralized zones, bedding is sub-vertical and large quartz breccia veins develop along the bedding (Figure 4). Moderately west-dipping shears extend across the bedding in these zones. Bedding-vein relationships indicate southwest-side-down kinematics during the early mineralizing event.

Upright north-trending folds and boudinaged zones are common in the Type 1 veins and suggest that the veins developed prior to strong horizontal east-west compression (D2-3 events). In contrast, the flat-lying Type 2 extension veins are undeformed and likely developed synchronously with the compressional events.

Further examples of polyphase deformation are shown by tightly folded Type 1 extension veins (Figure 5). The extension veins developed above extensional shears during early southwest-side-down movement. The veins are tightly folded by subsequent horizontal compression. In the first deformation phase, the bedding ‘opens’, then ‘closes’ during the later compressional event. Early extensional shears are reactivated as reverse shears.

Figure 2. a) Unconformable contact between strongly mineralized mudstone and the overlying Merougil Formation conglomerate (modified from Jones et al., 2019).
Figure 3. Gridded Sb data (30m grid) illustrates the marked change in Sb values from the altered mudstone to the overlying unaltered conglomerate unit. The mudstone unit dips 70° to the southwest and this accounts for the elevated Sb values to the west of the surface outcrop boundaries.

Figure 4. Schematic model shows bedding-vein relationships. In weakly mineralized zones, minor Type 1 extension veins develop steeper than bedding. In strongly mineralized zones, bedding is sub-vertical and large quartz breccia veins develop in the zone of enhanced dilation during south-west-side down movement.

Figure 5. a) Two distinct deformation phases are shown by overprinting relationships. Early southwest-side-down movement is indicated by the orientation of steep bedding-parallel extension veins above the west-dipping shears. These Type 1 extension veins are folded by subsequent compression and the early extensional shears are reactivated as reverse shears. The first event 'opens up' the bedding, the second event 'closes' the bedding; b) flat-lying Type 2 extension veins cut across the steep bedding-parallel Type 1 veins. Note the upright east-verging F2 fold in the Type 1 veins in the center of the face (modified from Jones et al., 2019).
4 Conclusions

The angular unconformity between the strongly mineralized mudstone and the overlying unaltered Merougil Formation conglomerate indicates that the main mineralizing event occurred prior to erosion and deposition of the conglomerate unit. The lack of alteration in the overlying conglomerate unit is consistent with deposition after the mineralizing event.

The strong modification of Type 1 veins by D_{2-3} horizontal compression also suggests that the mineralizing event occurred early in the deformation history. Gently dipping Type 2 extension veins consistently overprint the Type 1 mineralization and are not deformed. These veins likely developed during the later compressional events.

Bedding-vein relationships indicate southwest-side down kinematics and the mineralizing event may have occurred during early extension and development of the Merougil Basin.

Acknowledgements

Thanks to all the mine, resource and exploration geology teams for the ongoing field trips and useful discussions. Thanks also to David Douth for his insightful studies into the Invincible deposit.

References


Reverse shear, horizontal shortening and lode-gold mineralisation along the Mougooderra Shear Zone, Western Australia

Jamie J. Price, Tom G. Blenkinsop, Andrew C. Kerr
School of Earth & Ocean Sciences, Cardiff University, UK

Kathryn M. Goodenough
British Geological Survey, The Lyell Centre, Edinburgh, UK

Adrian J. Boyce
Scottish Universities Environmental Research Centre, UK

Clinton Kuehnapfel
Minjar Gold Pty., Golden Dragon Project, 70km S of Yalgoo, Western Australia

Abstract. Exploration for lode-gold deposits in the Archaean Yalgoo-Singleton greenstone belt of Western Australia is difficult, due to widespread, thick transported cover blanketing the bedrock from the surface. This study has employed detailed structural logging of core drilled along the unexposed Mougooderra Shear Zone, primarily from the 400 koz Silverstone deposit, in order to characterize the style of mineralisation present. Structural analyses at Silverstone reveal reverse kinematics of a steep (~65°) west-dipping shear zone, with associated veining of two principal types: foliation-parallel shear veins and extensional flat veins. Mineralisation conforms to the fault-valve model, whereby highly pressured fluids are responsible for reverse shear along a steeply inclined structure. Similar analysis on another deposit on a splay structure also demonstrates fault-valve style mineralisation, suggesting most lode-gold deposits in the belt formed during the same contractional episode. This is supported by preliminary S isotope data. A paragenetic study has revealed two discrete phases of gold associated with arsenopyrite and ullmannite (NiSbS) at Silverstone, associated with intense carbonate alteration in mafic and ultramafic host rocks. A better understanding of mineralisation style and paragenesis will help to provide a revised rationale to underpin exploration in a highly-prospective area.

1 Introduction

The Archaean Yilgarn Craton of Western Australia is recognised as one of the best-endowed geological terranes on Earth, hosting a diverse array of world-class orogenic-lode gold deposits. These lode-gold deposits have a range of common characteristics including a spatial association with regional structures, a distinct structural control and formation from low salinity aqueous-carbonic fluids. Previous research into lode-gold deposits across the craton has focused on the largest and well renowned deposits of the Eastern Goldfields, in the east of the Yilgarn Craton, and not fully investigated mineralisation in lesser endowed, but Figure 1. Simplified geological map of the central Yalgoo-Singleton greenstone belt, showing gold deposits, the Mougooderra Shear Zone.
nevertheless, highly prospective areas elsewhere.

The Yalgoo-Singleton Greenstone Belt (YSGB) is situated in the far west of the Yilgarn craton. The belt has a similar stratigraphy and deformational history as the Eastern Goldfields (e.g. Czarnota et al. 2010), but is currently host to fewer discovered gold resources. This may be attributed to minimal (<5%) outcrop, thick transported cover and a high degree of weathering, all of which make for a more difficult exploration environment (Watkins & Hickman, 1990).

Using a combination of structural logging of drillcore, oxide pit observations, and thin section analysis, the kinematics and style of lode-gold mineralisation present in the YSGB has been assessed and the mineral paragenesis determined. Such structural analysis is a crucial means of characterizing mineralisation and host structures, to ultimately aid future exploration in the region.

2 Geological setting

2.1 The Murchison Domain

The Murchison Domain is a relatively understudied region situated in the western part of the Yilgarn Craton, Western Australia. Its geometry represents a typical Archaean granite-greenstone terrane, with thin, north-west trending greenstone belts bound by vast swathes of felsic intrusives (Watkins & Hickman, 1990). The rocks of these greenstone belts record a complex and protracted history, including multiple phases of volcanism and sedimentation from 2960 Ma to 2720 Ma, each followed by deformation, metamorphism and the emplacement of felsic and mafic-ultramafic intrusive complexes (Van Kranendonk & Ivanic, 2009).

Recent structural mapping focused in the northeast of the domain has identified four major deformational events (D1-D4; Van Kranendonk et al. 2013), including a late stage of shearing along N-S structures (D4). The latest deformational phase, D4, is attributed as the main stage of formation of shear-hosted lode-gold deposits in the domain.

2.2 The Yalgoo-Singleton greenstone belt

The Yalgoo-Singleton Greenstone Belt (YSGB) is a ~120 km, north-south trending belt located in the southwest of the Murchison Domain (Fig. 1). The geology of the YSGB consists of multiple folded limbs of Neoarchean (2950-2800 Ma) supracrustal rocks, primarily felsic volcaniclastics and (ultra)mafic volcanics intruded by mafic-ultramafic differentiated sills (Ivanic et al. 2015). These units are overlain by the Mougooderra Formation, which comprises shale, sandstone and minor conglomerate. This undated metasedimentary package is 2-3 km thick and occupies the centre of the belt. The belt is bound by multiple phases of felsic intrusive rocks, and is dissected in the south by a post-tectonic monzogranite (Zibra et al. 2018).

Deformation in the belt is heterogenous, with narrow NNW-trending shear zones dissecting less deformed areas. The largest shear zone present, the Mougooderra Shear Zone (MSZ; Fig. 1), is a concealed ~60 km structure located at the boundary between the Mougooderra Formation rocks and underlying mafic-ultramafic volcanics and intrusives (Watkin & Hickman, 1990). Most discovered lode-gold deposits in the belt are situated along the MSZ, however, very little is known about the geometry and kinematic history of this unexposed structure.

3 Deposit-scale geology

3.1 The Silverstone deposit

The principal focus of this study, the 400 koz Silverstone deposit, is located directly on the MSZ (Fig. 2). The deposit currently consists of six oxide pits, extending 1.6 kilometres along strike, with 10-15 metres of transported cover at the surface. At Silverstone, the MSZ is moderate to steeply west-dipping resulting in a footwall that comprises shales of the metasedimentary Mougooderra Fm, and a hangingwall consisting of mafic-ultramafic units and interbedded shales. The latter units intersect the shear zone at an angle of ~20°, such that the hangingwall varies from ultramafic in the north, to mafic in the south (Fig. 2).

3.1 The Windinne Well deposit

The 100 koz Windinne Well deposit is situated on a N-S trending splay to the west of the MSZ within the greenstone package (Fig. 2). Mineralisation is hosted by
4 Structural analysis

Structural logging of drillcore has been undertaken in six holes intersecting the MSZ at Silverstone, and three holes at Windinne Well. Measurements have been taken for both planar features (foliations, bedding, veins) and linear features (mineral lineations, vorticity vectors), and corroborated with pit mapping of overlying oxide pits.

4.1 Silverstone

Our structural analyses at Silverstone identify a principal NNW-trending and west dipping (~65°) foliation, confirming the geometry of a metasedimentary footwall and mafic-ultramafic hangingwall to depths of at least 200 metres. In several instances, a steep down-dip mineral elongation lineation is found on foliation planes. Furthermore, a range of kinematic indicators, including quartz o-clasts, SC fabrics and sheared varioles (Fig. 3), reveal ubiquitous west-side up movement, demonstrating reverse kinematics of the MSZ. This is further supported by younging directions from graded bedding, with 5-10 metre scale isoclinal folding observed in the footwall metasedimentary units, and overturning of hangingwall units as they are transposed into the shear.

Two principal types of veining have been recorded at Silverstone: foliation-parallel shear veins and extensional flat veins. Cross-cutting relationships show a progression from early, foliation-parallel quartz-carbonate veins, to flat quartz-carbonate-sulphide veins and late calcite veinlets.

This vein geometry, along with reverse kinematics of a relatively steeply inclined structure, conforms to the fault-valve model of Sibson et al. (1988), requiring high pore fluid pressures to facilitate movement. In the fault-valve model, such highly pressured fluids develop near the brittle-ductile transition where pore spaces close and create an impermeable zone. Fluid pressure builds below this zone until pressures become high enough to induce failure along pre-existing structures (Sibson et al. 1988).

Some pyrite and arsenopyrite crystals are deformed into the foliation, whereas others occur as euhedral and undeformed crystals, consistent with mineralisation occurring in the late stages of shearing to post-shearing.

4.2 Windinne Well

At Windinne Well, a pervasive, steep (~80°), bedding-parallel foliation has been identified, in addition to a steep down-dip mineral lineation. Kinematic indicators, including sheared sulphide aggregates, demonstrate east-side-up sense of movement and thus near vertical reverse kinematics. Vein orientations are variable, but generally form two groups; bedding/foliation parallel and sulphide-bearing, shallowly inclined veins.

Similarities between Windinne Well and Silverstone deposits suggest they both formed via fault-valve behaviour, possibly as part of the same episode of crustal shortening.

5 Mineral paragenesis & gold occurrence

Our paragenetic study reveals the sulphide assemblage at Silverstone consists of pyrite, pyrrhotite and arsenopyrite, with minor chalcopyrite and ullmannite (NiSbS). In some parts of the ore zone, the sulphide assemblage is Sb-rich and relatively Fe-poor, with minerals including stibnite (Sb2S3), berthierite (FeSb2S3), chalcostibite (CuSbS2) and ullmannite, in place of the above typical sulphides.

There are at least two discrete gold bearing phases at Silverstone, comprising an early phase of euhedral arsenopyrite crystals (Fig. 4) and a later phase of gold-bearing antimony sulphides, typically ullmannite (Fig. 5). These observations are consistent along strike of the shear zone, with identical textures and associations to those at the Silverstone identified over 30 km south. Accessory minerals associated with gold mineralisation include rutile and monazite (phase 1), and scheelite and apatite (phase 2).

Alteration varies depending on the host protolith. For mafic protoliths, the alteration-assemblage is chlorite-sericite-albite-calcite, whereas in ultramafic protoliths to the north, the typical assemblage is talc-magnesite-fuchsite, with the localized development of listwaenite.


6 Preliminary sulphur isotope analysis

Preliminary conventional sulphur isotope analysis has been undertaken on a range of sulphide minerals from six deposits across the belt, primarily from those situated along the MSZ. A histogram of S isotope composition from samples along the MSZ is shown in figure 5. The collected δ34S data occupies a narrow range from -1.5 to +4.5 per mil, with most data from 0 to +4.5 per mil.

Four pyrite analyses from barren quartz-sulphide veins return values of +0.5 to -1.5 per mil, in contrast to pyrite associated with Au grade which measures +1.0 to +3.0 per mil. These values appear to be consistent both within the Silverstone deposit, and at other deposits along the length of the MSZ for 30-40 kilometres. Values for gold-bearing arsenopyrite are markedly higher than for pyrrhotite and pyrite associated with mineralisation – this is also consistent across the length of the shear zone.

The consistency of δ34S isotope data across multiple deposits supports structural analysis which indicates that mineralisation across the belt formed as part of the same contractional episode. It is plausible that variations in pH/fO2 is causing fractionation of sulphur isotopes as modelled by Ohmoto (1972) and Ohmoto & Rye (1979). It is unlikely that the variability in S isotope composition between earlier Au-bearing arsenopyrite and later pyrite is due to the tapping of multiple reservoirs.

7 Summary and conclusions

Deposits along the main Mughooda Shear Zone and those on second-order structures display reverse kinematics and fault-valve behaviour, and were likely formed as part of the same episode of crustal shortening. This is currently supported by preliminary S isotope data from deposits across the belt, which shows a consistent signature of +1 to +3 per mil for pyrite associated with mineralisation, and +4.0 to +4.5 per mil for gold-bearing arsenopyrite. Lode-gold mineralisation was replaced syn-shearing, as demonstrated by deformed sulphide aggregates and boudined arsenopyrite crystals. There is currently little evidence for strike-slip/transpressional strains commonly associated with lode-gold mineralisation elsewhere in the Yilgarn Craton.

At Silverstone, the ore zone has experienced intense carbonate alteration in both mafic and ultramafic protoliths, with a sulphide assemblage dominated by pyrite, pyrrhotite and arsenopyrite, but notably with an enrichment in Sb-bearing minerals. Two phases are directly associated with gold, comprising an early phase of arsenopyrite, and a later phase of gold associated with ullmannite (NiSbS).

Structural logging and analysis of oriented drillcore remains a crucial tool for understanding the geometry and style of mineralisation, especially in areas such as the Australian mid-west, where outcrop is minimal to nonexistent.

Acknowledgements

The authors acknowledge the support of Minjar Gold for providing access to drillcore, in addition to accommodation and logistical support during fieldwork. JP is supported by a NERC GW4+ Doctoral Training Partnership studentship from the Natural Environment Research Council [NE/L002434/1]. JP acknowledges the generous support of an SEG-CF grant towards fieldwork costs. Many thanks to Mrs. Alison McDonald for help during conventional S isotope analysis.

References


Stratigraphic and structural controls on Carlin-type mineralization in central Yukon (Canada)

Nicolas Pinet, Patrick Mercier-Langevin, Denis Lavoie, Benoît Dubé
Geological Survey of Canada, Canada

Patrick Sack
Yukon Geological Survey, Canada

Julia Lane
ATAC Resources limited

Abstract. Late Cretaceous Carlin-type mineralization at the Conrad prospect in central Yukon (Canada) is mainly hosted in Neoproterozoic limestone (and in a lesser amount in calcareous siltstone) in the core of a doubly-plunging anticline. The limestone unit is in fault-contact to the north and in stratigraphic contact to the south with non-calcareous siliciclastic units with low porosity and permeability. The upper part of the limestone unit that consists of lime mudstone, packstone, floatstone (deposited as debris flows) and calcareous siltstone and shale played an important role in channeling fluid flow. In more massive lithologies, fractured and brecciated intervals also focused fluid flow via the selective replacement of irregular and often complex pre-mineralization vein sets that were preferentially dissolved by acidic fluids early in the mineralizing process. Multiple feedback effects between sedimentologic, hydrothermal and tectonic parameters resulted in complex ore shapes and variable mineralization styles.

1 Introduction

Carlin-type deposits are formed from fluids often described as ‘passive’ or ‘opportunistic’ because the fluids are interpreted to have exploited a variety of pathways (Cline et al. 2005; Muntean 2018). The opportunistic nature of the fluids is mainly due to the relatively shallow depth (a few kilometres at most) of mineralization which results in a wide variety of ore zone shapes at the deposit scale.

In central Yukon, recently discovered Carlin-type orebodies are for the most part concordant with lithologic units at property scale (Tucker et al. 2018; Pinet et al. 2018; Pinet and Sack 2019). Orebody geometries are however more complex in detail and correlation between drill holes located a few tens of metres apart can be problematic. This study presents a reappraisal of the geometry and mineralization characteristics of the Conrad prospect. A similar approach for the nearby Sunrise prospect has been reported in Pinet and Sack (2019).

Figure 1. a. Geological map (simplified from Moynihan 2016). b. cross-section of the eastern Rackla belt in east-central Yukon

Gold from Orogenesis to Alluvial
2 Geological setting

Carlin-type gold prospects of central Yukon are located in the Rackla belt, a 5-15 km-wide fault and fold belt bounded to the north by the Kathleen Lake Fault and to the south by the Dawson Fault (Fig. 1A). The Rackla belt roughly coincides with the paleogeographic boundary between the Selwyn Basin and the Olgivie/Mackenzie Platform during the Neoproterozoic and part of the Paleozoic (Fig. 1A). This spatial coincidence suggests that depositional patterns were controlled by a major, long-lived, probably deep-seated, structure that may have been reactivated during mountain building. The succession is complexly folded and faulted (Fig. 1B) and experienced several phases of deformation (Steiner et al. 2018). Major faults have been interpreted as thrusts or backthrusts, but most of them bear a significant strike-slip component.

Carlin-type gold prospects in the eastern Rackla belt form the Nadaleen trend. Gold mineralization is predominantly hosted in Neoproterozoic limestones (with few mineralized intervals in siltstones) belonging to the Nadaleen and Gametrail formations (Windermere Supergroup; Moynihan, in press) and in mid-Paleozoic calcareous siltstones. The Conrad and Sunrise-Osiris prospects (cumulative inferred resource of 12.4 Mt at 4.23 g/t Au, 1.69 Moz Au; Atac resources website) exhibit characteristics consistent with Carlin-type mineralization including: i) host-sediments deposited in slope to base of slope settings; ii) alteration that includes partial to complete decalcification of mineralized intervals, and local silicification and argilization; iii) the ‘invisible’ nature of gold which occurs as rims of Au-bearing arsenian pyrite on pre-ore pyrite or as sub-micrometer particles; iv) the association of gold with Ti, As, Hg, Sb; v) the low base metal and Ag content (Tucker et al. 2018; Pinet and Sack 2019; Sack et al. 2019).

3 Conrad prospect

The Conrad gold prospect is one of the Neoproterozoic-hosted prospects in the eastern Rackla belt (Fig. 1). The host limestone unit forms the core of a doubly-plunging anticline and is in fault-contact to the north and in stratigraphic contact to the south with non-calcareous siliciclastic rocks with low porosity and permeability.

The oldest sedimentary unit is a vari-coloured thinly laminated mudstone and siltstone with quartz pebble conglomerate intervals. This unit is regionally correlated with the Ice Brook Formation (Moynihan et al., in press) and is found in the hanging-wall of the Nadaleen Fault, structurally overlying the Conrad prospect. The Nadaleen Fault is an east-striking, steeply-north-dipping (65°) fault with a damage zone up to several tens of meters in thickness.

In the footwall of the Nadaleen Fault, the limestone unit is a medium grey lime mudstone/wackestone (Fig. 2A) with some packstone (and minor grey to black siltstone). Toward the top of the limestone unit, close to the contact with stratigraphically overlying siliciclastic rocks, the succession is more diverse (Fig. 2B) and includes lime mudstone, packstone, floatstone and calcareous siltstone. Floatstone intervals (Fig. 2C) correspond to matrix-supported sedimentary breccia with angular fragments interpreted as debris flow deposits formed on a carbonate slope. Both the host limestone and the stratigraphically overlying siliciclastic rocks in the footwall of the fault are correlated with the Nadaleen Formation (Moynihan, in press).

Though the limestone host unit is poorly exposed, there is evidence of complex folding and faulting. Observations from diamond drill core indicate that the deformation style varies with rock competency. In the more massive and competent intervals, multiple generations of calcite (+dolomite/quartz) veins may locally represent up to 20% of the rock volume. In the more thinly bedded and less competent intervals, shearing on bedding planes and bed-restricted fractures predominate.

4 Mineralization

In the Conrad prospect, ore bodies are mainly hosted in: i) the steeply-dipping upper part of the limestone unit, close to its contact with stratigraphically overlying siliciclastics; ii) in the immediate footwall of the Nadaleen Fault; and iii) close to fault intersection zones (Fig. 3). Mineralized intervals are documented for 800 m along strike and to a minimum depth of 500 m. Contacts of mineralized zones are sharp and gold grades decrease from several ppm to background values in a few meters at most. Bedding is still visible close to, or even within, mineralized intervals.

Realgar and orpiment (±fluorite) are generally good visual guides for gold mineralization in the Conrad prospect. These minerals often post-date the main stage of gold mineralization. However, the spatial association of realgar and orpiment with gold mineralized intervals strongly suggests that these minerals formed in the late stage of a single event, not during a distinct hydrothermal pulse.

Decalcification is the main alteration type associated with gold mineralization and resulted in a significant increase of the rock porosity (Fig. 2H). The intensity of decalcification varies strongly, with some decimeter-scale intervals still reacting with HCl a few centimeters from decalciﬁed ore segments. Silicification and argilization are more discrete alteration styles.
Figure 2. Lithology, mineralization and alteration, Conrad prospect. Orange colors correspond to realgar. 

a. Typical lime mudstone interval with bedding parallel stylolites and several generations of calcite veins. 
b. mineralized alternation of finely laminated limestone and calcareous mudstone. 
c. mineralized matrix-supported floatstone interval. 
d. stratigraphic contact between a mineralized floatstone interval and barren limestone. 
e. realgar replacement of selected limestone beds and filling fractures and minor faults at high angle to bedding (S0). 
f. comparison between barren limestone with complex calcite vein sets predating the ore fluid event and a mineralized breccia. 
g. mineralized hydrothermal breccia with angular limestone clasts in a realgar-rich matrix. 
h. Thin section showing the increase in porosity (blue epoxy) due to decalcification. 
i. Mineralized gabbroic dyke with realgar and fluorite.

At the macroscopic scale, gold mineralization styles vary significantly, even in the same mineralized interval. These styles include selective replacement of mm- to cm-thick beds (Fig. 2E), mineralized fractures at high angle to bedding (Fig. 2E), preferential mineralization of matrix-supported floatstone intervals (Fig. 2D), dark, almost featureless decalcified intervals (high matrix-content debris flow deposits?), irregular veining associated with brecciated intervals and hydrothermal breccia (Fig. 2G).

A 0.25-4 m thick gabbroic dyke is intersected in drill holes, in the footwall of the Nadalen Fault. Assays from this Upper Cretaceous dyke (74.1 ± 1.0 Ma, Tucker et al., 2018) are commonly >1 g/t and the dyke is altered with realgar and fluorite (Fig. 2I). This evidence has been used to provide an older age limit for mineralization (Tucker et al. 2018). Recent LA-ICPMS U-Pb results on hydrothermal calcite associated with mineralization allow narrowing this time constraint and show that dyke intrusion was (within age uncertainties) syn-mineralization (Davis et al. 2019).

5 Discussion

In the Conrad prospect, the limestone unit forms a tight domal feature that constitutes a four way dip closure fold/fault trap for mineralizing fluids. The two low-permeability mudstone/siltstone units in fault (to the north) and stratigraphic (to the south) contact with the limestone acted as prospect-scale aquitards and exerted a first order control on fluid flow. Lithologic and structural parameters provided second-order control that resulted in complex ore shapes and variable mineralization styles (Fig. 3).

Interbedded lime mudstone, packstone, floatstone and calcareous siltstone in the upper part of the limestone unit are the most favourable host rocks for mineralization. A strong lithological control was also noted in the Sunrise prospect in which floatstone intervals are major hosts (Pinet and Sack 2019). Fracture density also influenced fluid flow. In most cases, fractures predate mineralization and highly fractured intervals are linked to specific beds, fault damage corridors or fold hinge zones. Fractures were infilled with several generations of calcite and dissolution of calcite by acidic, early stage mineralizing fluids resulted in increased porosity and permeability (Fig. 2H) which focused later gold-bearing fluids.

The factors favouring gold mineralization should not be considered separately as sedimentologic, hydrothermal and tectonic parameters show feedback effects which have resulted in complex ore shapes (Fig. 3).

Acknowledgements

ATAC Resource Ltd is thanked for the tremendous logistical and scientific support. This is a contribution to Natural Resources Canada’s Targeted Geoscience Initiative Program, Gold Project.
Figure 3. Schematic 3D view of the Conrad prospect. The shape of ore bodies (in orange) are schematic and mineralizing fluid pathways (green arrows) are interpretative. The internal geometry of the limestone unit is simplified and second order structural features are omitted for clarity.

References
Structural controls on ore formation at the Zaozigou gold-antimony deposit, West Qinling, China

Duncan C. McIntire¹, Kunfeng Qiu¹,², Haocheng Yu², Zongyang Gou², Richard J. Goldfarb¹,², Zhaoshan Chang¹

¹Colorado School of Mines
²China University of Geosciences

Abstract. Assessing the structural evolution of the large Zaozigou gold-antimony deposit in the context of the tectonic evolution of the Triassic West Qinling orogen can resolve important gaps in our understanding of the deposit formation.

Porphyritic ca. 250-215 Ma dacite intrusions intruded Triassic slates along existing planar features. Reaction skarns within the compositional layers of the slates, along with the loss of macroscopic foliation and genetic textures indicate contact metamorphism caused by the intrusions. As a the slates proximal to the intrusions became increasingly brittle and notably susceptible to faulting and fracturing.

Field relationships of local structures at the mine-scale indicate initial brittle faulting in a N-S orientation under a compressive regime, Shallow E-W striking faults are cut by steeply dipping ENE-striking faults, which in turn are cut by NE striking shallow faults, which are cut by a generation of NW striking shallow faults. All four fault generations are significant ore-bearing structures.

The relative timing of faults in the context of the northward convergence of the South China Block relative to the North China Block suggests that the ore-hosting structures at Zaozigou evolved through progressive counterclockwise rotation of the local principal stress axis. This was facilitated by dextral strike-slip movement along the regional Xiahe-Hezuo fault.

1 Introduction

The Zaozigou gold-antimony deposit in Gansu Province, China, is the largest actively producing gold deposit (118 t Au) in the southwestern domain of the West Qinling Orogen (Qiu and Deng 2017; Sui et al. 2019; Yu et al. 2019). The deposit is hosted by Triassic slates and, to a lesser degree, intrusive porphyritic dacite dikes. Gold is hosted within fault-hosted quartz+stibnite±dolomite lodes as well as in wallrock alteration haloes up to 20m wide. Wallrock alteration is dominantly sericitic, with illite and muscovite as the main alteration minerals. Chlorite and carbonate minerals are less abundant and minor wallrock silification is common. Wallrock alteration also includes disseminated arsenopyrite, pyrite, and stibnite, typically as selvages to quartz±sulfide veinlets. Textural evidence indicates that disseminated mineralization precipitated through sulfidation reactions between hydrothermal fluids and iron-rich mineral phases (biotite, chlorite).

Previous studies have described the meta-sedimentary ore-hosting rocks as silicified slates, as these rocks retain their compositional layering, but are notably more competent and less fissile than their unaltered slates located 2 km from the mine site. The “silicified” slates are only found in proximity to the Triassic dacite dikes in the area, which could suggest that magmatic-hydrothermal fluids had been responsible for the silicification of the slates. However, bulk rock geochemistry shows no significant increase in silica concentration over unaltered slates. Additionally, petrographic and infrared studies indicate of cordierite, scapolite, and andalusite are present solely in the “silicified” slate. It is therefore more likely that the influence of the Triassic intrusions was a thermal pulse leading to contact metamorphism of the slates and ultimately increasing the propensity for brittle deformation.

2 Structural controls on mineralization

The six most significant orebodies (M4, Au9, Au1, M7, M6, and M9) are manifest as quartz±stibnite±dolomite reverse fault-hosted lodes and veins. The hosting structures have been extensively measured and organized in the present study according to field observations of crosscutting relationships. The main faults are irregular, and typically 1-3m in width, although associated with narrower subsidiary faults with similar strike orientation but extremely variable dips. The fault margins commonly are characterized by brecciation. Primary quartz±stibnite±dolomite is hosted discretely within the bounds of major and minor faults and related veinlets. Mineralization is manifest as massive quartz and stibnite laminated lode veins with minor sulfidation of wallrock breccia clasts found within faults. The lode veins are juxtaposed with bleached wallrock alteration haloes up to 20m wide. Alteration is associated with disseminated arsenopyrite, pyrite, ±stibnite which is found in the highest proportions immediately adjacent to the primary-ore-hosting faults.

The orientation of structures follows a counterclockwise rotation from initial E-W striking structures to eventually NW-SE oriented structures (Fig. 1), in total representing a rotation of strike of 140°. However, the youngest generation of faulting may be associated with a separate tectonic event. If this is the case the fault orientations would have progressively rotated ~60° in a counter-clockwise direction. Microtextural relationships of stibnite within primary fault-hosted orebodies indicates syn-kinematic precipitation of stibnite. This would indicate ongoing sulfide mineralization of faults during the rotation of the major axis of compression.
The implications of syn-kinematic precipitation of primary fault-hosted sulfides suggest that mineralization occurred in pulses during the progressive deformation of Zaozigou, as described by Sibson (1988)’s fault valve model for quartz vein formation.

3 Tectonic evolution of Zaozigou in the context of the West Qinling Orogen

The tectonic history of the West Qinling Orogen in the Triassic is not universally accepted. Workers in the region generally favor a tectonic evolution in which the South China Block experienced northward subduction below the North China block (Kröner et al. 1993, Zhang...
et al. 2004, Zhang et al. 2001), however Dong et al. (2011) suggest the South China Block was moving towards ~30° northeast, while the North China Block was largely stationary. Both interpretations of the West Qinling tectonics could have produced structure and geometry observed at Zaozigou.

1). Purely northward movement of the South China Block colliding with the North China Block would have likely produced high angle reverse faults in the North Qinling terrane (Fig. 2). However, this would be at an angle with the Shangdan Suture Zone, likely resulting in dextral oblique reverse motion along the Shangdan Suture Zone, Guanyindazhuang-Lishishan Fault, and Xiahe-Hezuo Fault. Locally at Zaozigou, the dextral movement sense along the Xiahe-Hezuo fault would result in NW-SE primary compression. As collision between the South China Block and North China Block continued, the angle between the Shangdan Suture Zone and South China Block would decrease, resulting in a counter-clockwise rotation of local compressional axis at Zaozigou.

2). Movement of the South China Block toward 30° NE (Fig. 3) would result in a primary stress axis (σ₁) trending 30° NE to 210° SW. Secondary stress axis (σ₂) and minimum stress axis (σ₃) would be oriented perpendicular to σ₁. It is logical to conclude that σ₂ would

Figure 2. Schematic map of tectonic terranes of the West Qinling Orogen. Modified after Goldfarb et al. (2018).

Figure 3. Schematic map of tectonic units involved in the evolution of the West Qinling Orogen.
have been vertical, therefore $\sigma_2$ would be oriented such that the secondary stress axis would trend 120° SE to 300° NW. East-west striking reverse fault, M4 may have been produced by the initial N-S block movement, however as the resultant high-angle reverse faulting became progressively over-steepened, there would be a gradual transition from purely reverse faulting at the block convergence to oblique and eventually strike slip motion along the suture zone. The secondary stress axis related to the northeastern migration of the South China Block in the northwest and southeast West Qinling, would therefore become the local axis of greatest stress in the 120° SE to 300° NW orientation. The resulting strain would be shortening in a SE-NW direction, producing NE-SW striking reverse faults in brittle terranes.

4 Implications for exploration

High angle reverse faults striking NW-SE in proximity to the Xiahe-Hezuo fault should be considered highly prospective for economic gold mineralization. At Zaozigou faulting represents a dilational jog and transpressional environment at a major change in strike of the Xiahe-Hezuo fault. The Xiahe-Hezuo fault is likely a deep, regional scale fault which may be an important fluid conduit for metal-carrying metamorphic fluids. Rotation of the primary stress axis allows for multiple reactivation events along this shear zone in varying orientations. This allows for significant fracturing of rocks along the trend, and therefore increased fluid permeability, brecciation of basement rocks, and increased surface area for hydrothermal fluids to react with.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (41702069), and the Fundamental Research Funds for the Central Universities China (292018125, 292018141). We must also thank Zhaojin gold company and the Zaozigou mine staff for their hospitality and logistical support.

References


Metabasalts as sources of gold in Archean greenstone belts

Iain Pitcairn, Alexandre Peillod
Department of Geological Sciences, Stockholm University, Sweden

Clifford Patten
Institute for Applied Geosciences Geochemistry and Ore Geology Group, Germany

Jean Goutier
Ministère de l’Énergie et des Ressources naturelles, Canada

Carl Guilmette, Georges Beaudoin
E4m, Département de géologie et de génie géologique, Université Laval, Québec, Canada

Abstract. Abundant volcanic rocks in Archean greenstone belts have been suggested as potential sources of metals in Archean orogenic gold deposits. However, the behaviour of gold during the metamorphism of these rocks is poorly known. We present ultra-low detection limit gold analyses from a suite of variably metamorphosed samples from the La Grande subprovince, Québec, Canada. The median mass change value in the amphibolite and upper amphibolite facies sample sets compared to the greenschist facies samples is -56% and -79% respectively and 1 km³ of greenschist facies metavolcanic rock metamorphosed to amphibolite facies would produce around 2 tonnes of Au. These rock types are therefore potentially important metal sources for Archean orogenic gold deposits.

1 Introduction

The sources of metals in Archean orogenic gold deposits have long been debated. Suggested metal sources are wide ranging and include metamorphic devolatilisation of metasedimentary and metavolcanic rocks (Groves et al. 1998; Beaudoin and Pitre 2005; Gaboury et al. 2013), magmatic hydrothermal fluids (Burrows and Spooner 1985), meteoric fluids (Nesbitt 1991), the lower crust and sub-continental lithospheric mantle (Hronsky et al. 2012). In Phanerozoic orogenic gold systems, metasedimentary rocks are thought to be the main metal source with metal-bearing fluids being produced from these rocks during prograde metamorphic devolatilisation (Pitcairn et al. 2006a; 2015; Tomkins 2010). Archean deposits are hosted in granite-greenstone belts that are comparatively poor in metasedimentary rocks. These belts contain far greater abundances of volcanic than sedimentary rocks but it is unclear whether volcanic rocks have compositions appropriate for producing Au-rich metamorphic fluids during orogenesis. Tomkins (2010) showed that metamorphism of mafic rocks produces considerably less H₂S, the ligand which is required to transport Au during metamorphic devolatilization, and over a much smaller temperature window than sedimentary shales. Furthermore, mafic volcanic rocks are relatively poor in other elements such as As which are ubiquitously enriched in orogenic gold deposits (Tomkins 2010; Pitcairn et al. 2014; Patten et al. 2016).

Figure 1. Geological map showing the location of the La Grande subprovince in northern Québec, Canada. Samples were collected from the metavolcanic units in the Yasinski, Lac Gayer, and Rivière-La Forge areas. Modified from Sappin et al. (2018).

We report a set of major and trace element analyses including ultra-low detection limit Au analyses from a suite of metavolcanic rocks from the La Grande subprovince, Québec, Canada (Fig. 1). The metavolcanics rocks in this area show a strong metamorphic gradient from lower greenschist facies in the west of the terrane towards upper amphibolite facies in the east (Goutier et al. 2003; Gauthier et al. 2007). The results show the capability of metavolcanics rock to produce Au-bearing fluids during metamorphism and therefore the potential for these lithologies to be the sources of metals in Archean greenstone-hosted orogenic gold deposits.

2 Geological setting

The La Grande subprovince is located in the east-central
Superior Province, Canada (Fig. 1) and is composed of multiply deformed sequences of Archean volcano-sedimentary and plutonic rocks (Houlé et al. 2015). The La Grande subprovince comprises submarine volcanic sequences including 2820-2806 Ma Guyer Group (Goutier et al. 2002; David et al. 2012), the 2751-2732 Ma Yasisinski Group (Goutier et al. 2001), and sedimentary sequences overlying tonalitic gneiss basement (3452–2768 Ma; Davis et al. 2014), all of which is intruded by intermediate to felsic plutonic rocks (~2716–2709 Ma; Mercier-Langevin et al. 2012). The rocks in the La Grande area were subject to four major Archean-aged compressional deformation events (Goutier et al. 2001, 2003), and 3 associated metamorphic episodes (Goutier et al. 2003). A steeply dipping ENE trending D2 foliation is dominant in the area. The subprovince hosts the world-class Roberto gold deposit (~8.8 Moz Au; Fontaine et al. 2015) and several other gold and base metal mineral deposits.

3 Sampling and analytical methods

A suite of 90 samples was collected dominantly from the Yasinski, Guyer and La Forge groups. Weathered and mineralised samples were avoided. Precise metamorphic temperatures are not well constrained and so samples are grouped according to the metamorphic facies based on the bulk silicate mineralogy. The Yasinski Group samples comprise 4 subgreenschist, 32 greenschist and 16 amphibolite facies samples, the 18 Guyer Group samples are all amphibolite samples and the 10 La Forge Group samples are all upper amphibolite facies. Major and trace elements were analyzed by ALS Global and Au was analysed at Stockholm University following the ultra-low detection limit method of Pitcairn et al. (2006b) that has a 3σ detection limit of 0.02 ppb.

4 Geochemical classification of samples

The Yasinski Group samples comprise basalts (n=37; 45.1-53.2 wt.% SiO2), basaltic andesites (n=7; 48.6-56.1 wt.% SiO2), andesites (n=7, 58.2-62.1 wt.% SiO2), and dacite/rhyolites (n=2, 71.4-71.9 wt.% SiO2). The basalts show a tholeiitic to transitional affinity (Zr/Y<6.1 and Th/Yb<1.4, Fig. 2), the basaltic andesites and andesites a transitional to calc-alkaline affinity (Zr/Y>4.11 and Th/Yb>0.2), and the dacite/rhyolites a calc-alkaline affinity (Zr/Y>9 and Th/Yb>2.2; Fig. 2a). The Guyer Group samples contain basalts (n=5, 46.8-48.8 wt.% SiO2), basaltic andesites (n=3; 48-54.9 wt.% SiO2), andesites (n=4, 60.6-61.6 wt.% SiO2), and dacite/rhyolites (n=6, 68.6-70.9 wt.% SiO2). The basalts have a tholeiitic affinity (Zr/Y<3.6 and Th/Yb<0.8) and the basaltic andesites, andesites and dacite/rhyolite all have a calc-alkaline affinity (Zr/Y>4.7 and Th/Yb>0.9, Fig. 2). The La Forge Group is dominated by basalts (n=8; 46.7-50.5 wt.% SiO2) with one basaltic andesite (52.6 wt.% SiO2) and one andesite (61.6 wt.% SiO2) sample, and all except one are of tholeiitic affinity (Zr/Y<2.8 and Th/Yb<0.3; Fig. 2).

The volcanic rocks of the La Grande subprovince are suggested to have formed by interaction between a differentiated crust and Mg-rich magmas rising from a depleted mantle source (Seymour and Francis 1987; Skulski et al. 1988; Richer-LaFlèche et al. 2000; David et al. 2011; Sappin et al. 2018). The tholeiitic MORB-like basaltic samples are interpreted to be the erupted volcanic products of Mg-rich magmas emplaced at subcrustal levels with limited interaction with the differentiated crust (Sappin et al. 2018). The transitional to calc-alkaline magmatic series are interpreted to have formed from interaction between the Mg-rich magmas and the differentiated crust leading either to crustal contamination and assimilation fractionation processes or mixing between mantle-derived and lower crust anatectic melts (Skulski et al. 1988, Richer-LaFlèche et al. 2000; Sappin et al. 2018). There is no sharp transition between the tholeiites and the crustal contaminated calc-alkaline magmatic series but rather a continuum with increasing crustal components.

Figure 2. Geochemical characterization of the metavolcanic samples from the Yasinski, Guyer and La Forge groups from the La Grande subprovince, Québec, Canada. 2A: Na2O+K2O vs SiO2 diagram, 2B: Th/Yb vs Zr/Y diagram.
5 Discussion

5.1 Protolith composition and mass change during metamorphism

The metavolcanic rocks from the La Grande subprovince have undergone different magmatic processes and their primary Au content and therefore their potential for producing Au-bearing metamorphic fluids may vary significantly. The sub-greenschist and greenschist facies Yasinski Group samples are used to calculate the protolith metal contents for both the tholeiitic and calc-alkaline affinities. The tholeiitic basalts have median Au concentrations of 1.06 ppb, (range = 0.16-3.75 ppb) similar to modern day fresh MORB (median = 1.17 ppb, range 0.17-5.77 ppb). The decreasing Au content with decreasing MgO implies that Au behaves as a compatible element during the magmatic differentiation and suggests that the melt is sulphide saturated. The calc-alkaline series have higher Au content (median = 1.62 ppb, 0.45-20.1 ppb) and different distribution than the greenschist tholeiitic basalts and fresh MORB (Fig. 3). Gold concentration in the calc-alkaline magmatic series increases with decreasing MgO implying an incompatible behavior during magma-crust interaction by assimilation fractional crystallisation.

Magmatic differentiation curves for Au are calculated both for the tholeiitic and the calc-alkaline series from the greenschist samples of the Yasinski group. These magmatic trends are used to calculate mass variation associated with metamorphism for the Yasinski, Geyer and La Forge Group samples. The mass change in Au relative to these magmatic differentiation curves is calculated for each sample using the method described in Jowitt et al. (2012) using the following relationship:

$$\Delta Au = Au_c - Au_s$$

where $\Delta Au$ is the Au mass change, $Au_c$ the calculated protolith Au composition based on the MgO composition and position on the magmatic differentiation curve and $Au_s$ the measured Au value (Fig. 4). The median mass change value in the amphibolite and upper amphibolite facies sample sets compared to the greenschist facies samples is -56% and -79% respectively (Fig. 4). Both tholeiitic and calc-alkaline series rocks show significant depletions in Au in the amphibolite and upper amphibolite facies samples. Assuming an average composition of 1.3 ppb Au (based on a composition of 50% tholeiitic and 50% calc-alkaline affinity), an average density of 2.8 g/cm³, and an Au mass loss of -56%, 1 km³ of greenschist facies metavolcanic rock metamorphosed to amphibolite facies would produce around 2 tonnes of Au. Of the other elements commonly enriched in orogenic gold deposits such as S, As, Sb, Bi, Te, none of them show any significant mobility during metamorphism with the exception of As which shows slight decreases in concentration with increasing metamorphism. However, the As concentrations in the greenschist facies metavolcanic rocks of 0.45 ppm are more than an order of magnitude lower than concentrations in metasedimentary rocks of the same metamorphic grade (e.g. Pitcairn et al. 2017).

5.2 Implications for sources of metals in Archean greenstone-hosted orogenic gold deposits

Their abundance in greenstone belts combined with the observed mobility of Au in these rocks during metamorphism indicate that metavolcanic rocks can be important potential sources of Au in Archean greenstone belt hosted orogenic gold deposits. In large Archean greenstone belts such as the Abitibi belt in Canada that comprise around 40% metavolcanic rocks on surface, more than 100000 km³ of higher metamorphic grade metavolcanic rocks are interpreted to occur at depth (e.g. Kerrich and Ludden 2000). The fertility of the metavolcanic rock with respect to Au may vary
considerably. Our results show different fertilities for Au between the calc-alkaline and tholeiitic series in the La Grande subprovince. The behaviour of S during magmatic differentiation also strongly controls the availability of chalcophile elements for later metamorphic remobilization with sulfur undersaturated volcanic rocks commonly showing higher Au concentrations (Patten et al. 2016). Plume-related volcanic rocks are also known to have higher concentrations of gold (Webber et al. 2013; Pitcairn et al. 2014). The mass change for Au in other more fertile terranes may be considerably greater than reported here for the La Grande.

The lack of mobility of other elements enriched in orogenic gold deposits such as As and Sb indicates that metavolcanic rocks are unlikely to be the only source rock. Metasedimentary rocks are likely to be important sources of Au and the main source of As, Sb and S (Pitcairn et al. 2017). Magmatic hydrothermal fluids may be important local sources of metals in deposits enriched in Mo, Bi and Te (Pitcairn et al. 2017). Deposits formed from predominantly metavolcanic source rock should therefore show distinct compositions such as having much higher Au:As than deposits formed from metasedimentary source rocks. Interestingly, orogenic gold deposits in Archean greenstone belts that are As and Sb rich tend to be sediment hosted (e.g. the Roberto deposit) whereas those that are hosted in volcanic rocks are commonly relatively As and Sb poor.

Acknowledgements

We acknowledge funding from Natural Resources Canada and Fonds de Recherche du Québec Nature et Technologies (FRQ-NT).

References

Beaudoin G, Pitre D, 2005. Stable isotope geochemistry of the Archean Val-d’Or (Canada) orogenic gold vein field: Min Dep 40:59-75


Gaboury, D, 2013. Does gold in orogenic deposits come from pyrite and Sb rich tend to be sediment hosted (e.g. the Roberto deposit) whereas those that are hosted in volcanic rocks are commonly relatively As and Sb poor.


Jenner FE, O’Neill HSC, 2012. Major and trace analysis of basaltic glasses by laser-ablation ICP-MS. Geochemistry, Geophysics Geosystems 13


Patten CGC, Pitcairn IK, Teagle DAH, Harris M, 2016. Mobility of Au and related elements during the hydrothermal alteration of the oceanic crust: implications for the sources of metals in VMS deposits, Min Dep 51:179–200


654 Life with Ore Deposits on Earth – 15th SGA Biennial Meeting 2019, Volume 2
Abstract. The Neoproterozoic-Cambrian Dalradian Supergroup in Northern Ireland is host to significant Au mineralization: the largest deposit discovered to date is Curraghinalt (>6 Moz*, SRK Consulting (Canada) Inc., 2018), 17km NE of Omagh, characterized by WNW-ESE trending pyritiferous quartz-carbonate veins dipping c. 55-70° to the north. Petrographic examination of vein pyrite and analysis by Laser Ablation Inductively Coupled Plasma – Mass Spectroscopy (LA-ICP-MS) reveals four distinct generations of pyrite (Py1-4) that record a history of emplacement and modification during the Grampian orogeny (475-460 Ma). Py1 within early veins is broadly aligned with regional S2/S3 Grampian fabrics and records an early Zn-Ni signature (Median Zn 5,030 ppm; Ni 2,410 ppm). Py2 overgrowths have an entrained schistosity indicating growth during prograde development of S2/S3 fabrics; Au is elevated in Py2 with a median of 3.69 ppm (IQR 2.02-10.1 ppm) and is coincident with elevated Co and Ni. Py3, occurring within the vein swarm cutting the host penetrative fabric, exhibits elevated Ni (median 134 ppm, IQR 20.4-395 ppm). Electrum is encountered along fractures of Py3 that have been healed by auriferous pyrite (Py4) that exhibits a Bi-Te signature. Geochemically constrained pyrite can be a useful tool for targeting of Au mineralization across orogenic belts.

1 Geological context

Vein-hosted auriferous deposits occur in Ireland and in central Scotland, constrained within rocks of the Dalradian Supergroup.
tectono-stratigraphic terrane. This late Neoproterozoic to Cambrian succession is composed of siliciclastics, limestones and mafic volcanics which were deposited on the Laurentian margin between the late Neoproterozoic and Cambrian (c. 800-510 Ma; Daly et al., 2009).

During the Grampian Orogeny, an arc-continent collisional phase of the Caledonian Orogenic Cycle (475-405 Ma) which ultimately led to the closure of the Iapetus Ocean, the Dalradian Supergroup underwent polyphase deformation, reaching upper-greenschist to amphibolite facies metamorphic conditions (Fettes, 1979). Peak pressures and temperatures at upper greenschist facies were recorded in the Sperrins region of Northern Ireland at approximately 468 Ma (Chew and Stillman, 2009). The southern extent of the terrane is demarcated by a major SW-NE trending structure known in Ireland as the Fair Head – Clew Bay Line (FH-CBL), which is contiguous with the Scottish Highland Boundary Fault (HBF).

Occurrences along strike to the SW and NE of Curraghinalt are being actively explored, while active mining is taking place at Cavanacaw, approximately 30km to the south-west. Stratigraphically contiguous gold occurrences in Ireland are also recognized along the belt in the Ox Mountains of Co. Sligo.

Gold distribution in the Sperrin mountains region is considered to be influenced by the presence of three principle regional structures: the SSW-NNE trending Omagh Lineament, the SW-NE trending Omagh Thrust and the Sperrin fold (ESE-WNW to SE-NW axial trace), an F2 recumbent antiform (Earls et al., 1996); at Curraghinalt, E-W trending dextral strike-slip structures control the distribution of auriferous quartz veins.

2 Petrography

2.1 Pyrite

The sulfide mineralogy across the Curraghinalt deposit is dominated by pyrite, accompanied by chalcopyrite and galena. Of these, pyrite is the most abundant sulfide mineral and is observed within all vein types and in altered wallrock. A variety of pyrite morphologies ranging from 10 microns to over 1mm in size have been recognised, these include euhedral grains, overgrowths and healed fractures. Specific generations of pyrite have been recognised using petrographic and microanalytical criteria, herein designated as Py1-Py4; Py3-4 are ore-stages associated with discrete phases of visible gold in the form of electrum.

Py1 with distinct overgrowths (Py2) (see Fig. 3A) are identified within angular, subhedral grains located within veinlets dominated by carbonate, sulfide and minor quartz. Growth of Py2 with entrained minerals developing along the S2/S3 fabric suggests that these veins are the earliest recognised at Curraghinalt. Py1-Py2 grains are sub-millimetric in scale and bear late cross-cutting fractures. Py1 is largely homogenous in appearance while close inspection reveals micro-inclusions of galena and sphalerite occurring as clusters or aligned trails, suggestive of metasomatic alteration and distortion of the host crystal lattice. Within Py2, inclusions of ankerite and silicates exhibiting alignment to the crystal boundary and enveloping schistosity are observed. Visible gold is encountered in microfractures associated with major fractures cross-cutting both Py1 and Py2.

Py3 occurs within ‘D’ quartz veins (see Fig. 3B) cutting the penetrative S2/S3 fabric of the host rock and is associated with post-peak metamorphic conditions. Grains are euhedral to anhedral, may have angular or rounded edges and are coarse grained (<1 mm in size). In many observed veins, Py3 occurs as large (millimetric), cataclastic masses characteristic of abrupt brittle deformation. This phase carries irregular electrum inclusions within the grains themselves, observed at <30 µm in diameter, or as elongate blebs along boundaries and within micro-fractures. Microfractures appear to have been healed by pyrite (Py4), though this is petrographically indistinguishable from Py3.

Figure 3. (A) Reflected light image of Py1 and Py2 overgrowth phase in S2/S3 fabric-parallel vein comprised of ankerite and quartz (sample CT12, drill-hole 11-CT-99, 819.04-819.24m); (B) oblique spatial relationship of quartzose vein hosting ore-phase Py3 with the S2/S3 fabric of the host rock in sample CT20 (drill-hole 16-CT-342, ‘Grizzly’ vein zone, 199.83-199.93m).

Disseminated pyrite porphyroblasts (<50 µm) are also observed in the wallrock, in close alignment with fabrics, occurring proximal to auriferous veins hosting Py3. Fabric relationships and trace element geochemistry suggest that this phase is Py2.

2.2 Visible gold

Energy dispersive spectroscopic analyses (EDS/EDX) (n=23) of electrum associated with ore-stage Py3 in samples from the central and lower veins reveal mean concentrations of 86.05 wt.% Au and 11.12 wt.% Ag. Where inclusions are observed which may be associated with late healing phase Py4 (within micro-fractures), concentrations of gold are close to the overall mean for the sample set, at 86.14 wt.% Au, with 10.88 wt.% Ag.
Inclusions of electrum tend to be more argentiferous in central vein sampling (with average concentrations of 76.18 wt.% Au, 19.45 wt% Ag), than those observed in the lower swarm (averaging 87.20 wt% Au, 11.89 wt.% Ag).

Electrum was also encountered along the boundaries of Py3 grains within more brecciated vein samples in the lower swarm, where inclusions are less common. Concentrations for this type averages 87.9 wt.%, with a narrow range of between 87.9 to 88.1 wt.%.

Zoned inclusions (see Fig. 4) are observed within the central veins containing a Bi-telluride and electrum component, while a Ag-Te rim is also visible for some Bi-tellurides (averaging 60.24 wt.% Ag). This inclusion type is most common in samples from the central part of the deposit. In lower swarm samples, such inclusions are less common, and electrum tends to be most pervasive at junctions of fractures and along grain edges. Observations suggest a coeval relationship between Au, Ag, Bi and Te, particularly within central veins where tellurides are more common.

3.2 Py2 development

A bimodal distribution of Au is recognized within in-situ data collected, with a median value across the Py1-3 dataset (n=149) of 0.23 ppm Au (IQR 0.09-0.98). The highest median value of Au is observed within Py2 (3.69 ppm Au, IQR 2-10.1 ppm, n=34), with a maximum recorded value of 39.1 ppm Au. Conversely, ore-stage Py3 exhibits relatively low Au contents.

The presence of Au within Py2 confirms that an auriferous fluid was active within the system prior to mineralization within ore-stage Py3, constrained by previous workers to a maximum 10 Myr interval (462.7 - 452.8 Ma; Rice et al., 2016). This interval post-dates peak metamorphism contemporary with the final stages of Grampian arc-continent collision at 468 Ma.

LA ICP-MS depth profiles for spot analyses show homogenous levels of trace elements, lacking distinct spikes in Au supporting the presence of lattice bound Au in Py2.

3.3 Ore-stage: growth of Py3-Py4

LA-ICP-MS element mapping of Py3 grains (see Fig. 7) reveals enrichment of Ni (median = 134 ppm, n=137) and oscillatory element variations for both Ni and Co; in-situ analyses record interquartile ranges of 20.4-395 ppm for Ni and 10.2-260 ppm for Co. This record of compositional zonation suggests varying physio-chemical conditions during pyrite growth in this phase.

Elevated Au levels and coincident Bi and Te along with discrete electrum occur independently of lattice bound signatures (Ni-Co) in Py3 and cross-cut oscillatory growth zones. Such enrichments are found within fractures and cataclastic zones healed by pyrite (Py4), cross-cutting Py1, Py2 and Py3. This phase is petrographically indistinguishable from earlier phases, but is indicated by local enrichments in Au, Bi and Te along linear features.
that a change from a Zn-Ni fertile source (Py1) to one bearing a Au signature is recorded early (Py2) in the paragenetic sequence of pyrite. We propose that Au was mobilized with Bi and Te coincident with post-peak metamorphic conditions into late fractures which cross-cut Py1-3.

The timing of auriferous fractures post-Py3 suggests metamorphic devolatilization reactions, which release H2O, S, CO2 and Au during orogenesis, as a likely mechanism for the mobilization of Au into these fractures; such fluids migrate preferentially into pre-existing shears and fracture zones (Phillips and Powell, 2010). We propose that paragenetically constrained pyrite in Dalradian strata records a geochemical fingerprint (Au-Bi-Te) of orogenic fluids depositing Au across the Grampian orogen and may have practical use as an exploration tool for the prediction of Au emplacement.

Acknowledgements

We are grateful to Dalradian Gold Ltd. for access to the Curraghinalt drill-core inventory, for their contributions, feedback and support. At the Trinity College Dublin Geology Department, we would particularly like to thank Cora McKenna, Gary O’Sullivan, Thomas Riegler, Paul Guyett, David Chew, Colin Reid and Leona O’Connor whose advice was much appreciated. This study is funded through the Irish Centre for Research in Applied Geosciences (iCRAG) by Science Foundation Ireland (SFI) (grant number 13/RC/2092) together with European Development Funds and industry funding partners.

References


* The 2018 resource update (SRK Consulting (Canada), 2018) reports 6.35 Mt at 15.02 g/t for 3.066 Moz contained Au in the indicated categories, with 7.72 Mt at 12.24 g/t for 3,038 Moz contained Au in the inferred category. Further details are available at https://dalradian.com/curraghinalt-project/resources/
Gold mineralization in the Mesoproterozoic Karagwe-Ankole belt (Byumba, Rwanda): new insights from petrography and trace element mapping

Sander Wouters, Philippe Muchez
KU Leuven, Department of Earth & Environmental Sciences, Belgium

Stijn Dewaele
Ghent University, Department of Geology, Belgium

Pim Kaskes, Philippe Claeys
Vrije Universiteit Brussel, Department of Chemistry, Analytical, Environmental and Geo-Chemistry, Belgium

Abstract. A recent increase of interest in the various mineral deposits of the Central African Karagwe-Ankole belt (KAB) has led to many new discoveries and exciting research. Gold deposits in the KAB still have many unanswered questions concerning their formation conditions. The aims of this research are to determine the controlling factors on gold distribution at the Byumba deposit (Rwanda) and to resolve the relationship between the different vein generations and the tectonic evolution of the area. To achieve this, drill cores from the Byumba deposit were logged and sampled for further petrographic research and major and trace element mapping. Micro X-ray fluorescence (µXRF) is used for the identification and distribution of gold and of different types of alteration/mineralization. Five main phases of quartz veining are identified which can be linked to the different phases of deformation that are recognized in the KAB. Important phases of folding and shearing are distinctly present at Byumba and associated with sericitization and chloritization. Sulfides are predominantly present in the form of pyrite, with minor associations of arsenopyrite, chalcopyrite, pyrrhotite and covellite. Primary gold mineralization seems to be correlated to chlorite-rich shear veins. Gold occurs within an early quartz phase and not associated with pyrite.

1 Introduction and geological setting

Gold mineralization in the Central African Karagwe-Ankole belt (KAB) has been the subject of much debate (Brinckmann et al. 1994; Pohl et al. 2013; Koegelenberg et al. 2016). Notwithstanding decades of research, uncertainties concerning the metal source, fluid evolution and timing of the gold mineralization remain. In addition to gold, the Mesoproterozoic KAB is known for hosting spatially associated Nb-Ta, Sn and W deposits, making it an important metallogenic province in Central Africa (Pohl and Günther 1991; Fernandez-Alonso et al. 2012). It encompasses the eastern part of the Democratic Republic of Congo (DR Congo), northwest Tanzania, southwest Uganda, Burundi and Rwanda. Investigations after the metal source for the Nb-Ta-Sn-W mineralization hosted in pegmatites, greisens and peribatholithic quartz veins revealed a genetic link between the Nb-Ta-Sn-W mineralization and the early-Neoproterozoic leucogranites (Dewaele et al. 2011; Hulsbosch et al. 2016).

Central African orogenic gold mineralization has in general been linked to fold-and-thrust belt formation (Brinckmann et al. 1994; Koegelenberg et al. 2016). An exact age for this deformation stage and associated gold mineralization is however still under debate. Koegelenberg et al. (2015) defined an age of ~1326 Ma in the eastern domain of the KAB, where gold mineralization in north-western Tanzania is clearly not associated with magmatic intrusions (Koegelenberg et al. 2016). In contrast, a late Mesoproterozoic (1000-950 Ma) deformation is proposed by many different studies (Tack et al. 2010; Fernandez-Alonso et al. 2012; Pohl et al. 2013). The overlap in timing between deformation and G4 granite magmatism at 986 ± 10 Ma (U-Pb SHRIMP on zircons from the DR Congo; Tack et al., 2010) may suggest a possible genetic link. Important pegmatite Nb-Ta-Sn mineralization is associated with the latter...
magmatism (Hulsbosch et al., 2016); as well as the W-Sn vein-type deposits (Dewaele et al. 2015). Fluid inclusion studies of Sn, W and Au quartz veins by Pohl and Günther (1991) suggest that as opposed to Sn and W, Au mineralization is not caused by the 986 ± 10 Ma G4 magmatism, but related to deep crustal metamorphism. The latter would have been induced by crustal thickening immediately preceding granitoid magmatism and associated mineralization. In addition, there are ferruginous breccia zones which have been dated at 640 ± 28 Ma and are linked to Pan-African events (Rb-Sr muscovite-tourmaline; Brinckmann et al. 1994). Also Ar-Ar dating of muscovite from quartz-sulfide-gold saddle reefs at the Twangiza deposit (Kivu, DRCongo) gives a Pan-African age of 522 ± 15 Ma (Ar-Ar; Walemba 2001).

To resolve this long-lasting discussion, the study of the gold occurrence at the Byumba deposit (Rwanda) forms a great opportunity to investigate the gold distribution and its relationship with the typical veins, minerals and tectonic evolution of the KAB. In this study, µXRF element mapping is used for the identification and distribution of gold and the relationship with different types of alteration/mineralization.

2 Methodology

The Byumba gold deposit is situated ~40 km NNE of Kigali in the northern part of Rwanda, and was recently discovered by Desert Gold Ventures Inc. (Figure 1). Detailed core logging was performed on explorative drillings from the Byumba site with a focus on lithological variations, alteration, deformation structures, different vein generations and their relation to the ore grade. In total 9 drill cores (~1800 m) were logged and sampled for further petrographic investigation with thin and polished sections.

The major and trace element distributions and semi-quantitative abundance within thick, thin and polished sections were mapped using the Bruker M4 Tornado Micro X-ray fluorescence (µXRF) scanner, available at the Vrije Universiteit Brussel (de Winter et al. 2017). The measurements were executed using a Rh source and two XFlash 430 Silicon Drift detectors under vacuum conditions (20 mbar), with short acquisition times per spot size (1 ms per 25 µm) and maximized source energy settings (600 µA, 50 kV). No sample coating is required and the method is fully non-destructive. This high-resolution technique offers the opportunity to search for “invisible gold”, which is gold that could not be detected by means of standard petrographic microscopy.

3 Results and discussion

3.1 Lithology, vein generations and tectonic setting

Lithologically, the drill cores of the Byumba deposit consist of alternations of sand- to siltstones with organic-rich shales. Multiple quartz vein generations are identified within these metasediments, which underwent intense folding and shear deformation (see Figure 2a). Cleavage is well developed and dominantly axial planar. In mica-rich phyllites the cleavage can be crenulated. Alteration at the Byumba deposit is present in the form of pervasive chloritization, some sericitization, silicification and carbonatization.

The first quartz vein generation in the paragenesis of
the Byumba deposit is parallel to and folded along with the bedding, which is indicative of a pre-folding origin. Massive quartz veins, concentrated in the hinge zones of folds, are associated with massive pyrite and represent a second generation of veining, which is related to folding. In addition, some irregular and thin chlorite-rich veins also occur in fold hinges, but they have a more widespread distribution in the metasedimentary rocks. A third generation of quartz veins is found in fault-related fractures or along the faults themselves. Fourth generation quartz veins occur parallel to the cleavage and may occasionally be boudinaged, which indicates formation after folding and cleavage development. This quartz vein generation also crosscuts the sandstones at an angle of 45°-60°. This orientation gives these quartz veins, in combination with the cleavage parallel-nature of the veins, a sigmoidal geometry. Based on mineralogical variations, a minimum of two distinct sigmoidal quartz vein generations can be identified. The earliest generation is primarily composed of quartz, chlorite and sericite. Sigmoidal quartz and Fe-rich carbonate veins crosscut the former, implying a younger age. The presence of shear zones and sigmoidal quartz veins are an expression of a distinct shearing phase which post-dates folding and cleavage development. Intense chloritization and silicification and the occurrence of C'-type shear bands are related to this shearing. Meter-thick massive quartz veins which crosscut the folds, cleavage and the aforementioned quartz generations represent a final vein generation. Host-rock fragments are frequently enclosed inside these veins, which therefore embody a brecciation phase.

3.2 Mineralization

The main sulfide mineral at the Byumba deposit is pyrite. Other sulfides include arsenopyrite, chalcopyrite, pyrrhotite and covellite. Numerous pyrite generations occur in the metasediments and quartz veins. Many of these pyrites show evidence of resorption and sieve textures. Early pyrite generations are anhedral and contain inclusions of chalcopyrite. The presence of quartz-filled pressure shadows surrounding some of these pyrites is evidence for a pre-deformation origin. Euhedral pyrites are younger and associated with inclusions of pyrrhotite (see Figure 2c). Several of the later pyrite generations are associated with folding and shearing deformation phases. A distinct correlation between the late shear-related carbonatization and large euhedral pyrites illustrates this relationship.

Logging of the gold grade distribution revealed a correlation between shear zones and the gold content. This is further evidenced by μXRF results which show that the gold is hosted by an early dark grey quartz phase inside chlorite-rich shear veins (see Figure 3). Gold is often present in the form of invisible gold inside quartz but has very occasionally been microscopically observed as small disseminated blebs. The dark grey quartz phase which hosts the gold is an early expression of silicification in the generation of shear quartz veins. The milky white quartz is a later quartz phase of the same shear vein generation. None of the different pyrite generations present in the shear veins show an enrichment in gold on the element maps. No gold has been microscopically observed in the sulfides. In addition, μXRF shows a correlation between the gold and arsenic content of enriched zones inside the quartz veins and the host rocks. The latter may also be expressed by the presence of arsenopyrite inside the shear veins.

Gold blebs are also found at sandstone/shale lithological contacts (see Figure 2b). These are difficult to place in the paragenesis of mineralization due to their disseminated nature and non-association with a specific mineral phase. A secondary gold enrichment stage may be proposed by the presence of the high ore grade at the oxidation/reduction zone boundaries at specific depths in the studied drill cores.

4 Conclusion

The relative timing, paragenesis and character of the different quartz vein generations at the Byumba deposit can be compared with quartz veins studied at other deposits in Rwanda. At the Nyakabingo W-deposit, three different types of quartz veins are identified (Dewaele et al. 2016), which may correspond to the pre-folding and the often massive cleavage parallel shear veins observed in this study. The folding of the metasediments and early
quartz vein generations indicate a pre- to early orogenic origin for the latter. After folding and cleavage development a pervasive phase of shearing causes the formation of the cleavage parallel or sigmoidal quartz veins. The aforementioned shearing, which is also associated with brecciation, is recognized in various deposits around the KAB (Pohl and Günther 1991). W and Sn mineralization thus shows similar pre- and syn- to post-deformation veins as found at the Byumba gold deposit, but a direct correlation is still difficult to make.

Gold occurs in the form of invisible gold and in the form of small disseminated blebs. The presence of gold is accompanied by an enrichment in the arsenic content of the quartz and the presence of arsenopyrite. The observed textures of the pyrite point to sulfide recrystallization and remobilization which is often associated with low gold content in orogenic-type and metamorphosed gold deposits (Cook et al. 2009). Supergene enrichment of gold is identified at oxidation/reduction zone boundaries based on the ore grade variation inside the boreholes. Secondary gold mineralization is also identified by Brinckmann et al. (1994), which links the redistribution of the gold to Pan-African structural reactivation.

Acknowledgements

We would like to thank Desert Gold Ventures Inc., Francis Gatare and Alain Ntenge from the Rwanda Mines, Petroleum and Gas Board for their collaboration and contribution. This research is financially supported by Research Grant C14/17/056 of the KU Leuven Research Fund. P. Claeyx thanks Research Foundation Flanders - Hercules Program for financing the Micro-XRF instrument

References

Koegelenberg C, Kisters AFM, Kramers JD, Frei D (2015) U-Pb detrital zircon and ⁴⁰Ar-³⁹Ar muscovite ages from the eastern parts of the Karagwe-Ankole Belt: Tracking Paleoproterozoic basin formation and Mesoproterozoic crustal amalgamation along the western margin of the Tanzania Craton. Precambrian Res 269:147–161
Walemba KMA (2001) Geology, geochemistry, and tectono-metallogenic evolution of neoproterozoic gold deposits in the Kadubu area, Kivu, Democratic Republic of Congo.Faculty of Science,University of the Witwatersrand
The source of Au in Paleoproterozoic orogenic gold deposits: insight from the Central Lapland Greenstone Belt, Finland

Patten C.G.C., Kolb J.
Institute for Applied Geosciences, Department of Geochemistry and Ore Geology, KIT, Karlsruhe, Germany

Molnár F.
Geological Survey of Finland, Espoo, Finland

Pitcairn I.K.
Department of Geological Sciences, Stockholm University, Stockholm, Sweden

Abstract. Paleoproterozoic greenstone belts are prospective terranes for orogenic Au deposits worldwide and yet the source areas of the metals enriched in these deposits are not well characterized. In this study we investigate the role of metavolcanic rocks as the potential source of Au in the Paleoproterozoic Central Lapland Greenstone Belt, Finland. The metavolcanic rocks in this belt show mainly MORB and WPB character. The WPB have higher primary Au content than MORB due to a plume component. Using fresh MORB and WPB data as proxy for protolith composition, mass variation calculation shows that up 68±39% of the initial metavolcanic Au content is lost during upper amphibolite facies metamorphism (>550 °C). Mass balance calculation indicates that up to ~2640 t of Au has been mobilized during metamorphism which is one order of magnitude higher than the ~280 t Au endowment in the deposits. Metavolcanic rocks appears thus as fertile sources for Au in Paleoproterozoic greenstone belts. Moreover, this study highlights the importance to consider the type of metavolcanic rocks present within greenstone belts as they partly control the Au fertility of the source areas.

1 Introduction

Orogenic gold deposits are the product of complex large-scale processes which include the production of metal-rich fluids, the transport of these metal-rich fluids through the Earth’s crust, and the precipitation of the metals in structurally controlled sinks at various degree of metamorphism (Pitcairn et al. 2006a; Kolb et al. 2015; Goldfarb and Groves 2015). Recognition of geological formations as sources of metals, ligands or ore-forming fluids is an important step for understanding hydrothermal ore deposit formation. Although the mechanisms responsible for Au precipitation in orogenic gold deposits are fairly well constrained, the sources of the metals are still debated (Goldfarb and Groves 2015). In Phanerozoic orogenic gold deposits, metasedimentary units are the principal Au source (Pitcairn et al. 2006a, 2015) but in Precambrian greenstone belts, the scarcity of metasedimentary rocks and the abundance of metavolcanic rocks hint that the latter could also be a potential Au source (Goldfarb and Groves 2015; Augustin and Gaboury 2017). However, this has not been clearly demonstrated yet.
metasedimentary rocks and the metavolcanic rocks are characterized by komatiites, WPB and minor MORB. It is interpreted that these rocks were deposited in the continental margin rift zones of the Karelian craton (Hanski and Huhma 2005). The CLGB displays a relatively complex metamorphic pattern but it can be simplified into a zonation where the core of the belt is metamorphosed to greenschist facies while the borders are metamorphosed to mid-amphibolite facies up to granulite facies (Hanski and Huhma 2005).

The CLGB hosts numerous orogenic gold deposits, which are characterized by typical (Au-only) and atypical (Au-Cu ± Co, Ni, Mo, U) metal associations (Eilu et al. 2007). Most of the deposits formed under similar pressure-temperature conditions at 300-450 °C and 1-3 kbar and in similar lithological and structural settings.

In this study we investigate the potential role of metavolcanic rocks as the source for the Au and other elements enriched in the orogenic Au deposits. We specifically focus on the source of Au in the Kittilä group and on metal mobilization from MORB and WPB samples during metamorphism.

**2 Methodology**

Sixty eight metavolcanic rock samples from 26 unmineralised drill cores from the archives of the Geological Survey of Finland (GTK) have been collected for the purpose of this study. The drill core locations are widespread throughout the CLGB and the samples are representative of the various lithologies and metamorphic facies present in the Kittilä and Savukoski groups ranging from greenschist facies (~250 °C) to upper amphibolite facies (>550 °C). Major and trace elements were analyzed by ALS Global. Major elements were analyzed by XRF, trace elements by ICP-MS or ICP-AES and S and C by Leco Furnace. Ultra-low detection limit Au method (Pitcairn et al. 2006b) was carried out at Stockholm University. The CANMET reference material TDB-1 and USGS reference material CH-4 were analyzed for data quality control and yield accuracy of 3.3 % and 10.5 % and precision of 11.8 % and 26.3 % respectively.

**3 Whole rock data**

Metavolcanic rocks from the Kittilä and Savukoski groups are characterized by mid-oceanic ridge basalt (MORB, n=19), within plate basalt (WPB, n=25), komatiites (n=16) and boninites (n=6). The Kittilä MORB samples are basalts (40-52 wt.% SiO₂) and basaltic andesites (52-57 wt.% SiO₂) with tholeiitic to transitional affinity (Zr/Y<3.86 and Th/Yb<0.69) and have relatively flat REE profiles (La/Ybpm=1.72±0.7). Similarly, Savukoski MORB samples are basalts with tholeiitic to transitional affinity (Zr/Y<3.24 and Th/Yb<0.49) and have relatively flat REE profiles (La/Ybpm=1.91±1.81). The MORB samples from the Kittilä gp and Savukoski gp have a median value of 0.61 ppb Au (0.15-8.39 ppb), 1420 ppm S (26-6520 ppm) and 0.99 ppm As (0.20-82.1 ppm). The WPB samples from the Kittilä gp are also basalts and basaltic andesites but have slightly higher Na₂O+K₂O content than the MORB samples (3.9±1.1 wt.%). They have transitional to calc-alkaline affinity (Zr/Y>4.61 and Th/Yb>0.42), LREE enrichment (La/Ybpm=5.91±2.75) and significant Ta and Nb negative anomalies (Ta/Thpm=0.24±0.09 and Nb/Thpm=0.38±0.43). Similarly, the Savukoski WPB samples have transitional to calc-alkaline affinity (Zr/Y>4.61 and Th/Yb>0.42), LREE enrichment (La/Ybpm=6.3±1.81) and significant Ta and Nb negative anomalies (Ta/Thpm=0.69±0.36 and Nb/Thpm=0.76±0.45). The WPB samples have a median of 0.75 ppb Au (0.19-17.1 ppb), 946 ppm S (26-6050 ppm) and 2.11 ppm As (0.63-77 ppm).

**4 Discussion**

4.1 Tectonic setting

Although the MORB and WPB samples from the Kittilä and Savukoski groups formed in different tectonic environments and timing (Hanski and Huhma 2005) the similarities in major and trace element chemistry imply similar magmatic processes. The tholeiitic affinity of MORB samples from the Kittilä gp and their relatively flat REE profiles indicate a transitional MORB affinity corresponding to the Vesmajärvi formation (Hanski and Huhma 2005). The MORB samples are likely sourced from the primitive mantle (Fig. 2). The Savukoski MORB samples have a slight Th/Yb anomaly implying little crustal contamination while Kittilä MORB do not (Fig. 2).

In the Kittilä gp, the transitional to calc-alkaline affinity and the LREE enrichment of WPB samples are
characteristic of the Kautoleskä formation (Hanski and Huhma 2005). The WPB samples show significantly higher Th/Yb anomaly relative to MORB implying a stronger crustal contamination (Fig. 2). The WPB basalts are likely sourced from an enriched mantle source and high TiO$_2$/Yb values imply a plume component for the WPB samples (Fig. 2). This indicate gradual evolution from plume-related and continental crust-contaminated volcanic rocks (Savukoski, komatiite and WPB dominated) to primitive mantle-related volcanic rocks (Kittilä, MORB dominated) during the transition from the latest rifting stages of the Karelian orogen to oceanic crust type environment (Hanski and Huhma 2005).

4.2 Metavolcanic protolith composition
To determine the potential of mafic metavolcanic rocks as the source of Au it is paramount to constraining their primary magmatic content and the possible differences between MORB and WPB. We use 128 fresh glass data from Tatsumi et al. (1999) and Jenner and O’Neill (2012) along with our samples in order to better characterize Au behavior during magmatic evolution. Two different magmatic trends are calculated for MORB and WPB using Zr/Y ratios (Fig. 3) and these are used as proxy for Au protolith composition (Jowitt et al. 2012; Patten et al. 2016). Gold is strongly compatible during differentiation in MORB melts due to sulfide segregation (Fig. 3). In WPB, on the contrary, Au content is higher due to plume component (Webber et al. 2013) and constant during melt differentiation due to limited sulfide segregation (Fig. 3; Tatsumi et al. 1999).

During oceanic crust migration from the ridge to the orogen, the oceanic crust sustains seafloor alteration, mostly at greenschist facies. Seafloor alteration leads to Au re-distribution within the volcanic section and partial depletion in the sheeted dyke and plutonic complexes (Patten et al. 2016). Sulfur and As, unlike Au, are highly mobile elements during seafloor alteration and significant remobilization or enrichment can occur (Patten et al. 2016). The effect of seafloor alteration is highlighted by the wide S range (200-6500 ppm S) and high As concentrations (median=10.3 ppm) of MORB and WPB greenschist facies samples relative to fresh ones (640-1890 ppm S and median=0.18 ppm As; Jenner and O’Neill 2012). Magmatic differentiation trends, thus, cannot be used as proxies for protolith composition and median values of greenschist facies samples (1350 ppm S and 10.3 ppm As) are used instead.

4.3 Mobilization during metamorphism
To accurately quantify the Au variation due to metamorphism it is necessary to account for the protolith variation. To do so we use the method described in Jowitt et al. (2012) and mass changes are calculated from the magmatic differentiation curves using the following relationship:

$$\Delta Au = Au_c - Au_p$$

where $\Delta Au$ is the Au mass change, $Au_c$ the calculated protolith Au composition and $Au_p$ the measured Au value (Fig. 4). The Au mass variation uncertainty ($\delta \Delta Au=\pm37.7 \%$) is the quadrature addition of the MORB and WPB mass variation uncertainty which in turn is the quadrature addition of the normalized root mean square deviation of the magmatic trends ($\delta Au_{MORB}=\pm19.7 \%$ and $\pm31.8 \%$ for MORB and WPB respectively) and analytical uncertainty ($\delta Au_{WPB}=\pm3.3 \%$, using TDB-1). This mass balance uncertainty is high but is inherent to the uncertainty of Au distribution in the primary volcanic rocks.

Gold mass change in the greenschist facies samples (median=-37\%, Fig. 5) and in the lower amphibolite facies (median=40\%, Fig. 5) are too close to the Au mass variation uncertainty to be considered meaningful. For instance the apparently low value of the greenschist facies samples is strongly affected by 5 MORB samples with low Au content (0.18-0.39 ppb) but which are nevertheless within the MORB compositional array (Fig. 5). On the opposite, the apparently high value of the lower amphibolite facies samples is positively skewed by 5 samples with high Au content (2.85-17.1 ppb) most likely due to Au remobilization and local enrichment during seafloor alteration (Patten et al., 2016) or later overprint. Only the upper amphibolite facies samples show important enough mass variation (median=68\%) to be significant (Fig. 5). Additionally upper amphibolite facies samples have smaller Au range (0.17-2.95 ppb) than the greenschist and lower amphibolite facies samples (0.18-12.2 ppb and 0.15-17.1 ppb respectively) characteristic of Au mobilization during metamorphism (Pitcairn et al. 2006a, 2015). The S and As concentrations in upper amphibolite facies samples (median = 500 ppm S and 0.87 ppm As) are significantly lower than in the greenschist facies samples and yield depletion of 63 \% and 92 \% respectively due to metamorphism.

Combination of the Au, S and As mass variations and 3D modeling of the Kittilä terrane (Niiranen et al. 2015) enables to better constrain elemental fluxes during metamorphism in the CLGB. Niiranen et al. (2015) estimated that up to 1500 km$^3$ of the Kittilä gp base has
been metamorphosed to upper amphibolite facies (>550 °C). The metavolcanic proportion in the Kittilä gp is estimated at 85% (Niiranen, pers. com.) which correspond to 3.6 x 10^6 Mt of rocks using a density of 2700 kg.m³. Mass balance calculation using a protolith composition of 1.06 ppb Au (median value of both fresh MORB and WPB) indicates that up to ~2640 t of Au (~84 Moz) has been mobilized during metamorphism. This estimation is lower than that estimated by Niiranen et al. (2015) of 4425-7080 t Au but still one order of magnitude higher than the total reported Au endowment of the CLGB orogenic Au deposits (~280 t). Mass balance calculation of S and As indicates that up to 3.1 x 10^3 Mt S and 34 Mt As are also mobilized. The metavolcanics, thus, can also be the source of the S and As despite the presence of S and As rich metasedimentary rocks in the CLGB, which are also potential sources for these elements. The metavolcanic rocks, however, do not show systematic depletion in the metals enriched in orogenic gold deposits with atypical metal association (e.g. Au + Cu, Ni, Co, Mo, U) pointing toward an alternative source and a bi-modal source area system for the metals enriched in orogenic gold deposits (~2640 t). Mass balance calculation using a protolith composition of 1.06 ppb Au (median value of both fresh MORB and WPB) indicates that up to ~2640 t of Au (~84 Moz) has been mobilized during metamorphism. This estimation is lower than that estimated by Niiranen et al. (2015) of 4425-7080 t Au but still one order of magnitude higher than the total reported Au endowment of the CLGB orogenic Au deposits (~280 t). Mass balance calculation of S and As indicates that up to 3.1 x 10^3 Mt S and 34 Mt As are also mobilized. The metavolcanics, thus, can also be the source of the S and As despite the presence of S and As rich metasedimentary rocks in the CLGB, which are also potential sources for these elements. The metavolcanic rocks, however, do not show systematic depletion in the metals enriched in orogenic gold deposits with atypical metal association (e.g. Au + Cu, Ni, Co, Mo, U) pointing toward an alternative source and a bi-modal source area system for the metals enriched in orogenic Au deposits of the CLGB.

4.4 Implication for Paleoproterozoic orogenic Au deposits

This study confirms that metavolcanic rocks can be the source of the Au enriched in Paleoproterozoic orogenic Au deposits (Augustin and Gaboury 2017) on the contrary to Phanerozoic ones where metasedimentary rocks are the dominant source of gold (Pitcairn et al. 2006a, 2015). Additionally, this study highlights the importance of considering the type of metavolcanic rocks present in the greenstone belts and their primary Au fertility. The presence of plume-related WPB in the CLGB significantly increases the primary Au fertility of the metavolcanics. Similarly Augustin and Gaboury (2017) argued that the Au endowment in the Mana district of Man-Leo shield in the West Africa craton, one of the best endowed Paleoproterozoic Au province, is related to the presence of plume-related metavolcanic rocks in the source. Alternatively, calc-alkaline magmatic series (andesite to rhyolite) are enriched in Au relative to MORB and can also increase the Au fertility of greenstone belts such as in the Abitibi greenstone belt (Pitcairn et al. this issue).

Acknowledgement

This study was partly funded by the Academy of Finland supported MinSysPro #281670 project and by the Academy of Finland and DAAD travel grant.

References


Goldfarb RJ, Groves DI (2015) Orogenic gold: Common or evolving fluid and metal sources through time. Lithos 233:2–26


Jenner FE, O’Neill HSC (2012) Major and trace analysis of basaltic glasses by laser-ablation ICP-MS. Geochemistry, Geophysics Geosystems 13:


Patten CGC, Pitcairn IK, Teagle DAH, Harris M (2016) Mobility of Au and related elements during the hydrothermal alteration of the oceanic crust: implications for the sources of metals in VMS deposits. Miner Depos 51:179–200

Pearce JA (2008) Geochemical fingerprinting of oceanic basalts with applications to ophiolite classification and the search for Archean oceanic crust. Lithos 100:14–48


The paragenesis of veining and Au mineralisation at the Barsele Au deposit, Sweden

Evelina Rann, Iain Pitcairn
Department of Geological Sciences, Stockholm University, Sweden

Marcello Imaña, Kåre Höglund
Agnico Eagle Sweden AB

Abstract. The Paleoproterozoic Barsele Au deposit located in Västerbotten, Sweden is a granodiorite hosted deposit with Au mainly associated with multiple phases of quartz veins. The aim of this study is to constrain the sequence of veining and identify the mineralogical and textural host for Au in the veins. Based on form, texture, mineralogy, metal association and trace element concentrations, we identify 2 main vein generations. An early magmatic hydrothermal phase where irregular blue colour quartz with an Au-Mo-Bi metal association gives formation temperatures from titanium-in-quartz geothermometry of 625 ± 75ºC. The main-stage quartz which hosts the bulk of the Au shows textures and trace element concentrations consistent with formation at <350ºC. The Au in the main-stage veins is hosted in areas of recrystallised quartz associated with carbonate and sulphides which possibly formed late or post main-stage veining.

1 Introduction

The Barsele deposit occurs at the junction between the world-class mineralised Skellefte District in the east and the NW-SE “Gold Line” trend that includes the Knaften, Fäboliden, Svartliden, Stortjärnshobben and Bläken gold deposits (Bark & Weihe, 2007). The Barsele area contains a number of different mineralised zones including the Norra VMS deposit, and three clusters of quartz-Au veins that form the Avan, Central and Skiråsen deposits all of which are hosted in a 1.876 Ga ± 10 Ma early orogenic granodiorite (Thomas et al., 2019).

The aim of this project was to constrain the paragenesis of veining and gold mineralisation in the Qtz-Au vein deposits. We investigate vein textures, cross cutting relationships and the location of gold to identify the temporal evolution of Au mineralisation at the deposit. Vein samples collected from drill cores were further investigated by polarising microscopy and scanning electron microscopy (SEM). Trace elements in quartz were quantified using electron microprobe (EMPA) and used to differentiate between quartz vein generations and possibly constrain the temperature of mineralisation using the titanium-in-quartz geothermometer (Wark & Watson, 2006).

2 Regional geology

The Barsele deposit is located within Palaeoproterozoic 1.9–1.8 Ga supracrustal and related intrusive rocks (Fig. 1) that were deformed and metamorphosed during the Svecokarelian orogeny (Lundström et al., 1997; Mellqvist et al., 1999; Kathol & Weihe, 2005). The lowest stratigraphic unit in the area is the Bothnian Supergroup and consists of metasedimentary and intercalated volcanic rocks (Kathol & Weihe, 2005; Skyttä et al., 2012) and also metadacite dated to an age of 1959±14 Ma (Eliasson et al., 2001). The Bothnian Supergroup forms the basement to the Skellefte Group (1.89-1.88 Ga), of mainly felsic volcanic rocks (Allen et al., 1996) that formed during crustal extension event (D1) by using syn-extensional normal and transfer faults for emplacement (Bauer et al., 2011). The Skellefte Group of volcanic rocks are overlain by the Vargfors group, a dominantly sedimentary unit (1.88 - 1.87 Ga) and the local stratigraphy is comparable to some of the volcanic domains of the Skellefte District. The oldest intrusive rocks in the Barsele area are early orogenic, 1.89-
poor in visible Au which was observed only in one sample continuum of vein injection which due to being the most ore deposits (Rusk, 2012). Titanium -in-quartz method chemical and physical conditions for formation of types of trace elements which can be used as evidence for the Ti and Fe. Hydrothermal quartz has a wide variation of SX100 with 5 spectrometers for in- situ trace element on 18 thin sections at University of Oslo with Cameca geothermometer for quartz according to previous studies. The early -stage veins (Qtz -0) have a distinct form and spatially associated with carbonate. The Qtz-4 veins were 2D) or in fine grained recrystallised quartz (Fig. 2F) both Au is hosted in arsenopyrite grains as sieve texture (Fig. 2). Based on similarities in vein form, cross-cutting relationships, texture and mineralogy we suggest that Qtz-1 to Qtz -4 vein groups at Barsele represent a magmatic-hydrothermal stage of veining and Au mineralisation. 

3 Vein characteristics and trace element analysis

The quartz veins at Barsele have been previously categorised based on mineralogy, texture and accompanying alteration into five types (Unpublished report, Imaña, 2016); Qtz-0 - irregular wormy shaped vein types, often with a distinct blue colour that are cross-cut by all other veins (Fig. 2A), Qtz-1 - sinuose quartz ± carbonate veins, 0.5 to 30 cm in width (Fig. 2C), Qtz-2 - planar quartz veins with distinct alteration selvages from chlorite, biotite and centreline carbonate infill, Qtz-3 - show some of the characteristics of Qtz 1 and 2 but contain visible Au and/or scheelinite, and Qtz-4 – polymetallic quartz-carbonate veins that are very sulphide rich containing mainly sphalerite, pyrrhotite and galena with rare pyrite (Fig. 2G).

Based on our microscopy we can distinguish 2 main vein generations; early-stage and “main-stage” veining. The early-stage veins (Qtz-0) have a distinct form and colour and comprise fine grained polycrystalline quartz with irregular grain boundaries formed by grain boundary migration (Passchier & Trouw, 2005). They contain visible Au as electrum which is spatially associated with molybdenite, chalcopyrite, BiPbS minerals and native Bi (Fig. 2B). Based on similarities in vein form, cross-cutting relationships, texture and mineralogy we suggest that Qtz-1 to Qtz-4 vein groups at Barsele represent a continuum of vein injection which due to being the most abundant veins in the deposit we refer to as main-stage veining. There are differences between these vein groups, such as the sulphide content in the Qtz-4 veins (Fig. 2G and H), but the quartz textures are consistent. These veins are composed of fragments of older quartz showing undulose extinction and strain lamellae. The older quartz is separated by areas of finer grained polycrystalline quartz formed during dynamic recrystallisation (Fig. 2E). In the main-stage quartz veins Au is hosted in arsenopyrite grains as sieve texture (Fig. 2D) or in fine grained recrystallised quartz (Fig. 2F) both spatially associated with carbonate. The Qtz-4 veins were poor in visible Au which was observed only in one sample as an inclusion within pyrite.

Electron microprobe analysis (EMPA) was conducted on 18 thin sections at University of Oslo with Cameca SX100 with 5 spectrometers for in-situ trace element analyses on quartz. Elements analysed were Mg, K, Al, Ti and Fe. Hydrothermal quartz has a wide variation of trace elements which can be used as evidence for the chemical and physical conditions for formation of types of ore deposits (Rusk, 2012). Titanium-in-quartz method (TitaniiQ) has been tested and can be used as a geothermometer for quartz according to previous studies (Wark & Watson, 2006; Rusk et al., 2008). Qtz-0 veins had an average Ti concentration of 110 ± 33 ppm with a range from 40 to 215 ppm. Concentrations of Ti were below the detection limit of 16 ppm in all other vein types. Aluminium concentrations are also systematically higher in Qtz-0 veins (average = 286 ± 220 ppm, range 28 to 814 ppm) compared to other vein types where analyses range up to 600 ppm but 36% of analyses are below the DL of 18 ppm.

4 Discussion

4.1 Early magmatic hydrothermal phase

The early-stage veins are clearly distinct in terms of form, mineralogy, and metal association compared to the other vein types. The trace element contents are also distinct with early-stage veins having higher Ti and Al contents than the other main-stage veins (Fig. 3). Applying the titanium-in-quartz (TitaniQ) geothermometer developed by Wark and Watson (2006), and assuming 1) the presence of rutile in the granodiorite, and 2) pressures of 4 ± 2 Kbar, yields temperatures of formation of 625 ± 75°C. Previous work on Ti-in-quartz geothermometry reports higher Ti concentrations in higher temperature quartz, particularly that from magmatic hydrothermal systems (Wark & Watson, 2006; Rusk et al. 2008). We suggest that based on the trace element association, the vein orientation and distribution and the temperatures from Ti-in-quartz thermometry that early-stage veins represent an early magmatic-hydrothermal stage of veining and Au mineralisation.

4.2 Main-stage quartz veining at Barsele

Titanium concentrations in quartz of less than 10 ppm are suggested to indicate temperatures of <350°C (Rusk et al. 2008; Rusk 2012). We suggest that the main-stage veins at Barsele show textures and compositions consistent with formation at less than 350°C. The main-stage veins show distinct zones of recrystallisation of older quartz into finer-grained polycrystalline quartz with associated carbonate (calcite) and sulphides (arsenopyrite and pyrite). The visible Au in the main-stage veins at Barsele occurs within these zones of hydrothermal recrystallisation, either within the sulphides (Fig. 2D) or within the recrystallised fine-grained quartz (Fig. 2F). This indicates that the main-stage of Au mineralisation occurred either late relative to the emplacement of main-stage veins or post emplacement and most likely contains Au remobilised from early-stage mineralisation. The planar nature of the main-stage quartz veins most likely facilitated their recrystallisation during later deformation. In summary we observe 3 main mineralisation and veining events at Barsele; 1) early-stage magmatic hydrothermal quartz Au-Mo-Bi mineralisation that formed at 625 ± 75°C, 2) the main-stage quartz veining that formed at <350°C, and 3) the recrystallisation event that produced Qtz-carbonate-sulphide-Au mineralisation that may represent the later stages of the main-stage veining or a separate hydrothermal event.
Figure 2. Quartz veins and textures A) Blue early-stage veins (Qtz-0) with irregular structure, in AVA022ER. B) Electron backscatter image of early-stage vein in sample AVA022ER, showing native gold beside molybdenite and an unknown BiPbS mineral in quartz. C) Main-stage veins (Qtz-1) without alteration rim and with alteration rim (Qtz-2) in SKI035ER. D) Electron backscatter image of arsenopyrite with gold inclusions, in host rock, close to main-stage vein (Qtz-1). Sample CNT029ER. E) Transmitted light image of SKI025ER with large quartz cut by recrystallised younger quartz with calcite. F) Reflected light image of main-stage vein (Qtz-3) in SKI013ER. Au associated with calcite, arsenopyrite and recrystallised quartz. G) CNT031ER with a Qtz-4 vein characterised by sulphides (Sp, Po, Gn, Py, Apy). H) Reflected light image of sulphide rich main-stage vein (Qtz-4) in CNT031ER.
Figure 3. Plot of Ti vs Al concentrations in quartz from veins at Barsele from EMPA. The detection limit at 16 and 18 ppm for Ti and Al respectively. Qtz-0 veins are compositionally distinct from the others with higher Ti and Al.

Acknowledgements

We thank Agnico Eagle Sweden AB for access and discussions. We thank Tobias Bauer, Glenn Bark and Helen Thomas for discussions. Muriel Erambert at University of Oslo is thanked for assistance with EMPA.

References


Rusk, B., Lowers, H., Reed, M., 2008: Trace elements in hydrothermal quartz: relationships to cationolominescent textures and insights into hydrothermal processes. Geol 36:547–550


Polyphased gold mineralization at the Yaou deposit, French Guiana

Vincent Combes  
*Université de Lorraine-CNRS, laboratoire GeoRessources, Nancy, France / Auplata SA*

Aurélien Eglinger, Anne-Sylvie André-Mayer, Yoram Teitler  
*Université de Lorraine-CNRS, laboratoire GeoRessources, Nancy, France*

Christophe Scheffer, Arnauld Heuret  
*Université de Guyane, France*

Pierre Gibert  
*Auplata SA*

Didier Béziat  
*Géosciences Environnement Toulouse (GET), Université Paul Sabatier, France*

Abstract. The Yaou deposit, located in French Guiana within the Guiana Shield, is hosted by the Paramaca Paleoproterozoic greenstone belt. The deposit displays multiple intrusive bodies aligned along a shear zone. The local deformation stages show a progressive evolution from the ductile regime to the brittle one. The D$_{1/2}$ event is responsible for the main penetrative foliation with associated ductile veining while the D$_{3}$ phase is related to a sinistral shearing. An intrusive event affects the district and is identified as being syn-D$_{3}$. The following phase D$_{4}$ represents a transitional to brittle veining set located preferentially within intrusive bodies and along the shear zone. A local D$_{5}$ brecciation event is offsetting the D$_{4}$ veins and is overprinted by late D$_{5}$ veinlets. A multi-stage model for the formation of the gold mineralization is presented focusing on gold-bearing pyrite. At the macroscopic scale, the gold mineralization is polyphased with the D$_{3}$ shearing and the D$_{4}$ brittle events being auriferous. A total of 6 generations of pyrite are defined. Results of in situ analyses using LA-ICP-MS on pyrite show that pyrite Py$_{3}$ exhibits an Au-As correlation with a cobalt and arsenic rhythmic zonation. Diagenetic pyrite Py$_{0}$ are a potential primary source of submicroscopic gold having a low contribution to the total budget. Pyrite Py$_{3}$ shows some gold content due to remobilization of Au$_{D0}$. Gold in pyrite Py$_{4}$ is found as submicroscopic gold, as micro-inclusions and as infilling fractures in association with other elements such as Te, Ag and Bi. Most contribution to the Au system is from micro-inclusions and relatively few from both free gold and submicroscopic. Pyrite Py$_{5}$ shows some late remobilization.

1 Introduction

Defining the monophase or polyphase character of an auriferous mineralized system in an orogenic gold deposit is a key factor for exploration targeting. Various gold deposits have been identified as having a polyphase release of gold with protracted history of precipitation, remobilization and new input, as evidenced by Meffre et al. (2016), Fougerouse et al. (2017), Le Mignot et al. (2017) and Augustin et al. (2018).

The Yaou deposit, owned by the gold exploration and mining company Auplata, is located in French Guiana, South America, within the Precambrian Guiana Shield. Ore bodies are currently identified along a 4.5 km long structure, giving an average tonnage and grade of 22.9 Mt at 2.1 g/t (data published on stock market, Auplata 2018).

The aims of this study are (i) to establish the link between deformation stages, quartz-carbonate vein generations, gold-bearing sulfide generations, alteration styles, gold types/behaviors/concentration and gold events, (ii) to understand the role of the different units including intrusions and mylonite, and (iii) to discuss about the polyphase character of the auriferous gold system.

2 Geological settings

The Amazonian Craton consists of the Guiana Shield to the north and the Guapore Shield to the south and constitutes one of the largest pieces of the Columbia ‘puzzle’ (Bispo-Santos et al., 2014 and references therein). The nature and the distribution of gold deposits within the Guiana Shield are intimately controlled by the Transamazonian geodynamic evolution occurred between ca. 2.25 Ga and 1.95 Ga (Enjolvy et al., 2008) and subdivided in two main periods, a period of crustal growth followed by a period of crustal recycling (Vanderhaerghe et al., 1998). The Yaou deposit is located within the southern branch of the Paramaca Greenstone Belt at the border with the Central TTG Complex (Delor et al., 2003). The deposit consists in a rheologically controlled mineralized system associated with quartz-carbonate veins located mainly in intrusive bodies aligned in a 4.5 km structure striking N60° along a shear zone. Gold is itself carried by pyrite with rare free gold. Mineralized veins are hosted by (i) fine grained dioritic intrusive rocks, composed of hydrothermal albite, ankerite, sercite and
pyrite, and (ii) a mylonitized metasedimentary unit composed of quartz, chlorite and sericite. The surrounding area is characterized by a metabasite unit. Studies carried out by Milési et al., 2003, define gold mineralization associated to quartz-albite veins, to disseminated sulfides along strata and to folded and unfolded veins hosted by Paramaca volcaniclastic rocks.

### 3 Results

The observed deformation stages show a progressive evolution from the ductile regime to the brittle one. Phases D1 and D2 are well marked in the host lithologies (metabasites). The veins associated with D1 and D2 are boudinaged and folded. Quartz grains within these veins display evidences of recrystallization with Grain Boundary Migration (GBM). The D3 deformation stage is characterized by transcurrent shearing (NE-trending sinistral shear zone) and intrusions of intermediate magmas. A C/S3 fabric is observed together with a mylonitic gradient and millimeter scale hydrothermal pyrite with quartz-chlorite-calcite fringes. The D4 brittle deformation stage is characterized by quartz veins mostly hosted by dioritic intrusions, and more rarely cross-cutting the sheared metasediments and metabasites. A late breciation stage D5 affects the intrusive unit and the metabasite. The combination of drillcores observation, petrographic data and trace elements analysis allows to discriminate generations of vein and associated pyrite linked to deformation stages. Py0 pyrite is interpreted as diagenetic core within Py3 pyrite, the latter being associated with D3 deformation. Py4 pyrite occurs within D3 veins as well as in their alteration haloes. Py5 pyrite is developed within the D5 breccia cement. When comparing deformation stages, vein stages and alteration phases (including pyrite) data with auriferous zones along drill cores obtained from whole-rock gold analyses, it is clear that D3 veins and associated Py4 are responsible for high gold grade (average values of 1 to 4 g/t), although Py3 pyrites associated with D3 shearing may significantly contributes to the gold budget (up to 1.5 g/t). The D2 event is not auriferous (below 0.1 g/t). D5 breciation (less than 0.5 g/t when no D4 vein associated) hardly contributes to the whole mineralization. Gold releases are therefore associated with the D4 veining event and, to a lesser extent, with the D3 shearing event. The combined occurrence of Py0/3 and Py4 results in the highest gold grades zones (e.g. in the F75 drill core with meters intervals grading > 9 g/t). Ore shoots are mostly located in intrusive bodies and in the mylonite because of the high frequency of the D4 veins. Importantly, rare D4 in the metabasite return positive Au grades (about 0.5 g/t) but are not frequent enough to build an ore zone.

LA-ICP-MS analyses of trace elements within pyrite show that highest submicroscopic gold values are found in pyrite Py0 with a median of 1.1 ppm with outliers above 50 ppm. These outliers correspond to analyses conducted within As-rich zones of Py0 pyrites. Pyrite Py0 exhibits variably high arsenic content, above 200 ppm with a median value of 2800 ppm. Gold concentrations of analyzed pyrite Py2 are below the detection limits confirming that the formation of these pyrite was not related to any gold mineralizing event. This generation is characterized by elevated Ni concentrations (mean value of 8000 ppm). Py2 pyrites are arsenian pyrite with As content ranging from 25 ppm to 3000 ppm, high variations corresponding to As-rich rims and As-depleted rims. A positive correlation between Au and As is observed. The median Au content in Py3 pyrites, corresponding to invisible gold, is about 0.2 ppm. Cobalt displays variable concentrations ranging from 40 to 4800 ppm. The gold content in pyrite Py4 ranges from 0.3 to 7.5 ppm, with a median value of 0.75 ppm. Such a large variability in the gold content related to the presence of gold nano- to micro-inclusions within pyrite. Pyrite Py5 displays lower As and Co and higher Te and Bi contents compared to other pyrite generations. Gold micro-inclusions larger than 30 µm, associated with Py5, were also analyzed using LA-ICP-MS. These micro-inclusions are associated with Te, Ag, Bi, Pb (plus minor As, Ni and Co). The lattice is depleted in Au near gold micro-inclusions. Pyrite Py5 has trace elements composition relatively similar to that of the Py4 generation but with lower gold contents (median value of 0.4 ppm) and higher Ni content (median value of 190 ppm). Trace element analysis of pyrites shows that Py0, Py3, Py4 and Py5 are gold-bearing. Positive correlation for Au-Ag-Te-Bi in pyrite associated to D4 and positive correlation for Au-As in pyrite associated to D0 and D1 are evidenced. Pyrite exhibits a remarkable Te enrichment from generation Py2 to Py5, together with the decrease of the As content when building the deposit.

### 4 Discussion

#### 4.1 Function and contribution of each event to the model: a polyphased mineralization at the macroscopic scale

Each event documented in the present study has a specific role on the formation of the deposit. The relative amount of gold attributed to each event is shown in figure 1. First at D0, a stratabound diagenetic pyritization, located in a metasediment, is evidenced as being a primary source of gold.
A relatively weak contribution to the system is defined as the hosting unit is poorly developed in the area and pyrite $P_{Y_0}$ are not statistically abundant from core observation. The $D_0$ can be defined as an early gold phase but gold in $P_{Y_0}$ is not high enough to support a single source of gold. The ductile $D_{1/2}$ compression phase, giving the main penetrative foliation, shows no evidence of any contribution to the deposit formation. The importance of the $D_3$ shearing event in the gold mineralization is multiple. The intrusive bodies are spatially associated with the shear zone, having the same N60° trend with a less than 200 m spacing between the aligned intrusion/dykes and the shear corridor. Secondly, the $D_3$ shearing provides hydrothermal fluids to the system: the mineralization $D_3$ is controlled by the localized shearing, acting as a pathway for the circulation of fluids forming the $P_{Y_3}$ rims around pyrite $P_{Y_0}$. Locally the sheared metasediment host $D_4$ veins along the N60°E trend. The contribution of $D_3$ to the deposit formation is major whereas the contribution of Au$_{D3}$ to the budget from $P_{Y_3}$ is relatively weak as pyrite $P_{Y_3}$ is only present within the 30 m large $D_3$ band.

The role of the intrusion highlights the rheologically controlled aspect of the deposit, as auriferous $D_4$ veins are preferentially located within the intrusion. Due to rheological contrasts, veins are more likely to develop in the intrusions which are a favorable environment for fracturation, forming traps for auriferous fluids. The intrusive event may be associated with new gold input to the system, although the observation that rare $D_4$ veins...
within others lithologies are auriferous, argue against such interpretation.

In contrast, the epigenetic D4 event represents the main gold mineralization stage with a high frequency of both D4 veins and associated pyrite Py4 together with strong ankeritization. It is most likely associated with a new gold input, related to new hydrothermal fluids (ankerite rich) together with some remobilization of previous gold releases.

The D5 event is related to a late remobilization, within breccia due to both hydrothermal fluids and brittle deformation. The relative contribution to the system is weak, Py5 are auriferous but when no D4 brecciation is observed, gold assays are low (below 0.5 g/t).

A polyphased deposition of gold is therefore evidenced with at least 4 events. This is critical for exploration as gold can be located in various settings (Py0 in metasediments, D3 shear zone, D4 veins in intrusions and D5 breccia) by multiple remobilization and possible new gold inputs. The ore shoot locations are lithology controlled for AuD0 (metasediments), structurally controlled (shearing N60°) for AuD3 and rheology/lithology controlled for the AuD4.

4.2 Gold evolution, behaviors and speciation at the microscopic scale

The early gold AuD0 in diagenetic pyrite Py0 is present both as nano-inclusions and as solid solution in the lattice of the sulfide, as evidenced by LA-ICP-MS spectra patterns. Invisible gold is the only gold species in the initial sulfidation stage, closely associated to arsenic. AuD3 is also classified as invisible. Three gold species associated to the main event D4 are defined, namely, (1) anhedral micro-inclusions in Py4, (2) gold infilling deformation cracks in Py4 and (3) free gold grain situated in the D4 vein at the edge of Py4. The visible gold could be secondary, coming from remobilization of primary, invisible gold.

We identify two main positive correlation: invisible gold is linked to arsenic and visible gold is linked to silver, tellurium and bismuth. The contribution of invisible gold is relatively low (below 1 ppm in pyrite lattice). Most of the gold is identified as micro-inclusion and infilling fractured gold. We define an early low-grade enrichment (AuD0 to AuD3) followed by a later high-grade episode (AuD4).

5 Conclusions

Our data demonstrate that the gold mineralization is polyphased with a total of 4 auriferous events. Most of the mineralization is associated with one set of hydrothermal veins, (brittle D4 event). Gold micro-inclusions within Py4 pyrites predominantly contribute to the Au system, together with minor contribution from both free and submicroscopic gold. The ore shoot locations are lithology controlled for AuD0 (metasediments), structurally controlled (shearing N60°) for AuD3 and rheology/lithology controlled for the AuD4.

Acknowledgements

This study is part of Vincent Combes’s Ph.D. research at the Université de Lorraine at GeorRessources, Nancy, France. This research was funded by Auplata SA and benefited of the framework of the CREGU. This study greatly benefited from discussions and friendly support from Frédéric Tona. We are grateful to the GET Laboratory in Toulouse, France, for LA-ICP-MS analyses.

References


Geochemical signature of native gold from various Au-bearing deposits – implications for mineral exploration

Haiming Liu, Georges Beaudoin, Sheida Makvandi
E4m - Centre de recherche sur la géologie et l’ingénierie des ressources minérales, Département de géologie et de génie géologique, Université Laval, Canada

Simon Jackson
Geological Survey of Canada, Ottawa, Canada

Abstract. Native gold is a significant indicator mineral for gold-bearing deposits. The chemical composition of gold in diverse geological settings is a function of the composition of its parental hydrothermal fluids in diverse geological settings. Thus, trace elements contained in native gold could present a particular geochemical signature that can be used to discriminate gold from different mineralization types. This study characterizes the composition of native gold grains from various Au-bearing deposit types and yields discrimination models for application to mineral exploration for gold deposits. Trace element contents of gold from orogenic, epithermal and volcanogenic massive sulfide (VMS) deposits, were measured in-situ by laser ablation ICP-MS (LA-ICP-MS) to identify systematic changes in gold compositions associated with different mineralization environments, and, where possible, to identify the distinctive geochemical signature of Au in each hydrothermal system. The results suggest that Zn, Ni, Sb, Pd, and Te are the most significant discriminator elements to differentiate gold among different gold deposit types.

1 Introduction

Native gold occurs in a great variety of deposit types and its chemical composition is controlled by factors including transport media, fluid chemistry and precipitation processes (Chapman et al. 2009). Thus, the geochemical composition of native gold can fingerprint various Au-bearing deposit types (Chapman et al. 2017). Recent studies have focused on measuring major element concentrations in placer gold grains, which are used as indicators to identify the source of detrital gold in overburden areas (Chapman and Mortensen 2016). Combining morphological information and alloy composition, based on the relative proportions of Au, Ag, Pd and Hg, allowed identification of six genetic alloy types for placer gold in highly oxidizing hydrothermal environments (Chapman et al. 2009). Based on Au, Ag, and Cu components, ternary diagrams were used to distinguish gold from porphyry Cu, porphyry Cu-Au, and epithermal deposits (Townley et al. 2003). However, due to the limited numbers of elements determined, these diagrams were inconclusive for differentiating gold from epithermal deposits and that from orogenic gold deposits (Moles et al. 2013).

The development of the sensitive technique of laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) has allowed for accurate in-situ measurement of trace element concentrations in mineral matrices, which offers deeper insights into ore-forming processes and mineralization events (Cook et al. 2017; Reich et al. 2017). LA-ICP-MS has been used to provide quantitative analyses of trace element concentrations within placer gold. However, in-situ major and trace element analysis of native gold from various Au-bearing deposit types is not well documented and there is a lack of a powerful discriminant model to differentiate gold from different systems. This study characterizes the chemical compositions of gold grains from various geologic settings using LA-ICP-MS in order to build discriminant models that can distinguish different origins of native gold grains.

2 Methodology

A total of 628 gold grains were selected from forty-two Au-bearing deposits or districts worldwide (Figure 1), including orogenic deposits (e.g., Lucien Béliveau/New Béliveau, Sigma, Goldex from Canada, Kittilä from Finland, Sukhoi Log from Russia, St. Ives district, Fosterville from Australia, and Shangxiu from China, Cuiabá from Brazil), epithermal deposits (e.g., Little Florence, Ken Snyder, and Golden Arrow from USA, Fruta Del Norte from Ecuador, La India from Mexico), and volcanogenic massive sulfide deposits (VMS) (e.g., Boliden from Sweden, Ming, LaRonde and Quemont from Canada). The samples come from different geological settings, have a wide variety of mineralization ages and are hosted by different rocks. The purpose of the broad scope of samples is to capture the variance that may arise from different gold precipitation conditions, resulting from different hydrothermal fluids forming gold deposits. The deposits selected for this study are typical gold deposits that have been documented by previous researchers thus providing required background information. Petrographic analysis and sample descriptions were conducted using optical microscopy and scanning electron microscopy (SEM).

Gold grains were analyzed for major and minor elements at Université Laval (Canada) using a CAMECA SX-100 electron probe micro-analyzer (EPMA), equipped with five wavelength dispersive spectrometers, both using a 5 µm diameter beam with a voltage of 25KV and a current of 100nA. Trace elements contents in gold were measured using a Photon Machines Analyte 193nm...
Excimer laser ablation system coupled to an Agilent Technologies 7700x series quadrupole ICP-MS at the Geological Survey of Canada (Ottawa, Canada) and a Resonetics S-155-LR 193nm Excimer laser ablation system coupled to an Agilent 7700x quadrupole ICP-MS at the University of New Brunswick (Fredericton, Canada). Native gold grains were ablated in spot mode at 10Hz repetition rate, an energy density of 4.2J/cm² and a 25 to 45μm spot size depending on the gold size. Data acquisition included 40s for ablation and 20s for background measurement. Trace element concentrations were internally normalized to Ag values determined by EPMA. At GSC, the external standards, GSE-1G, Po726, and the synthetic gold standards (NA-AU-31, NA-AU-30 and AU-RM-2) were used for data calibration and quality control of LA-ICP-MS analyses. At UNB, the external standards, NIST610, MASS1, and the synthetic gold standard (NA-Au-31) were used for data calibration. Following Makvandi et al. (2016) and Barker and Rayens (2003), the imputed centered log-ratio (clr) transformed chemical data of gold, for the elements with less than 40% censored data were investigated by partial least squares-discriminant analysis (PLS-DA).

Figure 1. Distribution map of forty-two Au-bearing deposits studied including orogenic, epithermal and volcanogenic massive sulfide (VMS) deposits.

3 Results and discussion

Gold from orogenic gold deposits dominantly occurs as anhedral to subhedral inclusions in pyrite, arsenopyrite, chalcopyrite, and pyrrhotite. Gold also fills in the interstitial space between quartz, tourmaline and calcite grains (Figure 2A). Gold from epithermal deposits is characterized by the mineral assemblage pyrite ± sphalerite ± chalcopyrite ± galena. In some epithermal deposits, gold occurs as electrum with Au rich rims (Figure 2C). Gold can also occur as disseminated grains in equilibrium with bismuthinite in quartz veins (Figures 2B, C, D). Gold from VMS deposits commonly occurs either in veinlets filling fractures, or coarse grains in equilibrium with arsenopyrite, chalcopyrite, pyrite, tellurides, tourmaline, pyrhotite, bornite, and minor with tennantite-tetrathedrite (Figures 2D, E). In this study, gold grains with a homogeneous distribution of Au and Ag in backscattered-electron images (BSE) and EPMA maps were selected to determine their trace element compositions by LA-ICP-MS (Figures 2D, F, E).

As is shown in Figure 3, gold grains from different deposit types have distinct trace element compositions. For instance, gold from epithermal deposits is characterized by relatively high Te, Se, As, Pb, Zn, and Fe contents, but low Cd, and Cu contents. In contrast, gold from orogenic gold deposits contains relatively high Sb, and Cu concentrations, whereas Cr, Ni, and Fe concentrations are low. Gold from VMS deposits can be distinguished by relatively high Cu and S, but low Zn, Te, Se, Sb, Sn, Pb, and Fe concentrations. Generally, gold from epithermal deposits shows greater variations in Te, Se, Bi, As, Pb, and Zn relative to gold from orogenic gold deposits. However, gold from VMS deposits is characterized by larger variations in Pd, Bi, Sb, As, Pb, and Cu compositions of gold grains is discriminant for VMS, epithermal and orogenic gold deposits. This indicates the potential of trace elements signatures of gold grains in provenance discrimination of gold grains from unknown sources. The variation in chemical compositions of gold from various geological systems may be explained by different chemical compositions and physicochemical conditions of parent fluids and deposit mechanisms.
Figure 3. Multi-element box and whisker plots of trace element composition based on LA-ICP-MS data from epithermal, orogenic and VMS deposits. The red line indicates the minimum detection limits for LA-ICP-MS analysis.

PLS-DA is a supervised classification technique that allows discrimination of trace element compositions in gold from the three studied deposit types. The loadings biplot of first and second PLS-DA components (qw*1-qw*2) illustrates correlations among elemental contents and relationships among elements and deposit types. Cadmium, Sn, Bi, and Sb plotted in the positive first principal component (PC1) and positive second principal component (PC2) quadrant, and show a positive correlation. They have negative correlations with Ni, S, Cr, Co, Fe, As, and Zn, which have negative PC1 and negative PC2 scores (Figure 4A). Copper and Pd, plotted in the negative PC1 and positive PC2 quadrant, are negatively correlated with Pb and Te, which plot in the positive PC1 and negative PC2 quadrant.

Correlations among trace elements define the classification of gold analyses in a PLS-DA first and second scores scatter plot (t1-t2; Figure 4B). Gold from orogenic deposits forms a cluster with negative t1 values because of variably higher S, Ni, Cr, Cu, Fe, As, Zn, Co, As and Pd, and lower Sn, Sb, Te, Pb, and Bi relative to the average of the dataset (Figures 4A-B). Gold from VMS deposits mainly plots in the positive t1 and positive t2 quadrant due to covariation of Cd, Bi, Sb, and Sn (Figures 4A-B). Gold from epithermal deposits can be distinguished from the other two deposit types by positive t1 and negative t2 due to higher Fe, Zn, As, Sb, Te, Pb, and Bi, and lower S, Ni, Cu, Pd and Cd. Furthermore, elements such as Zn, Ni, Sb, Pd, and Te in gold, which plot at the periphery of the loadings biplot (Figure 4A), play a more significant role in distinguishing orogenic, epithermal and VMS deposits based on the gold composition in Figure 4B.

Gold samples plotting in the vicinity of each other in the t1-t2 subspace are characterized by similar trace element compositions. Gold grains carry the chemical characteristics of their parental fluids that are derived from their geologic settings. Thus, the variation in the chemical compositions of gold probably can reflect the differences in the chemistry of ore-forming fluids and geological settings where gold was precipitated. The Hg, Bi, Sb, and Te enrichments in gold from VMS and epithermal deposits are consistent with the composition of fluids related to volcanic systems. The enrichment of S, Ni, Cu, Pd and Zn in gold from orogenic deposits may be related to S-bearing auriferous fluids associated with orogenic belts.

Figure 4. PLS-DA of native gold LA-ICP-MS data classified by the studied deposit types. In this model. (A) The first and second loading plot (qw*1-qw*2) indicates correlations among elemental variables and deposit types. (B) The score plot (t1-t2) shows the distribution of gold samples projected for the first and second components.

To investigate the potential of PLS-DA model in the classification of gold deposit types, the LA-ICP-MS data of native gold from the Hollinger, McIntyre and Aunor orogenic gold deposits (Velasquez 2014) are projected into the t1-t2 subspace. Because S, Cd, Co data were lacking in the literature data, they were excluded in the dataset and a new PLS-DA diagram had to be defined to project the literature data (Figure 5). As illustrated in Figure 5B, the majority of the literature analyses of gold from orogenic gold deposits from literature were projected into the field defined by gold from orogenic deposits from this study. Thus, PLS-DA of gold LA-ICP-MS data yields robust discrimination models for classification of native gold from orogenic, epithermal, and VMS deposits.
Figure 5. PLS-DA of native gold compared with literature data from Hollinger, McIntyre and Aunor orogenic gold deposits (Velasquez 2014). (A) The loadings plot (qw*1-qw*2) for the first and second components indicates correlations among elemental variables and deposit types. (B) Projection of the compositional data of literature data into the defined discriminant model from this study. The three shade areas were drawn from the first and second components score plots.

4 Conclusion

The differences in composition between the chemical signatures of gold from different deposit types identified by EPMA and LA-ICP-MS are significant. The use of PLS-DA demonstrates the potential for trace elements in gold to be used as discriminators and the ability to build discriminant models to differentiate gold from orogenic, epithermal and VMS deposits. Our PLS-DA results suggest that gold from orogenic gold deposits is characterized by high Ni, S, Cu, and low Sb and Te compared to those from gold in VMS and epithermal gold deposits. Gold derived from VMS Au-rich deposits typically contains higher Pd, Cd, and Sn, and lower Zn, As, Fe, and Ti contents relative to that from the other two deposit types studied. In contrast, gold from epithermal deposits is characterized by high Te, Pb, Zn, Ti, and low Pd, Cu, and Ni. The most effective discriminator elements to classify gold from the three deposit types are Zn, Ni, Sb, Pd, and Te. Discriminant models defined by PLS-DA of trace elements in gold can be used to distinguish gold from orogenic, epithermal and VMS deposit types, which can be a useful tool to determine deposit types for mineral exploration.

Acknowledgements

Many thanks to NSERC and Agnico Eagle Mines Limited for funding the research. We thank Marc Choquette (Laval U.) and Brandon Boucher (UNB) for their assistance with EPMA and LA-ICP-MS analyses, respectively. Many thanks to Émilie Bédard (E4M) for improvements on this manuscript. Special thanks to Veronica Di Cecco (Royal Ontario Museum, Canada), Larry Pilgrim (Rambler Metals and Mining Canada Ltd), Pia Fagerström (Field Exploration Northern Fennoscandia, Bolden), Peter W. Stewart (The Valley Geological Services Inc.), David Pitre (Agnico Eagle Mines Ltd), Michael W. Ressel (University of Nevada), Stefano Salvi (Géosciences Environnement Toulouse – OMP, France) for providing samples for analyses.

References

Abstract. The Bagassi gold deposit is situated in the Houndé greenstone belt. It is a high-grade (1.8 million tons @ 11.47 g/t) deposit in which mineralization is located at the contact between volcanic mafic rocks and granitoids. Two types of mineralization were observed. (i) gold disseminated within sulfides within host-rock and ankerite-rich veinlets and (ii) as free particles within quartz-rich tension gashes. Two types of pyrite associated to gold events were identified. Py1 is generally overgrown by Py2 which contain native gold inclusions. LA-ICP-MS data reveal that Py1 is enriched in trace elements (Median Au = ~4 ppm, median As = ~9000 ppm) compared to Py2 which have median Au = 0.01 ppm and median As = ~320 ppm ppm. Py1 and Py2 show approximately the same range for Ni, Co, Zn, Te and Se and are both depleted in Cu, Sb, Ag, Bi and Pb (Median < 2 ppm). At 55 Zone gold mineralization refers to a single hydrothermal event associated to remobilized gold (gold fineness > 906). Earlier stage of this event consist of an As-Au rich fluid with incorporation of primary gold into As-rich Py1 lattice. The later stage implicates an Au-oversaturated fluids forming free gold nuggets in the quartz-rich veins related to second generation Py2.

1 Introduction

Orogenic gold deposits represent a major source for global gold production (Goldfarb et al., 2001). In these deposits, gold is generally associated to pyrite. Because of its abundance and its role in gold mineralization, textural, chemical and physical properties of pyrite have been extensively studied. (Large et al. 2007, 2009; Thomas et al. 2011; Deditius et al. 2014; Velasquez et al. 2014, 2018; Augustin et al. 2019).


This work investigates the distribution of trace elements in pyrite grains related to the different gold event of the Bagassi Gold deposit.

2 Geological setting

2.1 Regional setting

The southern part of West African Craton, the Man-Leo shied consists of an Archean domain (Kénéma-Man domain) to the west and a Paleoproterozoic domain (Baoulé-Mossi domain) to the east separated by the Sassandra fault (Feybesse and Milesi, 1994; Kouamelan et al. 1997) (Fig.1a). Geological formations of the Baoulé-Mossi domain also called Birimian formations were affected by a polyphase Eburnean orogeny between ~2150 Ma and 1980 Ma (Baratoux et al. 2011).

In western Burkina Faso, three deformation events have been defined by Baratoux et al. 2011. The first phase D1 (~2160 – 2120 Ma) has been distinguished as a penetrative metamorphic foliation S1. This phase corresponds to a shortening and is associated with the emplacement of TTG and granitoids ME1. A second phase D2 (2110-2109 Ma) is characterized by transcurrent shear zones that overprint the structural grain of this area. The late-Eburnean D3 or post-Eburnean (post-2109 Ma) is recorded only in some lithologies and is characterized by the development of crenulation cleavage and chevron or kink folds.

For many authors (Milesi et al. 1992; Beziat et al., 2008; Tshibubudze et al. 2013; Le Mignot et al. 2017; Goldfarb et al. 2017) this post-Eburnean phase is most favorable for gold deposits.

2.2 Bagassi gold deposit

The Bagassi gold deposit is situated in the Houndé greenstone belt in the Province of Balé in Western Burkina Faso (Fig.1b). It consists of two main high-grade gold deposits: the 55 Zone, study area of this work, which consists of a fully underground mine which is currently in production, and Bagassi South, whose production has just started. Other orebodies (109 Zone, 117 Zone, Haho, Kaho…) of the Yaramoko permit are economically less important.
The 55 Zone has proven and indicative ore reserves to a depth of 750 meters of 1.8 million tons grading 11.47 g/t gold. The mineralization is essentially located at the contact between mafic volcanic rocks and granitoids (Fig.1c) and is marked by a strong structural control (Hein 2015). Two types of mineralization have been observed: (i) disseminated gold associated to pyrite within altered host-rock and ankerite-rich veinlets and (ii) free gold in quartz-rich veins that develop pyrite rich proximal alteration in the host rock.

2.3 Veins System

In 55 Zone, mineralization is associated to dextral shear zones including a vein system which consists of two main vein types.

Type I, early stage ankerite-rich auriferous veinlets. They are made of ankerite (~60%), albite (~15%), quartz (<5%), chlorite (<2%), pyrite (~20%) and gold. Pyrite grains in these veins are characterized by chlorite pressure-shadow fringes.

Type IIa, auriferous laminated quartz-rich veins that show highest gold grades. Their width ranges from decimeter to several meters and they overprint the earlier Type I veins. Albite and ankerite ± calcite are the other main phases in the vein and quartz percentage increases with thickness of the vein. Gold is expressed as individual grains or as particles (1-300µm) at the vicinity of rare pyrite grain found in the vein. Pyrite is predominately located within the altered wall rocks haloes around the veins.

Type IIb, late stage milky quartz veins are the widest veins in 55 Zone and can reach more than 11meters; They are characterized by almost pure quartz and much less gold grains compared to type IIa.

3 LA-ICP-MS analyses on pyrite

LA-ICP-MS was used to obtain quantitative data of pyrite. In order to get the best signal during laser ablation, samples were mounted in epoxy resin and were polished using standard methods. Trace element contents in pyrite were determined at Géosciences Environnement Toulouse by using an ESI NWR193UC Excimer laser coupled to ThermoFinnigan Element XR. Spot diameters of 30 µm associated with repetition rates of 10 Hz with a laser fluency of 4 J.cm⁻² were used. For each analyze, following 20s of background acquisition, pyrite grain were ablated over the course of at least 60s.

4 Chemical and textural features of pyrites

Pyrite is the principal sulfide in the 55 Zone of the Bagassi gold deposit. Two pyrite generation associated to gold mineralization were identified according to petrological and chemical investigations. The division in pyrite generations is arbitrary, based on elemental zoning and textural relationships.

Py₁ is associated to type I veinlets in which it forms coarse-grained crystals and usually occurs as inclusion-rich core of Py₂ where the size is varying from 100 µm to 1,000 µm (Fig. 2a, b). It highlights the 55 Zone shearing event.

Py₂ is the most abundant variety and occurs as two subtypes of coarse-grained crystals of 300 µm to 3 mm (Fig. 2d, e, f). The first subtype of pyrite grains has been deformed and is characterized by chlorite strain fringes. Within these pyrites native gold occurs under different forms: as inclusions or infilling fractures in pyrite. Just like
Py₁, this first type highlights 55 Zone corridor foliations. A second subtype consists of mostly euhedral pyrite grains whose width ranges from 75 µm to 1000 µm. They form clusters and are randomly distributed. No native gold inclusions have been observed in this subtype. However, native gold can be found at the vicinity of these pyrite grains within the veins.

Chemical data show that Py₁ is enriched in an enriched in As, Au, Cu and Sb compared to later mostly inclusion-free Py₂ (Fig. 3). As and Au allow the best discrimination between Py₁ and Py₂ with highest As (7,000 to 13,300 ppm) and Au (0.3 to 10 ppm) concentrations found in Py₁ while Py₂ is characterized by much lower values of the same elements, As and Au ranging respectively from 150 to 830 ppm and <0.01 to 0.1 ppm. For other elements, Ni, Co, Cu, Sb, Se, Te, Ag, Zn, Bi and Pb, Py₁ and Py₂ show generally the same contents. The values of Cu, Sb, Ag, Bi and Pb are low in concentration (median <2 ppm).

Figure 2. a Backscattered electron images of deformed Py₂. b EPMA map showing As distribution between Py₁ and deformed Py₂. c, d Thin section microphotograph of undeformed Py₂ showing relation with native gold in quartz-rich type IIA vein.

5 Pyrite and gold mineralization

Py₁ forms As-rich zones overgrown by Py₂ (Fig. 2a, b). These As-rich bands mark a first fluid stage enriched in As and Au. This first stage is responsible of primary gold event in 55 Zone with invisible gold associated to Py₁ (Fig. 3).

Py₂: Trace element concentrations are less abundant in trace elements than As-rich Py₁. Petrological differences between the two subtypes of Py₂ can be explained by their location in the mineralized zone. In fact, Py₂ with strain fringes are situated along the 55 Zone shear zone corridor. This explains why they are strongly deformed and highlight 55 Zone corridor fabric. The other subtype of Py₂ is principally located in tension gashes associated to the 55 Zone corridor. They are not affected by deformation which explain their mostly euhedral shape (Fig. 2c, d). Py₂ distinguish another ore bearing fluid stage in the 55 Zone. These fluids are depleted in trace elements. Presence of numerous free gold grains in quartz-rich veins suggest an Au-oversaturated fluid. Regular boundaries and lacking of corrosion textures between Py₁ and Py₂ argue against a model of multiple events of sulfide precipitation. Py₁ and Py₂ illustrate a single great hydrothermal event with an early stage involving As-Au rich fluids and a later stage with an Au-oversaturated fluid.

In the Bagassi gold deposit, invisible gold can be found in the two generations of pyrite. In As vs Au diagram, all data plot below the Au solubility limit (Fig. 3) of gold in sulfides defined by Reich et al. (2005) for Carlin type deposits. As in pyrite from orogenic deposits controls the behaviour of Au in a similar way to that of Carlin-type systems (Dedithius et al. 2014). Several authors (Morey et al. 2008, Velasquez et al. 2014; Li et al. 2018) agree that occurrence of native gold as inclusions in pyrite crystal suggests exsolution/remobilization from earlier pyrite matrix. At 55 Zone, Py₂ containing native gold blebs are located along the 55 Zone corridor. Their high gold fineness (>906) may be the result of a remobilization process. As is the most abundant element after Fe and S and notable lack of arsenopyrite in Py₂ means that contribution of remobilized invisible gold from As-rich Py₁ in the 55 Zone deposit, should be low even absent. In this deposit most of gold grains co-precipitated with later Py₂ associated to later Au-oversaturated stage.

Figure 3. Binary diagrams of selected trace elements in pyrite types from 55 Zone. Gold solubility limit in As vs Au diagram is from Reich et al. (2005).

6 Conclusion

At 55 Zone of the Bagassi gold deposit petrological and
chemical analyzes on pyrites allow to distinguish two pyrites generations associated to gold mineralization: As-rich Py1 with high contents of As and Au and Py2 showing much less grade of the same elements. Both Py1 and Py2 are depleted in Cu, Sb, Ag, Bi and Pb.

Pyrite investigations revealed that, due to regular boundaries and lacking of corrosion textures between Py1 and Py2; gold mineralization is associated to a single great hydrothermal event which can be divided into two stages of ore bearing fluids. First stage is marked by As-rich Py1 is responsible of primary gold mineralization. Second stage is related to As-poor Py2 and is depleted in trace elements. Most of gold co-precipitated during the second stage with Py2.

Acknowledgements

This work has been supported by the NGO - Association le Soleil Dans la Main and the WAXI (West African Exploration Initiative) project. We would like to thank Roxgold Inc for providing logistical support and for giving access to drill core samples. We are grateful to GeoRessources (Université de Lorraine) and Laboratoire Géosciences et Environnement Minier (Université Ouaga1) for their technical support. Special thanks to Didier Béziat and GET (Toulouse) for pyrite trace element analyzes.

References


Synthesis of gold compositional data from petrography and detrital gold particles to characterize complex lode gold mineralisation

Carl P. Spence-Jones, Rob J. Chapman, David A. Banks, Graham W. McLeod
School of Earth and Environment, University of Leeds, UK

Abstract. Determining the contribution of individual episodes of mineralisation to the overall metal endowment of a gold deposit may be challenging, especially where veins are complex. We have applied a novel approach to address this problem which utilizes the variance of gold alloy compositions with environment of mineral precipitation. Studies at Curraghinalt (N. Ireland) and Cononish (Scotland) have linked gold compositions to paragenetic stage through classical petrography, and then correlated these compositional ranges to those observed in populations of detrital gold particles derived from erosion of the whole orebody. In this way the gold compositions which relate to the most important phase of mineralisation may be identified. The approach may, in some cases, be limited by the particle size ranges of gold, but can offer an efficient route to targeting the most important ore type and underpin further studies which develop deposit models.

1 Introduction

The nature and origins of fluids that create orogenic/mesothermal gold deposits are most commonly inferred from studies of the ore mineralization (Pitcairn et al. 2006; Goldfarb and Groves 2015). However, details of gold mineralogy are rarely reported, even though they may vary with each paragenetic stage. Information on gold composition is generally derived from petrographic studies of vein mineralogy within the orebody. Here we describe a new approach to characterizing the wider mineralisation which combines information from petrographic studies with data sets describing the composition of populations of detrital gold particles.

The gold within these deposits is present as a metallic alloy, which is a continuous solid solution of Au and Ag, the ratio of which is a function of physico-chemical parameters of the ore fluid (Gammons and Williams-Jones 1995). Compositional studies which identify the principle composition of the electrum therefore have the capacity to yield information regarding the pertinent mineralizing conditions within an ore body. Paragenetic descriptions of auriferous lodes report mineral species present. Unfortunately, gold is typically reported as either ‘gold’ or ‘electrum’ (native gold containing >25 wt% Ag) without the exact alloy composition given, or noting any variation there may be in the deposit (Spence-Jones et al. 2018; Mumin and Fleet 1995).

In order to assess the characteristics of a meaningful number of gold particles within a deposit large volumes of ore can be crushed & processed, however with this methodology the mineralogical context is lost, and gold particles <50 µm are difficult to recover by standard mineral processing equipment (Morrison et al. 1991; Chapman et al. 2017). While both petrographic and bulk sampling approaches generate information specific to the volume of ore studied, these are only a tiny fraction of the mineralized systems. The potential for variation in mineralizing conditions, and hence variation in gold alloy composition, mean that compositional data sets generated are likely to be unrepresentative.

Detrital gold particles are an erosional product of auriferous mineralisation. The high density of gold results in preferential retention in fluvial lags in which dense minerals may accumulate in specific sedimentary environments: for example, the ‘pay streaks’ of gold placer mines. Specialized field techniques for gold collection yield populations of particles derived throughout the eroded mineralisation such that the degree of compositional variation may be established (Chapman et al. 2018; Chapman et al. 2017). This study has characterized gold particles revealed in polished sections of ore and has also evaluated the information obtained from the study of populations of detrital gold particles collected from the environs of the orebodies.

2 Geological background to the studied lode systems

Two lode gold deposits, Curraghinalt (Northern Ireland) and Cononish (Scotland), within the Neoproterozoic Dalradian Supergroup were selected for study. The Dalradian Supergroup metasediments underwent metamorphism and deformation during the Grampian Orogeny, ~470 Ma (Stephenson et al. 2013b). The two deposits are separated by 235km, but are located along strike of each other within the Grampian/Caledonian orogenic belt, which extends from Britain and Ireland into Newfoundland in Canada.
2.1 The Cononish deposit

The Cononish deposit comprises a single composite vein hosted within the sub-vertical Eas Annie fault (041/89SE), which is a splay of the regional-scale Tyndrum Fault (Earls et al. 1992; Tanner 2014). The mineralogy and paragenesis of the deposit is described in Spence-Jones et al. (2018) and has been summarized here. The vein is up to 5m thick and records two main events; a pre-mineralisation quartz-pyrite vein, and later crosscutting gold-bearing veins. The gold-bearing veins have been characterized in petrographic studies which identify temporally constrained stages (Spence-Jones et al. 2018);

Stages 1-2, early gold mineralisation: comprises quartz veins with coarse pyrite (stage 1) hosting Au-Ag mineralisation within fractures containing hessite + electrum + galena ± altaite ± chalcopyrite (stage 2). Gold associated with this stage has a compositional range from 10 to ≈ 30 wt% Ag.

Figure 1. Simplified map of the Dalradian rock of Scotland and Northern Ireland within the Grampian terrane showing the location of the studied deposits after Stephenson et al. (2013a).

Stages 3-4, intermediate and later veins: cross cutting veins containing quartz with abundant chalcopyrite and galena, with subordinate pyrite, sphalerite, calcite and electrum. Distinctively, these veins contain >50% sulphides by volume and gold compositions from ≈ 30 to 90 wt% Ag.

Spence Jones et al (2018) interpreted the variation in gold composition in terms of progressive changes in the ore fluid over time; specifically, a marked reduction in tellurium fugacity in the ore fluids ascribed to fluid mixing. This conclusion was supported by S isotope studies which indicate that an early gold bearing (possibly magmatic) fluid was diluted progressively with larger proportions of crustal derived fluids during the ore deposition.

2.2 The Curraghinalt deposit

The Curraghinalt deposit comprises an array of sub parallel auriferous veins with the current deposit resource model containing 21 individual veins (Earls et al. 1989; McCaffrey and Johnston 1996; Wilkinson et al. 1999; Rice et al. 2016; Moloney 2012; Dalradian Resources 2018). Vein mineralogy was described by Wilkinson et al. (1999) and Rice et al. (2016). Both studies reported two stages of gold deposition; the early stage (Q2) gold composition is reported as 2 to 7 wt% Ag and later crosscutting vein hosted gold (Q4) is more silver rich, 11 – 20 wt% Ag, (Figure 2).

![Figure 2. Paragenesis for the Curraghinalt deposit (Rice et al. 2016) with gold compositions from (Wilkinson et al. 1999).](image)

3 Placer sampling

Over a thousand placer gold particles were collected from three drainages cutting the two study areas. These large sample sizes ensure that the populations are representative of the overall inventory of gold particles, <50µm in size, within the deposits. Curraghinalt Burn flows perpendicular to the vein array and two placer sampling localities were chosen to compare signatures from different groups of veins (labelled ‘1’ and ‘2’ in Figure 3). The Eas Anie Burn locality at Cononish includes sites above the flood plain of the Cononish River to minimize any effects of potential exotic gold particles. The Ag contents of Au alloy of gold particles from these populations are compared in Figure 3.

The populations of placer grains show that gold close to the mean of the detrital population is more abundant than gold of more extreme compositions. Thus, the distributions of gold sourced from the deposits is monomodal and approximates to a normal distribution. The detrital populations therefore identify the composition of gold that was deposited during the most significant mineralizing event within the deposit.
4 Results

4.1 Placer vs Lode at Cononish, Scotland

The compositional range of gold particles observed in polished sections of Cononish ore is compared to that of the detrital grains from Eas Annie Burn in Figure 4. The results indicate that stages 2 to 3 are the most significant contributors to the population of placer gold. Gold from stage 4 is a negligible contribution to the overall deposit, which indicates either an overall low abundance, and/or that the gold particles are too small to collect by standard panning techniques (i.e. <50µm). The correlation of the placer to the early vein stages is supported by the presence of the diagnostic early stage mineral hessite (AgTe₂), which is observed as inclusions within the detrital gold grains.

4.2 Placer vs Lode at Curraghinalt, North Ireland

Detailed petrographic work to date has focused on a gold bearing sample collected from the V75 vein. Vein mineralogy comprised two stages of mineralisation with the pyrite host of early low silver gold (3-5 wt% Ag) cross cut by later quartz carbonate veins containing gold with a higher silver content (12-18 wt% Ag). Figure 5 shows that the two ranges of gold compositions observed in the V75 vein are encompassed by the populations of placer gold particles, but do not account for the full compositional range. Both gold bearing stages in the V75 were observed to contain bismuth tellurides and bismuth tellurides inclusions were observed in the entire range of composition of gold particles in the detrital populations.

5 Discussion

The results reveal that the range of gold compositions at Cononish and Curraghinalt are distinct, and that in each case the later gold is more Ag-rich. The gold at Cononish has a far wider compositional range than at Curraghinalt which can be explained by the complexity of the fluid regimes which involve variable fluid mixing at different stages of the mineralisation process (Spence-Jones et al. 2018).

Comparison of the two Ag curves describing placer samples from Curraghinalt Burn show negligible differences indicating that the range of gold compositions is the same across the different veins. From this we can infer that the similar mineralizing conditions were present in each vein system. This inference combined with the observation that bismuth minerals occur throughout the entire range of gold compositions, questions published models for the Curraghinalt deposit.

The Curraghinalt results can be interpreted alongside published observations in one of two ways: either that the Q2 stage of Wilkinson et al. (1999) is the main event that produced the enrichment, with the range of electrum compositions being much wider than original reported; or...
the previously reported mineralogy of the Q4 vein stage is incomplete.

If Q4 does represent an important enrichment stage, which the detrital gold population supports, this implies that the continual evolution of ore fluids from a “Q2” style to a later “Q4” style over time likely existed. This would imply that Q3 has the potential to carry gold and could be an important vein stage on a deposit scale. If this is correct, Q3 style veining could fill in the gap currently present in petrographic gold particle compositions, seen in Figure 5. Furthermore, if bismuth tellurides are indeed present in the Q4 stage this questions the model of emplacement, of Q4, by a later chloride brine advocated by Wilkinson et al. (1999).

The data sets presented here show how information gained from analyses of gold particles illuminates aspects of ore paragenesis. Comparison of alloy compositional ranges of samples from hypogene settings can indicate whether mineralizing conditions were stable or evolving. Study of populations of detrital grains allows us to evaluate the variation in alloy composition across the deposit and to correlate important sub-signatures with specific mineral assemblages.

6 Conclusions

Studies of placer gold in tandem with classical ore petrography permit rapid evaluation of the most important phase of gold mineralisation in complex mineralizing systems. Characterization of both alloy compositions and mineral inclusions within gold particles provide independent routes to link detrital gold particles to specific stages in the paragenesis within the overall mineralizing system. The approach is straightforward, time efficient and relatively inexpensive. Consideration of the range of gold compositions can also suggest whether evolution of the hydrothermal system was continuous or if multiple discrete pulses of fluid were responsible.

Acknowledgements

CSJ was supported by a SEGf Graduate Student Fellowship. Scotgold Resources Ltd and Dalradian Resources are acknowledged for logistical field support and access to company information.

References


Dalradian Resources (2018) Dalradian announces a 46% increase in Measured & indicated gold ounces and a 32% increase in Inferred gold ounces in new Mineral Resource Statement TSX Toronto.


Quantification of gold grains morphology in alluvial sediments, Moulin River, Appalachian Province, Québec, Canada

François-Xavier Masson, Georges Beaudoin and Denis Laurendeau
Université Laval, Québec, Canada

Abstract. In quaternary sediments, gold grain morphology is used to estimate the distance of transport of the grain from the source. Gold particles are malleable and their shape is modified during transport. In alluvial deposits, the Wentworth flatness index, the Corey shape factor and the roundness are commonly calculated to characterize the grains. These parameters are applied on gold particles greater than 200 μm to quantify the shape modification with the distance of transport. The 3D X-ray microscope produces a 3D mesh tomography of the gold grain. This tool has an optimal resolution to characterize gold particles greater than 100 μm in size. 3D SEM photogrammetry provides a 3D textural model of the grain surface. This approach is appropriate to quantify gold grain shapes smaller than 100 μm. For both methods, the axial lengths, the surface area and the volume are measured in order to calculate shape parameters. For the same gold grain, these two methods yield accurate results with an error less than 10% for most shape parameters. Our results indicate an increase of the flatness and a decrease of the sphericity related to the distance of transport over 9 km for small gold grains in the Moulin River.

1 Introduction

In quaternary sediments, the evolution of gold grain morphology is a common exploration tool to estimate the distance of transport from the source (Hallbauer and Utter 1977; Giusti 1986; Eyles 1995; Knight et al. 1999; Townley et al. 2003; Barrios et al. 2015). In alluvial environments, the malleability of gold causes changes to the particle shape (Hérail et al. 1990; Craw et al. 2013; Kerr et al. 2017). The Wentworth flatness index (Wentworth 1922; Cailleux 1945), the Corey shape factor (Corey 1949) and the roundness (Powers 1953) are generally estimated based on the dimension of the sedimentary particle. A correlation between an increase of the flatness ratios and the distance of transport is frequently observed (Hérail et al. 1990; Knight et al. 1999; Youngson and Craw 1999).

In sedimentology, other parameters are used to quantify a particle shape (Blott and Pye 2008). The Janke (Janke 1966), the Aschenbrenner (Aschenbrenner 1956), the Williams (Williams 1965) and the Oblate-Prolate (Dobkins and Folk 1970) shape factors, the Krumein intercept sphericity (Krumein 1941), the maximum projection sphericity (Folk 1955) and the Aschenbrenner working sphericity (Aschenbrenner 1956) are defined based on the axial lengths of the particle. The estimation of the operational sphericity (Wadell 1933; Aschenbrenner 1956) and the degree of true sphericity (Wadell 1932) uses the surface area, the particle volume and the volume of the circumscribed sphere. The inscribed circle sphericity (Riley 1941) and the roundness of Wadell (Wadell 1932) are based on the diameter of the largest inscribed sphere, the smallest circumscribed sphere and the diameters of the curvatures of the particle corners.

This study aims to quantify these parameters for gold grains sizes greater than 30 μm. The morphology is characterized using two methods: (1) the 3D X-ray microscope and (2) the scanning electron microscope (SEM) coupled with photogrammetry. These approaches provide measurements of the particle dimensions, the surface area, the volume and the circle diameters needed to estimate morphological parameters. The variation of these parameters is then investigated for a suite of fluvialite samples over a distance of 9 km.

2 Geological setting and sampling

The Moulin River flows from the Volet lake to the Beauceville River on quaternary sediments, mainly composed of till blankets and veneers (Fig. 1). The gold grains were collected using a prospecting pan for large particles (> 100 μm) and by commercial processing made by Overburden Drilling Management Limited (ODM ltd) for small grains (< 100 μm). For this study, a grain collected at 2.45 km is analyzed with the...
3D X-ray microscope and the SEM to validate the grain characterization methodology for both methods, before taking measurements on the other samples.

3 3D X-ray microscope

The Xradia 520 Versa 3D X-ray microscope, from Carl Zeiss AG, is used to scan the grain and reconstruct 3D shape. The grain is installed in a plastic tube filled with a matrix of silica powder to support it in the middle part of the tube. The sample is rotated at 360° during the X-ray radiation. Raw images of the grain are acquired with the following parameters: 140.1 KeV, 68.9 µA, 0.70 µm of pixel size, LE6 filter, 3201 projections, x4 of optical magnification and exposure time of 2 seconds. The tomography is non-destructive and the grain can be recovered after scanning. Dragonfly (Object Research Systems) is a visualization software used to produce a 3D mesh of the gold particle from raw images (Fig. 2A). The dataset is defined by theoretical densities. These values change according to the scan environment and the analysis parameters. For this grain, the gold theoretical density is ranges from 37 770 to 59 392. This density is used to delimit the grain boundary and the dimension of the minimal bounding box to measure the long (L), the intermediate (I) and the short (S) axes (Fig. 2A). The surface area (Ap) and the volume of the particle (Vp) are based on the mesh properties (Fig. 2A). Three other parameters are measured on the X, Y and Z planes (Fig. 2A): (1) the average value of the smallest circumscribed circles (Dc); (2) the average value of the largest inscribed circle (Di); (3) an estimation of the curvature of all corners of the particle (ΣDr/n). PolyWorks (InnovMetric) is a mesh inspection software used to measure the maximum length which is related to the diameter of the smallest circumscribed sphere (Fig.2B). The thickness map of the grain is produced according to the surface normals at mesh points. This representation enables the detection of anomalies inside the gold grain, such as a void or an inclusion as shown at 0 to 25 µm depth (Fig. 2C).

4 3D SEM photogrammetry

The Quanta-3D-FEG (FEI) SEM is used to acquire images of the gold grain surface with secondary electrons. The gold grain is placed on a wood stick with a carbon tape to provide a conductive setup. The energy is fixed at 3 KeV to obtain high quality texture and surface details (Fig. 3A) needed for an optimal reconstruction. A minimum of 20 images of the particle are required to reconstruct the grain in 3D. Depending on the orientation of the grain on the wood stick, the stand is tilted (between 52° to 70°) so the part of the grain that is close to the base of the stand can be observed. The grain is turned around 360° and an image is taken every 18°. ReCap Photo (Autodesk) software produces a 3D textural mesh from these 20 SEM images using photogrammetry (Fig. 3B). However, the mesh is not calibrated. To calibrate it, we used a magnified SEM image with a striated surface (Fig. 3A). The striated reference surface is measured 5 times. The same striated surface is identified and measured on the model (Fig. 3B). Then, the reconstruction model is cleaned, the base is removed from the model and the hole created by removal of base in image is filled to calculate the surface area and the particle volume. The mesh coordinates are oriented and translated to the point cloud origin to facilitate the estimation of the minimal

Figure 2. (A) Orthographic projection of the gold grain (2.45 km) produced by Dragonfly from theoretical density values between 37 770 and 59 392. The blue part corresponds to the silica matrix while colored part belongs to the gold particle. The white line is the boundary of the gold grain. For each slice (X, Y and Z), the average value of the largest inscribed circles (Di), the average value of the smallest circumscribed circle (Dc) and the average value of the curvature of corners (ΣDr/n) are determined. The particle dimensions (L, I and S), the surface area (Ap) and the volume (Vp) are computed from the mesh properties. (B) The thickness map of the gold grain mesh is produced by PolyWorks. The maximum length is located and measured. (C) Thickness map of the (B) hidden face with a detection of inclusion or void at 0 to 25 µm depth.
PolyWorks is used to measure the maximum length and to infer the volume of the smallest circumscribed sphere (Fig. 3D). MeshLab (ISTI-CNR) is a 3D mesh processing software that is used to find a bounding box for the grain. The grain is rotated in X, Y and Z planes to find the minimal bounding box related to the dimension of the particle (Fig. 3E). The surface area and the volume are derived from the mesh properties (Fig. 3E). The same process is used to quantify smaller particles and gold grains with complex morphology (Fig. 3F).

5 Shape parameters

Table 1. Gold grain (2.45 km) shape parameters analyzed with 3D X-ray microscope and SEM. The difference (in %) is calculated by taking the 3D X-ray as a reference.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>3D X-ray</th>
<th>SEM</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L (μm)</td>
<td>283.44</td>
<td>297.5</td>
<td>5.0 %</td>
</tr>
<tr>
<td>I (μm)</td>
<td>174.52</td>
<td>176.4</td>
<td>1.1 %</td>
</tr>
<tr>
<td>S (μm)</td>
<td>124.89</td>
<td>123.8</td>
<td>0.9 %</td>
</tr>
<tr>
<td>Maximal length (μm)</td>
<td>300.17</td>
<td>302.5</td>
<td>0.8 %</td>
</tr>
<tr>
<td>Surface area (μm²)</td>
<td>136 933</td>
<td>135 135</td>
<td>1.3 %</td>
</tr>
<tr>
<td>Vp (μm³)</td>
<td>2 924 506</td>
<td>3 089 920</td>
<td>5.7 %</td>
</tr>
<tr>
<td>Vsc (μm³)</td>
<td>14 161 214</td>
<td>14 493 950</td>
<td>2.3 %</td>
</tr>
<tr>
<td>Flatness ratio (S/L)</td>
<td>0.72</td>
<td>0.70</td>
<td>2.8 %</td>
</tr>
<tr>
<td>Elongation ratio (L/S)</td>
<td>0.62</td>
<td>0.59</td>
<td>4.8 %</td>
</tr>
<tr>
<td>Equancy ratio (S/L)</td>
<td>0.44</td>
<td>0.42</td>
<td>4.5 %</td>
</tr>
<tr>
<td>Wentworth flatness index</td>
<td>1.83</td>
<td>1.91</td>
<td>4.4 %</td>
</tr>
<tr>
<td>Corey shape factor</td>
<td>0.50</td>
<td>0.54</td>
<td>3.6 %</td>
</tr>
<tr>
<td>Janke form factor</td>
<td>0.61</td>
<td>0.58</td>
<td>4.9 %</td>
</tr>
<tr>
<td>Aschenbrenner shape factor</td>
<td>1.10</td>
<td>1.18</td>
<td>1.7 %</td>
</tr>
<tr>
<td>Williams shape factor</td>
<td>-0.14</td>
<td>-0.16</td>
<td>14.3 %</td>
</tr>
<tr>
<td>Oblate-Prolate Index</td>
<td>4.24</td>
<td>4.74</td>
<td>11.8 %</td>
</tr>
<tr>
<td>Krumbein intercept sphericity</td>
<td>0.65</td>
<td>0.63</td>
<td>3.1 %</td>
</tr>
<tr>
<td>Maximum projection sphericity</td>
<td>0.68</td>
<td>0.66</td>
<td>2.9 %</td>
</tr>
<tr>
<td>Aschenbrenner working sphericity</td>
<td>0.87</td>
<td>0.86</td>
<td>1.1 %</td>
</tr>
<tr>
<td>Operational sphericity</td>
<td>0.59</td>
<td>0.60</td>
<td>1.7 %</td>
</tr>
<tr>
<td>The degree of true sphericity</td>
<td>0.72</td>
<td>0.76</td>
<td>5.6 %</td>
</tr>
<tr>
<td>Inscribed circle sphericity</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roundness of Wadell</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 presents the results of the estimation of 3D X-ray microscope and SEM parameters for the same grain. The difference between the two methods is given taking the 3D X-ray microscope values. There is less than 10% difference for parameters with the exception for the Williams shape factor and the Oblate-Prolate index. According to the classifications of Blott and Pye (2008), the gold grain at 2.45 km is slightly to moderately flat, moderately elongated, moderately non-equant, prolate (rod-like) and has the form of an elongate block or a prolate spheroid. The Krumbein intercept sphericity, the maximum projection sphericity and the degree of true sphericity reveal that the particle is moderately spherical. But the operational sphericity corresponds to a low spherical particle and the Aschenbrenner working sphericity to a highly spherical grain. However, for the same grain, both methods give the same range of values. 3D X-ray microscope provides additional results on the inscribed circle sphericity and the roundness of Wadell.

Figure 4. Shape parameters for small gold grains (< 100 μm), with linear correlations straight lines, along the Moulin River.

These parameters suggest that the grain is moderately spherical and sub-angular. The results for small grains (< 100 μm) along the river show an increase of the flatness index and a decrease of the sphericity when the distance of transport increase (Fig. 4). The linear correlations of
the Corey shape factor and the sphericity factors decrease towards 0.40 - 0.50 that correspond to the value for a flat and a low spherical particle.

6 Discussion and conclusion

In exploration, the shape of gold is used to give indication about the mode of transport and to estimate the travel distance from the source whereas the chemistry of gold is being investigated to determine the source of gold (Hérail et al. 1990). Most quantitative studies are based on gold grains larger than 200 μm (e.g. Knight et al. 1999; Youngson and Craw 1999; Townley et al. 2003; Barrios et al. 2015) but a large part (> 75%) of gold grains is smaller than 200 μm such as in the Athabasca River (Giusti 1986). Also, an automated method can be used to quantify gold grain shape (Crawford and Mortensen 2009), but the results are only in 2D and the volume is not calculated.

The current study presents two methods to characterize the shape of gold grains in 3D varying in sizes and geometric complexity. The 3D X-ray microscope provides an accurate and a total reconstruction of the grain shape. The dimensions (L, I, and S), the surface area, the volume and the diameter of inscribed and circumscribed circles are measured on the mesh. This approach provides more physical parameters than the SEM to quantify the morphology of gold particles with sizes greater than 100 μm. However, the resolution is not optimal to analyze particles smaller than 100 μm, such that methods based on 3D SEM photogrammetry are more suitable to characterize the morphology of small gold grain. The lack of calibration and the partial reconstruction are the main drawbacks of this approach but the results are similar to those obtained with 3D X-ray microscope for the same gold grain.

Considering that: (1) the first gold grain collected in the river as the origin of the shape modification; (2) the river is the only transport agent that changes the shape of gold in addition to the glacial transportation; (3) there is only one possible source of the gold, thus excluding the affluents, we conclude that based on the estimated parameters on small grains, the Moulin River shows an increase of the flatness and a decrease of the sphericity during transport.

Acknowledgements

The authors thank Émilie Bédard and Roman Hanes for help with gold sampling, Stephane Gagnon for SEM analysis at Université Laval and Rui Tahara for tomography analysis at McGill University (IQBI project).

References


Wentworth CK (1922) The shapes of beach pebbles.


Youngson JH, Craw D (1999) Variation in placer style, gold morphology, and gold particle behavior down gravel bed-load rivers; an example from the Shotover/Arrow-Kawarau-Clutha River system, Otago, New Zealand. Economic Geology 94:615-633
Detrital gold, heavy minerals and sediment geochemistry elucidate auriferous mineralization in southeast Ireland

Moles, Norman R.
School of Environment and Technology, University of Brighton, UK

Chapman, Robert J.
Ores and Mineralization Group, School of Earth and Environment, University of Leeds, UK

Abstract. Recently published Tellus geochemical data for sediment fines in SE Ireland show extensive Au anomalies in north Wexford, but few anomalies in Wicklow despite historical extraction from the Goldmines River. Discovery of bedrock sources is hampered by glacial dispersion and scarce bedrock exposure. Here we describe a novel approach to characterizing regional gold metallogeny which involves the synthesis of data sets from stream sediment surveys, analysis of heavy mineral concentrates (HMCs) and detrital gold. Mineralogical characterization of HMCs and 2160 gold grains from 40 localities in the auriferous region provides a clear indication of proximity of gold to source and genetic origins. Detrital gold in the south of the region (Wexford) is most likely derived from the widespread stratabound Au-As-Fe-S reported by exploration companies, whereas the distinctive Pb-Bi-As mineral inclusion signature in detrital gold from the Goldmines River area is suggestive of a magmatic influence. Combining data sets from the different techniques yields superior information than is possible using each approach in isolation.

1 Introduction

Regional exploration for rare and precious metal enrichment traditionally uses multi-element geochemical analysis of the fines (<150 µm) fraction of stream sediments, however these data can be misleading in glaciated regions with complex geology or due to anthropogenic influences. In particular, the extreme density of gold results in highly localized concentrations within fluvial sediments, an effect exacerbated as gold particle size increases. Thus classical stream sediment sampling may under-represent gold. Conversely, establishing placer-lode relationships for gold can be challenging if only gold particles are collected because the particles may be recycled into successive surficial environments. Heavy mineral concentrates co-collected with gold particles may be used to investigate spatial relationships between sediments and local lithologies. Here we compare the spatial distributions of data from sediment fines with distributions of heavy mineral concentrates (HMCs) including detrital gold in southeast Ireland, where the relationships are poorly understood between historically exploited Cu-Au volcanogenic massive sulphide (VMS) mineralization, placer gold, and widespread Au anomalies in stream sediment fines.

2 Geology and mineralization

Southeast Ireland comprises a NE-SW oriented belt of Cambrian – Ordovician sedimentary and volcanic rocks that were deformed and metamorphosed during later Palaeozoic orogenic events (Gallagher et al. 1994). Lower Ordovician thick laminated mudstones of the 'Ribband Group' were followed by clastic sediments and volcanic rocks of the Duncannon Group (Brück et al. 1979). In Wicklow the latter incorporates the Avoca Volcanic Group (AVG) which comprises dominantly rhyolitic lavas, chloritic tuffs and slaty mudstones.

A major period of shearing towards the end of the Caledonian orogeny generated NE-oriented deformation zones, one of which occurs in the Avoca – Goldmines River area. The Leinster Granite batholith and satellite granitic plutons, including the Croghan Kinshelagh complex south of the Goldmines River, were emplaced into these actively deforming shear zones (Gallagher et al., 1994). Recent geochronological and geochemical studies (Fritschle et al. 2018) have established that the Croghan Kinshelagh complex comprises discrete older and younger units. The older granite is correlative with AVG volcanism and has been deformed with a penetrative fracture cleavage similar to the AVG rocks, whereas the younger granite intrusion is undeformed.

Metalliferous mineralization in SE Ireland comprises the Avoca VMS deposit (100,000 tonnes Cu, Tietzsch-Tyler et al. 1994; Williams et al. 1986), minor epigenetic Cu-Pb-Zn-Bi-Au mineralization in BIF on the Moneyteige –Ballycoog Ridge adjacent to the Ballinvalley River (Fig. 4) (McCardle & Warren 1987; Ixer et al. 1990; Milner & Mcardle 1992) and Au, W, Sn and Pb-Zn mineralization associated with hydrothermal fluid circulation accompanying late Caledonian shearing and granite intrusions (McCardle et al. 1989). Throughout the study area, company exploration has identified visible gold within Au-As-Fe-S mineralization in both stratabound- and shear zone-hosted quartz veins.

In 1795, the Goldmines River area was the scene of Ireland's only historical gold rush (Maclaren 1903). It has been estimated (Reeves 1971) that up to 300 kg of placer gold was recovered from gravels in the Ballinvalley and Monaglogh Rivers (Figs. 2 and 4) and surrounding area. Some of the gold was very coarse-grained, the largest mass being the 'Wicklow nugget' weighing 22 ounces (682 g). However, despite intense exploration, bedrock sources have not been identified.

Exploration in the region has recently benefitted from
a release (Knights & Heath 2016) of high precision re-analyses of fine fraction sieved stream sediments originally collected in the 1980s (O’Connor & Reimann 1993). Over 2000 samples had been obtained at a density averaging 1 per 4 km². About 5% returned elevated concentrations of gold in the range 0.1 to 1.5 ppm (Fig. 1). Samples with >0.5 ppm Au are mostly located in a NW-SE trending belt between Camolin and Carnew in north Wexford. There appears to be no spatial association between bedrock geology and Au enrichment in sediments, indeed the belt is perpendicular to the ‘Caledonian’ trend and crosses outcrops of both Ribband and Duncannon Group rocks. In the Avoca – Goldmines River area, values of Au >0.1 ppm occur in only one Tellus sample, from the Coolbawn River, but not at other localities of historical gold winning.

3 Methods and results

3.1 Detrital gold characterization

New data describing the alloy compositions and mineral inclusions within 1541 detrital gold particles was augmented by a similar data set for 619 grains reported by Chapman et al. (2006). A total of 40 localities in south Wicklow and Wexford are represented. Although gold was recovered at every locality, abundances varied enormously (Fig. 2A). In north Wexford, scattered sites returned relatively high abundance against a background of average to low abundance. The coarse particle size and rough morphology of gold grains from near the former placer working (‘Red Hole’) in the Ballinvally River

![Figure 1](image1.png)

**Figure 1.** Au concentrations in fine fraction sediments in SE Ireland, showing an area of relatively high values in north-central Wexford and mostly low values in Wicklow and Carlow. Tellus map reproduced with permission from the Geological Survey of Ireland. Red box indicates the study area shown in Figure 2.

![Figure 2](image2.png)

**Figure 2.** Outline geology of the study area with symbols at sample sites indicating (A) detrital gold abundance, with “high” indicating concentration previously sufficiently high to support historical exploitation in the Goldmines River area, and (B) median %Ag categories at sites from which 4 or more gold grains were obtained.
strongly suggests very local derivation, as suggested by Maclaren (1903). Rough gold characteristic of proximal derivation was found at Ballygarrett and Boley Lower in Wexford, while elsewhere much of the gold is flaky indicating transport and less proximal derivation.

Electron microprobe analyses of gold alloy in grain cores revealed that Ag is ubiquitous, whereas Cu and Hg are detected only sporadically. A generic form of the cumulative frequency curves of wt% Ag in Wexford samples allowed their characterization using a single median value. Three class intervals of median wt% Ag (low <5.5, medium 5.5-7.5, high >7.5) were selected and the spatial distribution of these categories is presented in Fig. 2B. No spatial association is apparent between Ag content and underlying lithology, HMC mineralogy, or ice flow direction in Wexford.

In the Goldmines River area, correlation of Ag range with inclusion type has yielded three generic gold types (Fig 3). The majority of galena and native bismuth inclusions, grouped because of their intimate association, occur within gold containing <9 wt % Ag which we refer to as type 1. Most arsenopyrite inclusions are hosted by gold grains of c. 9-14 wt% Ag, referred to as type 2. Type 3 gold contains >14 wt% Ag and lacks inclusions of galena, arsenopyrite or chalcopyrite found in types 1 + 2.

Comparison of wt% Ag ranges of gold types 1-3 against the bulk assay of historically recovered gold (7.82% Ag) recorded in returns to the Irish Mint (Kinahan 1882) shows Type 1 gold to be the most important overall signature. Consequently Type 1 gold probably represents the most attractive target for future exploration projects.

The mineral inclusion assemblage of Wexford gold also shows a galena-arsenopyrite signature. Bismuth minerals are absent whereas chalcopyrite, sphalerite and pyrite are more common than in the Wicklow samples. This inclusion mineralogy is compatible with the compositional range of Phanerozoic orogenic gold recorded throughout the British and Irish Caledonides as summarized by Chapman et al. (2000).

3.2 Heavy mineral characterization

Semi-quantitative analysis of mineral abundances in HMCs was undertaken to investigate resistate particle mobility in the surficial environment and potentially identify mineral species genetically linked to gold mineralization. As shown in Fig. 4, HMC mineralogy is diverse in the Goldmines River area with differing proportions of hematite, magnetite and ilmenite in adjacent tributaries. There are no clear associations between HMC mineralogy, gold abundance and the proportions of the gold types. However in Wexford, atypical HMC mineralogy at Askamore, which included abundant cassiterite and ferberite, correlates with a distinctive gold signature which, in combination, indicate a local source of granite-associated Au mineralization.

4 Implications for bedrock mineralization

Given the current limited understanding of in situ Au-bearing mineralization in SE Ireland, we can apply the spatial associations between detrital gold abundance,
microchemical signatures, and bedrock geology to re-evaluate previous hypotheses for the source of gold in the Wicklow placers. The potential of Avoca as a source may be discounted on the basis of ice flow directions (McArdle & Warren 1987), patterns of heavy mineral distribution (Fig. 4), and gold abundance and Ag contents (Fig. 2). The potential for the BIF-hosted mineralization on the Moneyteige Ridge to represent an example of Type 1 gold has been discussed above, although elsewhere Type 1 gold is hosted by other lithologies.

The differences in signatures of sample populations of detrital gold from within individual drainages (Figs. 3 and 4) leads us to favour a model in which intra-valley mineralization with magmatic-hydrothermal characteristics (gold type 1 with bismuth inclusions) supplemented gold from the local stratabound Au-As-Pe-S style (gold types 2 and 3) to form rich gutter placers in ravine-like settings in the Goldmines River particularly the Red Hole.

The decoupling of gold types from HMC mineralogy suggests that in the Goldmines River area, bedrock gold mineralization is not lithologically controlled. Instead, mineralization is likely to be controlled by tectonic structures and proximity to the Croghan Kinshelah granite. This concurs with Standish et al. (2014) who, in interpreting lead isotope ratios in placer gold from southeast Ireland, favour two separate mineralization events associated with the Early Caledonian orogenesis and with Late Caledonian granite emplacement.

5 Evaluation of exploration methods

All three approaches are mutually supportive: sediment fines analyses provide a basis for more labour-intensive targeted gold grain studies, which in turn highlight specific gold-element associations useful for interpretation of placer–lode relationships from gold grain studies. Microchemical characterization of gold establishes genetic relationships and clear links with known types of hypogene mineralization.

Acknowledgements

We thank John Ashton of New Boliden Tara Mines Limited for supporting the sampling program in Wexford, and IMC Exploration Group plc for their support of follow-up fieldwork in Wicklow. The University of Brighton provided facilities for XRD, SEM and XRF analyses of heavy mineral concentrates. The University of Leeds provided EMPA and SEM facilities for analysis of the gold grains. We are indebted to Colin Kimberley and John Krecn, Christopher Reynolds, Christopher Smith and Hamidullah Waizy for their assistance with sampling and analysis.

References


Placer gold provenance, a site study comparing placer and lode gold chemistry and inclusions Black Mountain, Alaska

Erin E Marsh¹, Robert J Chapman², David T Adams¹, Jakub Skrzynecki²
¹U.S. Geological Survey, Denver, Colorado, USA
²University of Leeds, Leeds, UK

Abstract. Eastern Alaska is a region well-endowed with placer gold deposits, but only two significant lode deposits are in production (Pogo and Ft Knox). This study explores the potential for microchemical studies of placer gold to elucidate specific lode-placer relationships and to contribute to a wider understanding of gold metallogeny in the region. Gold grains from the Gray Lead and Blue Lead Extension lode prospects on Black Mountain and placer grains from drainages near the prospects were sectioned and analyzed for trace element chemistry and mineral inclusion counts. Results indicate that the gold placer samples in the drainages immediate to the lode samples have comparable mineral chemistry, but lower in the drainages additional chemical and textural signatures are noted, suggesting the presence of undiscovered occurrences. The distinctive Pb-Sb-As-S signature of the mineral inclusion chemistry is similar to that previously recorded in orogenic settings of Cretaceous age on the Alaskan-Yukon border. Identification of such signatures provides an efficient means to characterize undiscovered lode sources and to aid in exploration. Here we report results from a unique setting in Eastern Alaska where placer and lode gold are available for comparison.

1 Introduction

Mineral inclusion count and placer gold geochemistry have been used in the Yukon and British Columbia for provenance discrimination (Chapman et al. 2010a, b, 2011, 2018; Chapman and Mortensen 2016). Eastern Alaska is well known for hosting rich placer fields such as the 40-mile and Fairbanks districts, with only a few known significant lode deposits (e.g., Pogo; Fort Knox). This is due in a large part to the poor geologic exposure in the region, which coupled with having only a few known significant deposits, has resulted in disputes on lode deposit models in the region. The Black Mountain area is an unique study area as it provides lode and placer sampling for comparison to set a baseline for a placer signature/source model, which will help with mineral exploration and defining the metallogenic make-up of mineralization in the Yukon Tanana Terrane.

2 Geologic Setting and Mining History

The Black Mountain area is within the Goodpaster mining district of the Tintina Gold Belt in eastern Alaska, approximately 110 miles southeast of Fairbanks (Fig. 1). Though not as well-known as the Fairbanks and 40 mile district for it’s placer production, the Goodpaster district is host to a few placer deposits and the well-endowed Pogo lode gold deposit. Several lode occurrences have been explored in the Black Mountain area, with historical mining taking place in the early 20th century (Rombach 1999; Flanders 2010). The lode occurrences on Black Mountain are hosted in (i.e. Blue Lead Extension) or along the margin of Mesozoic granites and Paleozoic meta-sedimentary rocks (i.e. Gray Lead) of the Yukon-Tanana Terrane (YTT). Gold deposits and occurrences hosted within the YTT include porphyry, orogenic, and reduced intrusion-related systems (Allan et al. 2013). Regionally, the YTT is structurally set between the parallel strike-slip Farewell-Denali and Kaltag-Tintina Faults. Between these regional structures are a series of northeast trending faults, including the Black Mountain tectonic zone, where the study area sits (Flanders et al. 2010 and references therein). Tibbs Creek, the creek off the west flank of Black Mountain, and Central Creek, which is to the west of the Tibbs Creek drainage, were previous placer producers (Rombach 1999).

3 Methods

In total, eight placer gold and three lode samples were collected from the study area. The placer gold grains were collected from four tributaries draining Black Mountain leading into Tibbs Creek and two locations along Tibbs Creek, as well as in one location along
Central Creek, a drainage to the west of Tibbs Creek. The area is densely vegetated, providing a challenge for access and workable material for sampling in the drainage. Surface samples were collected from Gray Lead and the eastern and western outcrops of Blue Lead Extension. These three sample were processed by electric pulse disaggregation using the Selfrag Lab system in the standard closed vessel with pulse power of 150,000 volts at a repetition rate of 5 Hz. Sample sets of gold grains were mounted in one-inch rounds following Chapman et al. (2000), during which textural observation where made with optical microscopy. Microanalytical work was done at the USGS Denver Microbeam Laboratory. Major and trace element analysis of the electrum was done on the JEOL JXA-8900 Superprobe, outfitted with five wavelength dispersive spectrometers, operated at an accelerating voltage of 20 keV, a beam current of 50 nA, and a beam diameter of < 1 µm. Mineral inclusion counts were conducted using an Oxford XMAX50 EDS with Silicon drift on a FEI Quanta 450 FEG SEM operating at 20kV by taking BSE images and acquiring EDS spectra for each mineral inclusion. Mineral inclusions are observed with optical microscopy, SEM imaging to be physically and texturally intergrown within the gold grain (Fig. 2).

4 Results

Placer grain morphology for the most part is rough. Following the empirical shape classification by Knight et al. (1999), out of the 137 grains from the Central Creek and Black Mountain placers, 102 are angular/irregularly shaped, 18 are irregular, and 17 are irregularly rounded or rounded.

Mineral microchemistry of the electrum grains from both lode and placer samples contain a range of Ag and Hg +/- Sb, Ni, Cu, Zn, and minor Bi, Pb, Co. The Ag content in the electrum for the Black Mountain placer and lode samples range from 4.9-39.7 wt% and 4.8-27.2 wt%, respectively (Fig. 3). Central Creek electrum samples contain 4.9-39.7 wt% Ag. The Black Mountain placer sample suite contains minor Cu and Co and a higher range of Hg and Ag than the lode sample suite (Fig. 4). The Black Mountain lode sample suite mineral chemistry shows little to no Cu, but minor Pb and higher Bi than the placer samples suite. The Central Creek placer sample suite had no Pb or Co and a slightly higher Sb signature.

Inclusions observed in the placer samples include boulangerite, stibnite, aurostibnite, stibiconite, chalcostibnite, antimony alloy, pyrite, pyrrhotite, arsenopyrite, chalcopryite, sphalerite, galena, as well as ankerite, iron oxide, mica, clay, and quartz. The lode samples contained each of these except for chalcopryite and the addition of andorite, bismuthinite, Bi-tellurides, and Bi-Au-tellurides. Within the lode samples, Grey Lead alone has the bismuth- and tellurium-bearing minerals as well as less antimony-bearing inclusions, whereas Blue Lead Extension samples are rich in arsenopyrite and stibnite +/- boulangerite, andorite, and sphalerite mineral inclusions.

5 Discussion

Parallel studies of alloy compositions and inclusions revealed in polished sections of gold grains comprise the methodology of ‘microchemical characterization’. Consideration of the microchemical signatures of gold from the lode sources reveals subtle differences, only some of which are replicated in the populations of placer gold grains. Such patterns are common in gold from orogenic settings (e.g. Chapman et al. 2010a,b) and may be used to infer the presence of undiscovered sources. In the present study, an additional source is required to explain the signature in gold from lower Antimony and Tibbs Creek samples. The Ag cumulative percentile plot

Figure 2. SEM BSE image of a grain collected from the A) lower Tibbs Creek site and B) separated from Gray Lead lode sample. Note the bright thin electrofined (Groen et al. 1990) pure gold rim on the placer grain. Only minerals clearly intergrown with the electrum were counted in this study.

Figure 3. Cumulative percentile plots of Ag in A) Placer creek samples except for Central Creek and B) lode gold samples from Gray Lead (GL), Blue Lead Extension East (BLEE), and Blue Lead Extension West (BLEW). Only three grains were collected from Johnson Creek, insufficient data for this plot.
shows that the population of gold grains from lower Antimony Creek is more complex than can be explained by a simple downstream dispersion of upper Antimony Creek material, as the highest Ag population from Antimony Creek is not seen in the lower Tibbs Creek sample. There is a pronounced break in slope at ~23 wt % Ag in gold from lower Antimony Creek that is absent in the Tibbs Creek sample. The hypothesis of a source local to the Tibbs creek placer is consistent both with the larger accumulation of gold at that point and the morphology of the gold which is suggestive of very limited fluvial transport.

Additionally, the Hg vs Ag plot (Fig. 4) shows higher Hg and Ag content in gold from Antimony and Tibbs Creek than grains derived from the Gray Lead and Blue Lead Extension lodes. Gold grains from Central Creek exhibit a similar Ag vs Hg pattern but with a larger range than those of the Black Mountain lodes. The overall similarity strongly suggests a similar lode source type for the Black Mountain and Central Creek placers.

In addition to distinct gold chemistry in Antimony Creek-Lower Tibbs Creek and the Upper Tibbs samples, there are also differences in the mineral inclusions, intergrown within the gold (Fig. 5). In this approach to characterizing inclusions, only primary minerals are included as these provide the clearest indication of hypogene mineralogy. Upper Tibbs Creek gold contains fewer arsenopyrite inclusions, more pyrite and, lacks the diverse suite of antimony minerals found in gold from Lower Tibbs Creek and Antimony Creek, having only a few inclusions of just antimony-gold alloy. Thus, differences between the alloy signatures of the placer samples are also reflected in their inclusion suites. These factors, together with evidence from morphological studies all indicate the presence of undiscovered mineralization near the floor of the Tibbs Creek valley, and this area could form a future exploration target.

Figure 4. Plot of EMP Ag vs Hg measurements. Traced areas are extent of the lode sample EMP data. BLEE = Blue Lead Extension East; BLEW = Blue Lead Extension West; GL= Gray Lead

The dominant stibnite- boulangerite- arsenopyrite inclusion signature of the gold reported here is atypical for most orogenic gold mineralization both globally (Chapman et al. 2009) and in most of the contiguous terrane in the Yukon (Wrighton 2013). However, it closely resembles that observed in placer samples from the Moosehorn Range on the Alaskan Yukon Border (Fig. 5; Wrighton 2013). Allan et al. (2013) determined a Cretaceous age for Moosehorn mineralization, similar to that at the Coffee Prospect, western Yukon, where the mineralization also exhibits a strong Pb-Sb-As-S signature, both of which are interpret by Wrighton (2013) and MacWilliam (2018), respectively, as orogenic Au deposits. Identification of the microchemical signatures in gold from placer areas where the source style of mineralization is uncertain can help to inform our understanding of regional metallogeny.

6 Conclusion

Microchemical characterization and consideration of gold grain morphology from placer and lode sources in the Black Mountain area suggests the presence of an undiscovered lode gold source in the Tibbs Creek valley. Identification of a very similar microchemical signature in
the gold sample from Central Creek suggests that this style of mineralization is more than a local occurrence. Furthermore, the similarity of this microchemical signature to that of gold from the Moosehorn Range provides evidence for a generic Pb-Sb-As-S signature associated with orogenic gold mineralization of Cretaceous age.

Our application of microchemical characterization of populations of placer gold grains in an area where understanding of placer-lode relationships is limited, suggests there are one or more hitherto undiscovered placer-feeding lode gold sources. In addition, the potential wider benefits of this method to understanding regional metallogeny have been demonstrated.

Acknowledgements

We would like to thank Thomas Strong and Chris Holm-Denoma for help with the Selfrag and Garth Graham and Ryan Taylor for collection of the BLEE and GL samples as well as reviews of early versions of this abstract. Any use of trade, firm, or product names is for descriptive purposes of the methods process only and does not imply endorsement by the U.S. Government.

References


Groen, JC, Craig, JR, Rimstidt, JD, (1990) Gold-rich rim formation on electrum grains in placers, Can Min 28:207-228


Abstract. A significant amount of the gold extracted today is sourced from orogenic deposits where it is concentrated in very high-grade quartz veins. The local elevated gold concentration in the veins appears to exceed the gold solubility expected in hydrothermal fluid in mid-crustal conditions. Accordingly, the gold transport mechanism and/or deposition processes associated to the formation of the ultra-high grade veins remains contentious. Here, we present Transmitted Electron Microscopy (TEM) analyses conducted on a high-grade quartz vein (>100 g/t Au) from the world-class Callie orogenic gold deposit (14.6 Moz Au). The TEM analyses are focused on a silica inclusion (~2.5 µm wide) enclosed within a gold grain and the results reveal that the inclusion is composed of amorphous silica that contains numerous Au nanoparticles which vary in size between 0.5 to 11 nm. The preservation of amorphous silica and Au nanoparticles indicates that the formation of colloidal Au and Si might have played a significant role in the formation of high-grade gold veins.

1 Introduction

The growing cost of gold exploration together with surficial resource depletion requires new impetus in our understanding of how high-grade orebody form. The concentration of Au into high-grade quartz veins (>> 100 g/t Au) from the world-class Callie orogenic gold deposit (14.6 Moz Au). The TEM analyses are focused on a silica inclusion (~2.5 µm wide) enclosed within a gold grain and the results reveal that the inclusion is composed of amorphous silica that contains numerous Au nanoparticles which vary in size between 0.5 to 11 nm. The preservation of amorphous silica and Au nanoparticles indicates that the formation of colloidal Au and Si might have played a significant role in the formation of high-grade gold veins.
et al. 1975; Ahmad et al. 2013; Bagas et al. 2014). The Tanami Group was first deformed and metamorphosed by an inferred NW-directed collision (Li et al. 2014; Bagas et al. 2010). The Tanami Group was affected by a second shortening event which is associated with dolerite dykes and granitic pluton emplacement between c. 1830 and c. 1780 Ma (jaccheri 2017; Bagas et al. 2010). Some of the magmatism was coeval with the gold mineralization in the Granites-Tanami Orogen, which formed between c. 1805 and 1790 Ma (Bagas et al. 2010; Cross et al. 2005; Fraser et al. 2012; Petrella et al. Accepted).

The stratigraphy is affected by three main deformation events (summarized in Figure 2); 1) a N-S oriented shortening event (D1) expressed by a tight folding of the stratigraphy along a fold axis that trends ~ N110 and dips ~80° to the SSW, 2) an E-NE to W-SW shortening and main mineralization event (D2) responsible for the formation of several structural pathways along a S2 foliation that trends from N060 to N110 and steeply dips from 60° to 75° to the SSE. The structural pathways are host to gold and are characterized by a high density of quartz-veins which are oriented parallel to the structural pathways; 3) a E-W oriented shortening event (D3) expressed by reverse faults oriented NW-SE to N-S and dipping ~ 50° to 60° to the E. The faults are associated with low angles carbonate-rich veins (Petrella et al. Accepted).

The ore at DBS includes vein-hosted and stratabound styles which are hosted in different units of the Dead Bullock Formation (Petrella et al. Accepted). The vein-hosted style has the highest Au grade (averaging 6 g/t Au; Schmeider et al. (2018)) and consists of visible gold hosted in quartz veins in decarbonized siltstone units. In contrast, the stratabound style is lower grade (averaging 2 g/t Au) and is associated with disseminated sulfides in iron-rich stratigraphic horizons. Both mineralization types result from the same mineralizing event associated with D2 and dated at c. 1805 Ma (Petrella et al. Accepted).

2. Method

2.1 Transmitted Electron Microscopy (TEM)

A high-grade gold-bearing quartz vein (sample N700_9672B @82.5m; Figure 3A) was selected for this study. We prepared a thin foil of approximately 10 x 10 µm size from a polished thin section at the interface between an Au grain and its quartz host (Figure 3B and C). The foil was prepared using a Tescan Lyra Ga+...
focused ion beam coupled with a scanning electron microscope (FIB-SEM). In-situ lift out techniques was used to mount the TEM foil onto a copper grid. The foil was thinned to ~100 nm, followed by a low kV (2 kV) ‘clean up’ routine to remove Ga+ ion surface implantation. The foil was then analyzed using a Talos FEG TEM operating at 200 kV accelerating voltage. Both instruments are housed at the Microscopy and Microanalysis Facility (MMF) at Curtin University’s centralized research infrastructure hub, John de Laeter Centre (JoDLC).

4 Gold nanoparticles associated to high-grade mineralization

From the selected sample, a foil was extracted that includes a quartz grain and a gold grain containing a silica inclusion (Figure 3B and C). Sub-rounded silica inclusions of 1 to 2 µm are common in the Au grains from this sample. The targeted inclusion is approximately 2.5 x 0.5 x 1 µm in size, sub-rounded to elongated and located close to the outer border of the Au grain. The TEM bright field images reveal the presence of a cluster of numerous Au nanoparticles within the silica inclusion mainly located along the contact with the Au grain. The Au nanoparticles are rounded and their size varies between 0.5 to 11 nm. Within the clustered area, the lattice continuity within the Au nanoparticles indicates the presence of numerous individual particles. The lattice continuity and selected areas electron diffraction (SAED) pattern acquired over the gold nanoparticles cluster, confirms the presence of multiple individual crystals of Au.

Electron diffraction of the quartz grain shows the presence of a single crystal, however, electron diffraction in the silica inclusion revealed a complete absence of crystalline structure, and therefore the presence of amorphous silica can be assumed.

In this study we present TEM analysis from a high-grade Au vein at the world-class Callie deposit that show numerous Au colloids trapped in an amorphous silica inclusion preserved within a gold grain. The estimated pressure and temperature of formation of the Callie ore system is 70 to 130 MPa and 240° to 360°C respectively (Mernagh and Wygralak 2007) and the mineralization is estimated to have formed at c. 1805 Ma (Petrella et al. Accepted) which make the preservation of amorphous silica inclusions very remarkable. Amorphous silica generally consists of spherical nanoparticles of SiO or SiOH groups. The crystallization of amorphous silica into quartz, which consists of a re-ordering of the atoms and an increase in density, is mainly linked to the removal of water from the amorphous silica phase (Herdianita et al. 2000; Rodgers et al. 2004). When Si nanoparticles are linked in a coherent three-dimensional aggregates they form a silica gel (Iler 1979), consequently, we propose that a silica gel containing Au nanoparticles was deposited in the vein.

Therefore, the finding of naturally occurring Au nanoparticles within a Au grain supports the involvement of colloidal Au in the formation of high-grade veins predicted by Herrington and Wilkinson (1993). The presence of Au colloid in the mineralizing fluid might explain Au concentration that exceeds the expected Au solubility in the fluid.

The results presented in this study suggest that Si and Au colloids might contribute in forming high-grade gold intercepts. The preservation of amorphous silica inclusions opens further research probing into their composition and potential contribution to the hydrothermal system.

Acknowledgements

This study is part of a PhD project started in March 2016 at the Centre for Exploration Targeting at UWA. Newmont Mining Corporation, the Australian Postgraduate Award and the Mineral Council of Australia are gratefully acknowledged for financial support to this project. Newmont Tanami geologists are thanked for providing site access, support and insightful discussions. This study is partly supported by the Hammond and Nisbet fund at UWA.

References


Geochronological and multi-isotopic evidence for the genesis of the post-magmatic and deeply-sourced Daliuhang orogenic gold deposit, Jiaodong, China

Kai Feng, Hongrui Fan
Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, China

David I. Groves
Centre for Exploration Targeting, University of Western Australia, Australia

Abstract. The Daliuhang gold deposit (>20t gold) is located in the central Penglai-Qixia belt of the giant Jiaodong gold province, eastern China. The ore-hosting Guojialing granodiorite and pegmatite were formed at 129.0 ± 0.6 Ma and 126.2 ± 0.6 Ma, respectively. Syn-ore monazite, with a U-Pb age of 120.5 ± 1.7 Ma, represents the timing of gold mineralization. Noble gas isotopes of pyrite indicate that the initial ore-forming fluids were deeply-sourced from the sedimentary wedge overlying the subducted plate and mantle during early Cretaceous paleo-Pacific plate subduction. There is a narrow variation of δ³⁴S values (3.7−8.3‰) of ore pyrite, which also suggest that the initial ore-fluid and some of the sulfur component were derived via subduction-related devolatilization. The elevated δ³⁴S values of the ore-related pyrite are partly ascribed to mass fractionation and partly to a contribution from sulfur leached from crustal host rocks. This interpretation is also supported by Nd isotope ratios of monazite, which correlate well with the ore-hosting rocks. This study highlights the combined roles of deeply-derived fluids and intense interaction with upper crustal rocks in the formation of Jiaodong gold deposits.

1 Introduction

The Jiaodong Peninsula is the largest and most productive gold province in China, with more than 4500t of gold resources (Fan et al. 2016; Yang et al. 2018). Located in central Jiaodong and hosted in early Cretaceous granodiorite, the Daliuhang deposit is a typical auriferous quartz vein-style gold deposit. This deposit has high-grade gold ores (20g/t on average), and locally contains visible gold (Chang et al. 2013). There are abundant mafic and felsic dykes that are broadly coeval with gold mineralization in the mining district. Thus, the Daliuhang deposit represents an excellent example to investigate the possible genetic relationship between Au mineralization and magmatism.

In this study, the U–Pb age of hydrothermal monazite in the ores was obtained to delineate the precise timing of gold mineralization. In addition, the U-Pb ages of zircon from ore-hosting granite, a pegmatite dyke and two mafic dykes were obtained, collectively, to determine the timing of relevant mafic and felsic magmatic events. In-situ sulfur isotopic analyses on gold-hosted pyrite, in-situ Nd isotopic analyses on hydrothermal monazite, and He–Ar isotopic analyses on primary ore-forming fluids entrapped in pyrite, were conducted in order to place constraints on the sources and temporal evolution of the ore-forming fluids, and also on the possible sources of sulfur and ore metals. The integrated results allow a better understanding of the genesis of the Daliuhang deposit.

2 Regional and ore deposit geology

The Jiaodong Peninsula is located on the south-eastern edge of the North China Craton. It comprises the Sulu ultra-high pressure orogen in the southeast and the Jiaobei Terrane in the northwest (Fig. 1). Almost all gold deposits are distributed in the Jiaobei Terrane, which mainly comprises Precambrian basement rocks and Mesozoic magmatic intrusions and volcanic-sedimentary sequences (Zhai and Santosh 2013). The Jiaodong gold province is divided, from west to east, into the Zhaoyuan-Laizhou, Penglai-Qixia and Muping-Rushan belts (Fig. 1). Most gold deposits are hosted in the Linglong and Guojialing granitoids or their contacts with the basement metamorphic rocks. The distribution of gold deposits is controlled by a set of NE- and NNE-trending crustal-scale faults zones. Gold deposits have been traditionally classified as disseminated-style and auriferous quartz vein-style (Fan at al. 2007).

The Daliuhang gold deposit, with a proven reserve of >20t gold, is situated in the northern segment of the Penglai-Qixia gold belt. Granitoids are widely distributed in the mining district, and include the late Jurassic Linglong gneissic biotite granite and early Cretaceous Guojialing granodiorite. Late-magmatic pegmatite and aplite dykes are well-developed within the Guojialing granodiorite. The ore bodies are mainly hosted in the Guojialing porphyritic granodiorite. The mineralization occurs predominantly in the form of massive auriferous quartz veins. The No. 103 vein is the most important and representative orebody in this district, with a length of 2.5 km and a width of approximately 0.2 to 2 m. It generally strikes 020°–045°, dips 50°–80° SE. The gold grade varies from 1.06 to 160.02 g/t, averaging 20.09 g/t. The alteration halos include an intense sericite-quartz alteration zone, followed by sericitization, silicification, and K-feldspar alteration zones.
Four stages of mineralization in the ore-bearing lodes have been recognized based on crosscutting relationships between veins and mineral textures within them. Stage I is characterized by coarse-grained milky quartz with sparsely disseminated fine-grained pyrite (Py1) that contains no gold mineralization. Stage II is represented by quartz-pyrite veins. Pyrite in this stage (Py2) is euhedral to subhedral, and is compositionally homogeneous in BSE images. Some visible gold grains occur either along the grain boundaries or within fractures of Py2 (Fig. 3a). A few monazite grains were also identified as inclusions in Py2 grains or adjacent to their margins, showing a close spatial association with pyrite (Fig. 4a-b). The anhedral monazite grains have variable diameters (5–100 μm) and are compositionally homogeneous under BSE images. Stage III veins contain coarse-grained quartz and pyrite, with subordinate galena, sphalerite and chalcopyrite (Fig. 3b-c). Locally, stage III minerals are superimposed on Py2, forming an irregular, dark inner core (marked as Py2-altered) with fine-grained galena overgrown by a bright outer rim of arsenian Py3 (Feng et al. 2018 and our unpublished data). Irregular electrum grains occur along grain boundaries of Py3 where they display a close paragenetic association with galena (Fig. 3b). Stage IV is represented by milky carbonate-quartz veins with minor pyrite (Py4). Stages II and III represent the main gold mineralization episodes.

**Figure 1.** Geological map of the Jiaodong gold province, showing the major gold deposits and lithological units (Wen et al. 2015).

**Figure 2.** Photographs of major wallrocks and various mineralized veins. a Multiple pegmatite dykes intrude into Guojialing granodiorite; the earlier pegmatite-1 is crosscut by later pegmatite-2; b Guojialing granodiorite and pegmatite are crosscut by mafic dyke; c Quartz vein (Stage I) and its adjacent sericite-quartz alteration, sericitization and silicification; d Representative specimens of quartz-pyrite veins (Stage II) which are crosscut and overprinted by quartz-galena-pyrite vein (Stage III).

**Figure 3.** Microscopic images showing occurrences of visible gold and textural features of pyrite from main mineralizing Stage II and III. a Coarse-grained Py2 and visible gold grains occur in fractures; b Visible gold grains intergrown with galena along grain boundaries of the Py3; c Py2-altered (core) and Py3 (rim) are both infilled by galena; d Oscillatory-zoned Py3 that has overgrown the porous Py2-altered. Representative δ34S values are shown in figure c (via SIMS) and figure d (via LA-MC-ICPMS).

**3 Geochronology**

Hydrothermal monazite dating indicates that the gold mineralization occurred at 120.5 ± 1.7 Ma (Fig. 4). It places the age of gold mineralization at least five million years younger than the latest granitic magmatic activity indicated by the ca.126 Ma age of pegmatite dykes that intruded the ca. 129 Ma Guojialing granodiorite. The above robust dating results show a measurable age gap between the ore-hosting intrusion solidification and gold deposition, such that gold mineralization cannot have a direct association with granite magmatism. This is also supported by the 40Ar/39Ar ages of pristine biotite from Guojialing granodiorites (124.5-124.0 Ma, Li et al. 2003), indicating that the intrusions have cooled below ~350°C before gold mineralization.

The contacts between granitic intrusions and Precambrian basement rocks are particularly favourable sites for mineralization, with heterogeneous stress and inhomogeneous strain between different rock units focusing ore-fluid infiltration (Groves et al. 2018). Note that some syn-ore mafic dykes (121.1 ± 0.7 Ma), with no obvious wallrock alteration, are interleaved with nearby auriferous quartz veins within the same fault zones in the adjacent Heilan’gou deposit. Given the spatial and temporal association between gold mineralization and mantle-derived mafic rocks, the ore-controlling faults are inferred to have great vertical depth extension (Zhao et
Figure 4. a–b: Representative monazite crystals, coexisting with pyrite; c: The U–Pb Tera–Wasserburg Concordia diagram for monazite; d: the 206Pb-corrected 206Pb/238U weighted mean age al. 2012; Zhu et al. 2015) and to have facilitated the advection of deeply sourced fluids to the site of gold mineralization at shallower crustal levels.

4 Origin of ore-forming fluids and ore metals

On a 3He versus 4He plot, samples from the Daliuhang deposit lie between the crustal and mantle curves (Fig. 5a), indicating mixed sources between those two reservoirs. As a result, the mantle contribution from the current study is estimated to be between 20% and 40%. The 36Ar/39Ar ratios (327–574) of fluids in pyrite are much lower than those of deeply-derived mantle fluids (≥12000, Burnard et al. 1997), but slightly higher than the atmospheric value of 295.5, which indicates a significant atmospheric influence. In addition, there is a broadly positive correlation between 36Ar and 3He (Fig. 5b). The most logical interpretation is that there has been addition of an atmospheric noble-gas component into the mantle through subduction (Gautheron et al., 2005; Broadley et al., 2016). Therefore, it is deduced that ore fluids were derived via devolatilization of the sedimentary wedge, with its atmospheric component, and oceanic crust or overlying mantle lithosphere during subduction of the paleo-Pacific plate beneath the eastern North China Craton in the early Cretaceous (Zhai and Santosh 2013; Goldfarb and Groves 2015 and references therein).

Hydrothermal monazite has initial Nd isotopic compositions overlapping those of the ore-hosting Guojialing granodiorite (Fig. 6b). Thus, REE components in the ore-forming fluids were most likely extracted from the Guojialing intrusions along the fluid flow path. The ore-forming fluids that formed the Jiaodong deposits are characterized by lower REE concentrations (the bulk of sulphide ore in Xinli gold deposit: average 71 ppm; Zhao et al. 2015) than Guojialing granodiorites (average 309 ppm; Li et al. 2019). This interpretation is consistent with the rarity of REE-bearing minerals (mainly as monazite) in the ores. Thus, the Nd isotope ratios of ore-forming fluids are sensitive to input of REE from wallrocks via fluid-rock interaction.

5 Conclusions

at Daliuhang, similar to other deposits in the Jiaodong gold district (Fan et al. 2016). In concert with the noble gas data, these positive δ34S values are consistent with a model in which some sulfur was derived from mantle-crustal mixing processes at depth related to devolatilization during subduction of the paleo-Pacific plate (Deng et al. 2015; Zhu et al. 2015; Goldfarb and Groves 2015). However, it is inevitable that such fluids would scavenge additional sulfur from upper crustal rocks during advection, making it difficult to unequivocally define the ultimate fluid source. Compared with early-stage Py1, ore-related pyrites (Py2 and Py3) have higher δ34S values (6.7–8.3‰), with corresponding calculated δ34S values of 8.6–10.2‰ for ore-forming fluids (ln34α

Pyrite/H2S=1.9‰, Syverson et al. 2015). Considering the limited amount of Py1, mass fractionation during precipitation of pyrite seems unable to explain such elevated δ34S values (Ohmoto 1972; Zheng and Hefes 1993). In this case, an external 34S-enriched source appears to be required. It is proposed that some sulfur from the Jinghuan Group (δ34S: 8.2–12.0‰, average 9.7‰; Zhang and Chen, 1999) was leached into the ore-forming system. This interpretation is also supported by elevated As concentrations of ore-related pyrite (Feng et al. 2018 and our unpublished data), with As commonly enriched in meta-sedimentary rocks (mean 3.32ppm) relative to Guojialing granodiorite (mean 0.25ppm) and Linglong granites (mean 0.38ppm) as determined by Ding et al. (1997).

There is a narrow variation of δ34S values (3.7–8.3‰)
The U-Pb age of 120.5 ± 1.7 Ma for hydrothermal monazite represents the timing of gold mineralization at the Daluinhang gold deposit. It places the age of gold mineralization at least five million years younger than the latest granitic magmatic activity indicated by the ca.126 Ma age of pegmatite dykes that intruded the ca. 129 Ma ore-hosting Guojialing granodiorite. Therefore, a genetic relationship between gold mineralization and early Cretaceous magmatic-hydrothermal activity is negated. Noble-gas isotope ratios are consistent with a model in which ore forming fluids were initially derived from devolatilization of the subducted slab and overlying sediment wedge and interaction with overlying mantle lithosphere during paleo-Pacific plate subduction in the early Cretaceous. The deeply-sourced fluids migrated upwards along crustal-scale faults, defined by the occurrence of widespread mafic dykes, scavenging sulfur and REEs from upper crustal rocks into the ore-fluid, thus devolatilizing the subducted slab and overlying sediment wedge and interaction with overlying mantle lithosphere during paleo-Pacific plate subduction in the early Cretaceous. The deeply-sourced fluids migrated upwards along crustal-scale faults, defined by the occurrence of widespread mafic dykes, scavenging sulfur and REEs from upper crustal rocks into the ore-fluid, thus creating mixed mantle-crustal signatures in isotopic ratios of ore minerals and fluid inclusions within them. During the main ore stage, gold was initially incorporated into arsenian pyrite, but later was deposited as native gold as sulfur activity decreased in an already low-S fluid.

Acknowledgements

Drs. Xin Yan, Kuidong Zhao, Yueheng Yang and Guoqiang Tang are thanked for their help during analyses of the SEM, LA-ICPMS, LA-MC-ICPMS and SIMS, respectively.

References

Goldfarb RJ, Groves DI (2015) Orogenic gold: Common or evolving fluid and metal sources through time. Lithos 233:2–26
Gold from Orogenesis to Alluvial  707

Mineralization, alteration and age of the host at the Barsele orogenic gold deposit, northern Sweden

Helen V. Thomas
Luleå University of Technology, Sweden

Marcello Imaña, Kåre Höglund
Agnico Eagle Sweden AB

Christopher Mark
University College, Dublin, Ireland

Thomas Riegler, Claire Florence Ansberque
Trinity College, Dublin, Ireland

Tobias Bauer, Glenn Bark
Luleå University of Technology, Sweden

Abstract. The Barsele Gold deposit is located near Storuman in Northern Sweden. Mineralization is hosted in approximately N-S to NW-SE trending D3 oriented quartz-carbonate veins and microfractures located in a granodiorite intrusion dated at 1.872 Ga ±11 Ma by this study. Gold is primarily free milling with a minor proportion occurring as invisible gold associated with sulphide minerals.

1 Introduction

The Barsele prospect is located in the Storuman area and forms part of the so-called Gold Line, a NW-SE trending belt of anomalous gold concentration in the till overburden c. 50 km southwest of the Skellefte district. As well as Barsele the deposits in the belt include Knaften, Fäboliden, Svartliden, Stortjärnhobben and Blaiken (Bark & Weihed 2007). The Storuman area hosts both volcanic-hosted massive sulphide (VMS) and orogenic gold mineralization at Norra and Barsele respectively (Fig. 1).

Gold mineralization at Barsele occurs mainly as free gold and electrum, with a minor portion present as refractory gold associate with arsenopyrite and pyrite. Arsenopyrite occurs throughout the paragenesis at Barsele, but is not always associated with strong gold enrichment. Tungsten occurring as scheelite is also variably associated with gold. Other phases present include pyrrhotite, pyrite, chalcopyrite, galena, sphalerite, tetrahedrite/tennantite.

The characteristic elongated shape of the intrusion along a regional D2 shear suggests that the deformation is roughly coeval with deformation dated in the Skellefte district at 1.87 Ga (Skyttä et al., 2012 and references therein). This confirms the area as a south-westward extension of the Skellefte district with interesting implications for gold deposit formation in the area as the structural setting and granodiorite host combine to provide a favourable host for orogenic gold mineralization.

Further work in this project is expected to confirm the Norra VMS deposit, hosted in NNW-SSE trending D1/D2 structures, as younger than the Barsele gold deposit, as is common in the Skellefte district (Allen et al., 1996; Bauer et al., 2011). Mineralization at Norra consists of reduced assemblages containing pyrrhotite, chalcopyrite, dark sphalerite and gold-bearing arsenopyrite.

Geochemical data analysed here includes assay data (multi element, after 4 acid digest) and hyperspectral core scanning. Textural observations are based on drill core study as well as petrographic study under the optical microscope. Samples for petrographic study were mounted in resin blocks and analysed using Scanning Electron Microscopy (Zeiss Merlin FEG-SEM-EDS/WDS) and Laser Ablation Inductively Coupled Mass Spectrometry (Thermo Scientific iCAP Qc, coupled to an ESI NWR193 laser) at Luleå University of Technology, Sweden.

2 Regional geological framework

The Barsele prospect is located within Palaeoproterozoic supracrustal and associated intrusive rocks (Fig. 1). Bedrock in the area consists of 1.9–1.8 Ga supracrustal and associated intrusive rocks that were deformed and metamorphosed during the Svecofennian orogeny (Lundström et al., 1997; Mellqvist et al., 1999; Kathol & Weihed, 2005). The Storuman area borders the Skellefte district to the east. North of the Skellefte district Palaeoproterozoic and reworked Archaean rocks form the Norrbotten craton. South and east of the study area, metasedimentary rocks of the Bothnian Basin occur, so the Storuman area represents a kind of transitional zone between two major tectonic units.

The lowest stratigraphic unit in the area consists of metasedimentary and intercalated volcanic rocks of the Bothnian Supergroup (Kathol & Weihed, 2005; Skyttä et al., 2012). The Bothnian Supergroup forms the inferred basement to the 1.89–1.88 Ga, mainly felsic volcanic rocks of the Skellefte Group (Allen et al., 1996; Kathol et al., 2011). VMS deposits formed dominantly as sub-seafloor replacement in volcanoclastic and sedimentary
rocks and partly as exhalative deposits within the stratigraphically uppermost part of Skellefte Group volcanic rocks (Allen et al., 1996) utilizing the syn-extensional faults as fluid conduits (Bauer et al., 2014). Studies from the nearby Skellefte district indicate that the Skellefte Group volcanic rocks are overlain by a 1.88–1.87 Ga, dominantly sedimentary unit called the Vargfors Group (Allen et al. 1996).

The oldest intrusive rocks in the district are early orogenic, 1.89–1.88 Ga granitoids, diorites and gabbros, including a quartz-monzodiorite in Barsele dated at 1880±4 Ma (Eliasson et al., 2001).

The main compressional deformation event (D2) took place at 1.88–1.87 Ga and resulted in folding, reactivation of the syn-extensional faults and related transposition of VMS deposits (Bauer et al., 2011). The latest major deformation event at 1.82–1.80 Ga (D3; Weihed et al., 2002) is inferred to have resulted from east-west crustal shortening causing reactivation of major syn-extensional high-strain zones with reverse kinematics (Bergman Weihed et al., 1996; Bauer et al., 2011; Bark & Weihed, 2012; Skyttä et al., 2012). Gold deposits south and east of the Barsele area are classified as orogenic gold deposits and are related to the E-W crustal shortening event at 1.80 Ga (D3; Bark 2008).

Figure 1. Geological map of the Storuman area. Modified after Kathol et al. (2005) and Krispinsson (2018). Coordinates in SWEREF99. Thick black lines represent major structures in the area. The vein orientation in the Barsele Gold Deposit is controlled by N-S trending D3 structures; with the Norra VMS deposit hosted in roughly E-W trending D2 structures. From Bauer et al. (2019).

3 U-Pb and trace-element analysis of zircon

Zircons from seven granodiorite samples were selected for trace element (Ti, REE) and U-Pb isotopic analysis, conducted at University College Dublin using a Thermo Scientific iCap Qc ICPMS, coupled to a Teledyne Analyte G2 193 nm excimer laser mounted with a two-volume cell. Analytical parameters and data reduction were similar to those described by Mark et al. (2016), except that the primary standard for trace-element analyses was GZ7 zircon (Nasdala et al., 2018). For six samples, zircon were mounted conventionally in resin, ground to expose internal surfaces and polished, following which cathodoluminescence images were acquired to guide placement of laser spots (n = 162). Zircons from the remaining sample were placed intact on adhesive tape (n = 13); the laser was then rastered over the grain surfaces in order to ablate only the most recent zircon growth.

Figure 2. Results of zircon U-Pb analysis. Red – analyses used for discordia calculation, including raster analyses; grey – conventional spot analyses; blue – data from subset of conventional analyses yielding highly discordant data. Inset: upper intercept age calculated using only weighted-means of equivalent conventional analyses.

Following exclusion of a small number (n=10) of inherited grains and highly discordant outliers, all remaining analyses which yielded single-analysis concordia ages with probability of concordance ≥ 0.001 were assumed to fall on a two-end-member mixing line. The Isoplot plug-in for Microsoft Excel (Ludwig, 2012) was used to generate weighted-mean isotopic ratios for all analyses which were equivalent for each conventionally-analysed sample. These six weighted-mean values define a discordia with an upper intercept of 1.872 ± 11 Ma (2σ), which we interpret as the age of crystallisation, plus a poorly defined lower intercept. Together with the raster analyses, the weighted-mean values define a discordia with an upper intercept of 1.869 ± 11 Ma, and a lower intercept of 225 ± 17 Ma. Finally, one conventional sample yielded a few (n=13) analyses which exhibited highly discordant portions of the downhole signal. The age significance of these is unclear; they may represent isotopic mixing between >2 end-members, or a separate discordia produced by an event intermediate between intrusion and Triassic zircon overgrowth.
Crystallisation temperatures calculated by Ti-in-zircon thermometry (Ferry and Watson, 2007) yield temperatures scattered between c. 800-900 °C for the grains recording intrusion; the raster analyses yield nominal temperatures of c. 900-1200 °C. Given the absence of a HT overprint, the latter are interpreted as evidence for Mesozoic crystal growth during the breakdown of a Ti-bearing phase, and are not meaningful. REE spectra were relatively uninformative.

4 Mineralization

Mineralization at Barsele is hosted by an early orogenic metagranodiorite that intruded at 1.872 Ga ±11Ma (this study) during emplacement along an WNW-ESE D2 structure to give an elongated shape.

Figure 3. LA-ICPMS map showing trace element evolution in overgrowths of arsenopyrite. Red: Gold; Green: Copper, Blue: Antimony.

Multiple generations of veining occur at Barsele with most veins hosting varying amounts of sulfide minerals including arsenopyrite. However, the relationship between sulfide mineralization is not simple with no direct correlation between gold grade and proportion of sulfide minerals, trace element concentrations in assay or presence of absence of scheelite. This is complicated by the protracted sulfide precipitation history illustrated in Figure 3.

Vein types described by Agnico Eagle geologists (Imaña, 2016) are classified based on visual observations in drill core and geochemical assay data and are described as Qtz-0 to Qtz-4. Qtz-0 are early, syn crystallization in nature, while Qtz-1 to 4 appear to overlap paragenetically during the main stage of mineralization. Gold is present in most vein types from Qtz-0 grey wormy quartz veins, to later Qtz-1 to 4 quartz-carbonate veining. These vein stages are characterized further in Rann and Pitcairn (2019).

Figure 4 shows an SEM (scanning electron microscope) map of a Qtz-4 polymetallic vein from a high grade sample, where quartz precipitation is accompanied by the addition of sulfides and electrum. Quartz-carbonate veins hosting base metal sulfides (Qtz-4) appear to occur late in the deposit evolution and are characterized by the presence of varying amounts of arsenopyrite, galena, pyrrhotite, pyrite, chalcopyrite, tennantite/boulangerite sulfosalts and bismuth bearing minerals. Arsenopyrite occurring in these veins differs from arsenopyrite elsewhere in the Barsele deposit as it is strongly included by galena.

Tourmaline veining occurs early in the deposit evolution, but after Qtz-0, as it has been observed to be cross cut by the quartz vein sets Qtz-1 to 4. Alteration associated with tourmaline veining consists of variable amounts of fine-grained arsenopyrite, and bleached haloes proximal to the veins indicating local albition of the host rock (few cm wide).

A decreased ratio of As/Sb in the central part of the deposit is consistent with the presence of Pb sulphides and sulphosalts and may represent lower temperature parts of the system.

5 Hydrothermal alteration

Hydrothermal alteration at Barsele is typical of an orogenic gold system. Proximal to veins fine-grained arsenopyrite occurs as cm-wide haloes, accompanied by weak bleached haloes as a result of a sulfidation reaction where iron is removed from the host to form sulphide minerals in the veins.

Chlorite occurs as a common alteration mineral, replacing biotite and other Fe-Mg bearing minerals and as selvages to Qtz-2 veins. There may be a weak association between veining and alteration of white mica composition as seen in hyperspectral core scanning, but this appears to be confined to very proximal areas. Very early and probably synvolcanic chlorite alteration also occurs in the shear zones at the Barsele gold deposit unrelated to gold mineralization, but associated with Zn.
enrichment.

6 Conclusions

Based on new dates presented here for the host rocks to mineralization, the Storuman area appears to be a westward extension of the Skellefte District. Gold mineralization appears to be orogenic in nature with the granodiorite host providing a favourable structural host for veining rather than a source for most of the gold. Further work is planned to investigate a possible source for the gold and to date the mineralization itself. The possibility that mineralisation is Triassic in age, perhaps linked to postulated Mesozoic unroofing of Paleozoic sedimentary cover (Larson and Tullborg, 1998), will be considered.

Acknowledgements

The authors thank Agnico Eagle Sweden AB for support, access and discussions. Iain Pitcairn and Evelina Rann are acknowledged for discussions. This work was funded by the EraMin project “Gold insight” and the ARN project (Alternative Mineral Raw Materials in Northern Sweden), funded by the European Union, through the Swedish Agency for Economic and Regional Growth and the Norrbotten County Council respectively.

References


Imaña, E.M., 2016: Barsele project: Structural compilation, lithogeochemistry and alteration, Unpublished internal report for Agnico Eagle AB.


Tracking an Archean orogenic gold deposit evolution through multiple sulfur isotopes

Dennis Sugiono, Nicolas Thébaud, Marco L. Fiorentini, Laure Martin
Centre of Exploration Targeting, School of Earth Sciences, University of Western Australia, Australia

Crystal K. LaFlamme
Department of Geology and Geological Engineering, Université Laval, Canada

Jamie Rogers, Giovanna Lorusso
Northern Star Resources, Australia

Abstract. The ability to detect mass-independent fractionation of sulfur (MIF-S) with reliable precision at the micro-scale has opened a new dimension in tracking changes of hydrothermal fluid conditions and sulfur reservoirs. Orogenic hydrothermal fluids often transport gold associated with sulfur complexes. However, the origin of sulfur in these fluids remains elusive.

Furthermore, the mechanism for gold precipitation is yet to be fully understood. Interpretation of widespread $\delta^{34}$S values in the past indicate a severe limitation in distinguishing between changes in P-T-pH-FO$_2$ conditions versus a change in sulfur reservoirs. To address these knowledge gaps, we apply multiple sulfur isotope analysis to rocks in the structurally controlled Kanowna Belle deposit, Kalgoorlie Terrane of Western Australia, where five temporally-distinct vein sets intrude different Archean lithologies. Results yield a consistent positive MIF-S ($\Delta^{33}$S = +0.05‰ to +0.39‰) with highly variable $\delta^{34}$S values (-10.46‰ to +12.47‰) across different vein sets. These results are consistent with previous sulfur isotope results in other orogenic gold systems across the Yilgarn Craton and are compiling to show that the hydrothermal fluids source sulfur away from the precipitation site. Gold is later released from hydrothermal fluids through thermodynamic changes as preserved by the $\delta^{34}$S spread in mineralised vein sets.

1 Introduction

The advancement of analytical techniques in sulfur isotope analysis using Secondary Ion Mass Spectrometry (SIMS) has enabled the in situ analysis of the ratio of $^{34}$S and $^{33}$S compared to $^{32}$S with high precision. Thanks to these technical advances, it is now also possible to conduct in-situ multiple sulfur isotope analyses with high spatial resolution across a sulfide-bearing hydrothermal paragenetic sequence while preserving textural context (LaFlamme et al. 2018a).

Orogenic gold deposits are structurally controlled deposits that commonly formed during late to post-peak metamorphism within orogenic belts throughout the crust (Goldfarb and Groves 2015). The source of orogenic gold fluids is, however, still poorly constrained with researchers suggesting origin from; (1) magmatic or mantle (Xue et al. 2013), (2) gold-rich lamprophyres (Rock and Groves. 1988), (3) devolatilization of subducting slab (Goldfarb and Groves 2015; Selvaraja et al. 2017; LaFlamme et al. 2018), (4) meteoric fluid (Hagemann et al. 1994), (5) metamorphic devolatilisation (Phillips and Powell 2010; Tomkins 2010), (6) local sediments, especially carbonaceous shales (Large et al. 2011). Further, the precipitation process of gold in orogenic gold systems is also still not well understood, and has been described as a result of; (1) fluid mixing (Mikucki 1998), (2) fluid-rock interaction (Palin and Xu 2000) and (3) rapid changes in either temperature, pressure and oxygen fugacity of fluids (Palin and Xu 2000; LaFlamme et al. 2018a).

Gold transport in orogenic systems is thought to be mainly achieved by bi-sulfide complexes and/or with radical ion tri-sulfur complexes acting as ligands for Au (Seward 1973; Pokrovski and Dubessy 2015). However, early application of sulfur isotopes to trace the source reservoir was inhibited by the inability to distinguish between the change of sulfur source versus the change of thermodynamic conditions affecting the sulfur as it is transported and deposited. Sulfur isotope analyses have been used for the investigation of both source and changes in thermochemical processes within various hydrothermal processes (LaFlamme et al. 2018; Thébaud et al. 2018). The recognition of Archean-sourced sulfur through the signature of mass-independent fractionation of sulfur (MIF-S) (Farquhar et al. 2000; Farquhar and Wing 2003) added another dimension to sulfur isotope application. Symbolised as $\Delta^{33}$S, MIF-S is an indelible trace of the reservoir in which a mantle-derived sulfur should have $\Delta^{33}$S of 0, whereas sulfur affected by Archean atmospheric processes through short wavelength (<340 nm) photolysis should have $\Delta^{33}$S ≠ 0 (Farquhar and Wing 2003). Therefore, with the combination of both, it is now possible to monitor how hydrothermal fluids evolve though time (LaFlamme et al. 2018a).

The Kanowna Belle deposit, which contains multiple style of mineralisations that occur across different lithologies (Davis et al. 2010) offers a fantastic opportunity to further test this technique. In this natural laboratory, the application of multiple sulfur isotopes may help to discover the effects of different host rock lithologies on the hydrothermal fluids sulfur composition. Furthermore, this study is our first application of our recently developed techniques on pyrite and arsenian pyrite to objectively tracking the evolution of hydrothermal fluids within Archean orogenic gold systems leading into
a more consistent genetic model for Archean orogenic gold systems.

2 The geology of the Kanowna Belle deposit

The world-class 6 Moz Kanowna Belle deposit is situated in the gold-rich Kalgoorlie Terrane of the Archean Yilgarn Craton of Western Australia. The regional basal stratigraphy comprises the 2.72 to 2.69 Ga mafic-ultramafic volcanism (Kambalda Sequence; Tripp 2013). The Kambalda Sequence is overlain by the Black Flag Formation, which is dominated by felsic volcanoclastic units and polymictic conglomerate (Tripp 2013). Unconformably overlying the Black Flag Formation is the Panglo member polymictic conglomerate unit (Tripp 2013). The main intrusion in the Kanowna district is the Scotia batholith, located in the core of the Scotia-Kanowna anticline (Ross et al. 2004).

The lithological architecture of the Kanowna Belle deposit can be split into two main groups: the Footwall sequence at the north side of Fitzroy Fault and the Hanging wall sequence at the south (Figure 1). The Footwall sequence consists of the Golden Valley member and intercalation of footwall felsic volcanoclastic units. The Golden Valley member is part of the Black Flag Formation and comprises of sandstone and sparse interbeds of polymictic conglomerate (Tripp 2013). The Hanging wall sequence consists of the Kambalda sequence and Grave Dam member. The Grave Dam member is part of the Black Flag Formation and comprises thickly bedded felsic polymictic volcaniclastic breccia interbedded with feldspathic sandstone and polymictic conglomerate (Tripp 2013). Multiple types of intrusions were observed within the Kanowna Belle deposit geology, consisting of lamprophyre dykes, an aphyric felsic porphyry and the Kanowna Belle Porphyry (2655±6 Ma, Ross et al. 2004; Bull et al. 2017). Part of the Scotia batholith, the Kanowna Belle Porphyry is a feldspar-rich dacite with quartz-feldspar groundmass.

Figure 1. Geological map of the Kanowna Belle deposit (modified after Neumayr et al. 2005; Bull et al. 2017)

2.1 Deformation sequence and vein paragenesis of the Kanowna Belle deposit

The structural expressions in the Kanowna Belle deposit were formed through multiple events of local deformation events (Figure 2). The earliest recorded deformation in the Kanowna Belle deposit is D0 extension, which is related to the formation of the mafic-ultramafic Kambalda Sequence and deposition of the Golden Valley member and Grave Dam member (Tripp 2013). The first contractional event (D1) results in the emplacement of the Kanowna Belle Porphyry and the early formation of the ENE-WSW trending Fitzroy Fault. D1 is syngenetic with the emplacement of gold bearing carbonate-chalcostibite-pyrite-telluride-electrum veins (V1) exclusively hosted within the Kanowna Belle Porphyry adjacent to Fitzroy Fault. The next deformation stage is NE-SW shortening (D2) preserved as a regional foliation (S2) observed across all lithologies in the Kanowna Belle deposit. Early barren sericite-chlorite-pyrite stringers (V2) also formed during D2 and occur pervasively across all lithological packages at the deposit. This is followed by a N-S shortening event (D3), which led to the formation of mineralised quartz-carbonate-pyrite-gold veins (V3a) filling sub-parallel reverse faults to the Fitzroy Fault syngenetic with the shallow dipping extensional veins (V3b). This deformation event is followed by an auriferous ENE-WSW shortening (D4), which may have occurred synchronously with D3. The D4 deformation formed sinistral NW-SE Troy shear zones with quartz-pyrite-gold veins (V4a), steep barren quartz extensional veins (V4b) and late quartz-tourmaline veins (V4c). Both V3a and V4a mineralisation assemblages are strikingly different. The deformation of the Kanowna Belle deposit ended with the late normal movement of the Fitzroy Fault (D5). With the exception of gold-mineralised V1 veins which is exclusively hosted within Kanowna Belle porphyry, all other veins sets were hosted across different lithologies in the Kanowna Belle deposit.

3 Methods

Geological and structural observations on core and underground exposure permitted the definition of the vein paragenetic sequence, which provided the framework for further analytical investigations. Representative sulfides which are associated with different vein sets were sampled for further analysis. Mineralogical petrography and characterisation of the ore mineral assemblage was realised using optical microscopy together with Scanning
Electron Microscopy and Energy Dispersive X-ray Spectroscopy.

Multiple sulfur isotope analyses utilised the Cameca IMS1280 SIMS at the University of Western Australia. Cylindrical samples (around 2.8 to 3.2 mm in diameter) of spatially and temporally constrained sulfides were embedded within the 8 mm from the centre of a 1 inch mount together with a small chip of Sierra pyrite (see below). Trimmed mounts were coated with 30 nm of Au and loaded with a standard block inside the sample chamber. A focused Cs+ beam with an impact energy of 20 keV and beam current of 2.2-2.3 nA in Gaussian mode, rastered the sample surface to create a 10 µm analytical spot. More detailed procedures are defined in LaFlamme et al. (2016).

The sulfur isotopes 32S, 33S and 34S, were simultaneously recorded through three Faraday Cups using amplifiers with 1010 Ω (L2), 1011 Ω (L1), and 1011 Ω (FC2 or H1). Measurement of sulfide standards was integrated into early and in between the analyses to correct the drift, monitor external standard repeatability and correct for instrumental mass fractionation. Matrix-matched reference materials used to normalise isotope ratios were the Sierra pyrite (δ34S = 2.17 ‰; Δ33S = -0.02‰) and Nifty-b chalcopyrite (δ34S = -3.58 ‰; Δ33S = -0.06‰) (LaFlamme et al. 2016). Measurement error (2σ) on the pyrite is about δ34S = ±0.34 ‰; Δ33S = ±0.22‰ and the chalcopyrite is δ34S = ±0.48 ‰; Δ33S = ±0.34‰.

4 Sulfur isotope results

Multiple sulfur isotope results were acquired on sulfides that form within the vein sets across different lithologies that hosted them as described above (n=231). Results show widespread δ34S values ranging from -10.46‰ to +12.47 ‰, and small variation of Δ33S, ranging from ±0.05‰ to ±0.39‰ (Figure 3. A, B) with two Δ33S outliers from the V4 vein set (Δ33S = ±0.45‰ and +0.58‰). The pyrite in the gold-bearing chalcostibite-telluride rich V1 veins exhibits a homogenous metals composition but shows a large δ34S variation from -8.63‰ to +5.77‰ (n=54). The barren V2 (ser-py) veins pyrite do have a smaller variation of δ34S (-6.31‰ to +0.29‰; n=30). The gold bearing V3a (qtz-carb-py) pyrites exhibit a large variation of δ34S (-7.58‰ to +2.01‰; n=47). The isotopic signature of the larger euhedral V3 pyrite grains can be subdivided according to their different zoning. The core of the pyrite yields a sulfur isotope content of δ34Savg = +0.06‰ (n=13). The gold-related arsenic rims in the other hand have lighter isotopic component (δ34Savg = -5.39‰; n=9) with the outer rims have slightly heavier sulfur isotopic component (δ34Savg = -3.72‰; n=3) (Figure 3. C). The V4a pyrite is also in equilibrium with gold precipitation, however, is less well zoned compared to the V3 pyrite. The gold-associated V4a (qtz-ser-py-au) pyrite has the largest variation of δ34S (-10.46 ‰ to +12.47 ‰; n=97). The zoning of most V4a pyrite grains is distinguishable and carries similar characteristics to V3 pyrite with δ34Savg of the core (-2.23‰; n=49), arsenic rims (-5.38‰; n=20) and outer rims (-5.21‰; n=9) (Figure 3. C). The late V4c (n=3) measured through the chalcopyrite have sulfur isotope signature of δ34S = -0.93 ‰; -0.62 ‰; -1.13 ‰.

5 Constraining the source and processes occurring within Archean orogenic gold

Through the combination of multiple sulfur isotopes and vein paragenesis, it appears that mineralisation at the Kanowna Belle deposit tapped a rather homogeneous sulfur reservoir throughout the emplacement of the different vein generations. The various host rocks to mineralisation at the Kanowna Belle deposit exhibit little to no influence in contributing sulfur to the system, as indicated by the homogeneous and exclusively positive (Δ32S = +0.05‰ to +0.39‰; with two positive outliers) MIF-S signature. Through multiple sulfur isotope analyses, we are now able to reliably distinguish between the mixing of sulfur reservoir or thermochemical processes that are recorded by the sulfides. In the Kanowna Belle deposit, there is a clear indication within the gold bearing V1, V3a and V4a that there are important thermochemical processes (shown by the large spread of δ34S values and constant Δ33S) that occur throughout the
hydrothermal systems that lead to precipitation of gold within the Kanowna Belle deposit (Figure 3.). The increase in oxygen fugacity is known to decrease the $\delta^{34}$S values in sulfides (Palin and Xu 2000). Therefore this shift of $\delta^{34}$S values to lighter sulfur isotopes in the gold-bearing arsenic rim of pyrites in Kanowna Belle implied that the hydrothermal fluids became more oxidised. This change in oxygen fugacity lead to the precipitation of gold without involving any mixing of different sulfur reservoirs in the arsenian pyrite.

Our compilation of sulfur isotope data collected from various Archean orogenic gold systems across the Kalgoorlie terrane from this work and our previous work (LaFlamme et al. 2018a; Thébaud et al. 2018) present a remarkable consistency in their sulfur isotope pattern. In most instances, we observe high variation of $\delta^{34}$S in auriferous veins and low variation but consistently positive $\Delta^{34}$S in the 2.65 Ga orogenic gold deposits of the Yilgarn Craton (between 0 to 1‰). This data may be implying that Archean orogenic gold systems has an amalgamated source that seem to be dominated by a mantle sourced sulfur with some to minimal recycled sedimentary sulfur contribution. This results supported recent interpretations that auriferous hydrothermal fluid sulfur was sourced from either devolatilization of subducting slab (Selvaraja et al. 2017; LaFlamme et al. 2018) or possibly gold enriched sub-continental lithospheric mantle (Tassara et al. 2017).

Acknowledgements

This project is principally supported by Northern Star Resources Pty. Ltd. The main author would like to acknowledge SIRF funding from UWA for this PhD project. We thank CMCA-UWA for the access and training in using their facilities.

References


A refined view of the ‘Mesoarchaean gold event’

Nicolas J. Saintilan1,3, David Selby1, Joshua Hughes4, Denis M. Schlatter2, Jochen Kolb3, and Adrian Boyce4
1Department of Earth Sciences, University of Durham, UK
2Helvatica Exploration Services GmbH, Zürich, Switzerland
3Institute of Applied Geosciences, Geochemistry and Economic Geology Group, Karlsruhe Institute of Technology, Germany
4Isotope Geosciences Unit, SUERC, East Kilbride, Glasgow, UK
5Present address: Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Switzerland

Abstract. The controversial ‘Mesoarchaean gold event’ might have added the bulk of all gold to the juvenile continental crust at the onset of crust generation by plate tectonic processes at ca. 3.0 billion years (Ga). Here, we connect the ‘Mesoarchaean gold event’ to the precipitation of ca. <3.19–2.98 Ga seafloor massive arsenopyrite accompanying ca. <3.19–3.01 Ga basalt magmatism. Hydrothermal alteration mobilized As, Re, Os and Au from serpentinites of lower crustal harzburgite cumulates to yield arsenopyrite with invisible gold. In major shear zones, retrograde greenschist-facies metamorphism caused local dissolution of arsenopyrite, reset its Re-Os geochronometer, and liberated gold which was deposited as native gold with pyrite at 2.66 Ga. The initial Os isotope ratios of Neoarchaean arsenopyrite (187Os/188Os = 0.13 ± 0.02) and gold-bearing pyrite (0.12 ± 0.02) overlap with an estimated 187Os/188Os ratio for the Mesoarchaean mantle (0.11 ± 0.01, calculated by using the present-day values of 187Re/188Os = 0.435 ± 0.055 and 187Os/188Os = 0.130 ± 0.001 for a primitive upper mantle; Meisel et al. 2001; Carlson et al. 2005) and preclude contribution of radiogenic crustal Os. This ca. 2.66 Ga lode gold mineralization may bear testament to the endowment of Earth’s stabilizing continental crust through metamorphic upgrading of bulk gold originally extracted from the Mesoarchaean mantle.

1 Gold in the continental crust

The continental crust enrichment in gold (Au), up to economic levels, has occurred in a variety of gold deposit types from Mesoarchaean ‘palaeoplacers’ to Miocene magmatic-hydrothermal deposits (Groves et al. 1997, 2001; Frimmel 2007). Rather than a magmatic-hydrothermal deposits (Groves et al. 1997, 2001; Frimmel 2007). Rocks of the Witwatersrand Basin as ‘palaeoplacers’ minimum of 40% of the bulk Mesoarchaean gold has ‘Mesoarchaean gold event’ (Frimmel 2007). Although a evolving continental crust during a so-called giant concept by which the bulk of gold was added to the temporal distribution of gold deposits has favoured the proportion of komatiites in Earth’s crust from ca. 3.20 Ga (Greber et al. 2017), the preferred hypothesis for the the pervasive silicification of sub-seafloor volcanic rocks greenstone belts for lode gold deposits is explained by preservation bias, the low fertility of Palaeoarchaean ‘subduction zone’ setting (Kisters et al. 2012; Szilas et al. 2013, 2014; van Hinsberg et al. 2018). In the fragment of the North Atlantic Craton in south-west Greenland, the greenstone belts hosting the Tartoq Group contain lode gold mineralization (Fig.1a; Nielsen 1976; Appel and Secher 1984; Kolb et al. 2013; Steenfelt et al. 2016). The Mesoarchaean Tartoq Group comprises mafic rocks with well-preserved primary magmatic structures (e.g., pillow lavas, volcanic breccias) together with serpentinites of harzburgite cumulate protoliths (Szilas et al. 2013, 2014). These rocks have been interpreted as a remnant of a <3190–3012 Ma oceanic crust involved in an accretionary complex (Kisters et al. 2012; Szilas et al. 2013, 2014; Polat et al. 2016). Accretion and stacking of hydrated oceanic crust between 3012 and 2824 Ma caused the formation of felsic mylonites in thrusts and imbrication of the Tartoq Group rocks with voluminous tonalite-trondhjemite-granodiorite (TTGs; Nutman et al. 2004; Polat et al. 2016) by the melting of thickened oceanic crust (Nagel et al. 2012; Hastie et al. 2016) in a repeatedly-aborted ‘subduction zone’ setting (Kisters et al. 2012; Szilas et al. 2013, 2014; van Hinsberg et al. 2018).

The Nuuluk Greenstone Belt was originally metamorphosed to the amphibolite facies (~580°C, ~4.5 kbar) when imbricated into the TTGs (Szilas et al. 2014, van Hinsberg et al. 2018). Retrograde greenschist-facies mineral assemblages overprint the peak amphibolite-facies paragenesis within shear zones comprising anastomosing networks of quartz-ankerite ± pyrite veins, which are locally walled by fuchsite ± tourmaline ± talc, and cut through massive sulphide bodies (Fig. 1b; King. 1985; Petersen 1991; Evans and King 1993; Szilas et al. 2014, van Hinsberg et al. 2018). Tourmaline thermometry and the retrograde assemblage of chlorite-albite-epidotite-titanite-calcite in the mafic rocks attest of conditions of 380 ± 50°C at a pressure below 1 kbar (~4 km depth; van Hinsberg et al. 2018). Two 25-m-wide and ca. 5-km-long shear zones (i.e., the Western and Eastern Carbonate Zones – WCZ & ECZ, Fig. 1b; King 1985; Kolb et al. 2011, 2013) host gold mineralization: (1) as 5 to 20 μm anhedral grains in arsenopyrite and pyrite (or in fractures in those minerals) in massive sulphide layers (up to 20 ppm Au; Evans and King 1993), and (2) in discordant, pinch-and-swell veins composed of fine-grained quartz and
euhedral pyrite which are enclosed and displaced by syn-
tectonic fuchsite (up to 100 ppm Au; Appel and Secher
1984; Evans and King 1993).

3 Serpentinite and seafloor massive
arsenopyrite bodies

In the WCZ, arsenopyrite is bereft of common Os and
only contains radiogenic 187Os. Two aliquots of euhedral
to subhedral coarse-grained (ca. 1–2 mm) arsenopyrite
in between layers of younger medium- to coarse-grained
subhedral to anhedral pyrite (ca. 0.25–2 mm, sub-
sample TTQ-02-01 “sub-01”, Fig. 1b) yields reproducible
and precise Re-Os data (1.51–1.53 ppb Re and 51.5–
51.7 ppt 187Os) with overlapping Re-Os model dates of
3136 ± 31 [33] Ma and 3184 ± 40 [42] Ma (1.1–1.3%,
2σ, with [x] including the 187Re decay constant uncertainty;
Smoliar et al. 1996). In addition, four aliquots of euhedral
to subhedral very coarse-grained (>2 mm) arsenopyrite
associated with quartz and younger very coarse-grained
pyrite (sub-sample TTQ-02-02 “sub-02”, Fig. 1b) yield
reproducible, but slightly less precise Re-Os data (2.12–
2.59 ppb Re and 67–78 ppt 187Os) which yield
overlapping Re-Os model dates of 2967 ± 168 [173] Ma,
Ma and a weighted average of 2986 ± 98 Ma (Fig. 2a; n
= 4, 95% confidence, MSWD = 2.1). The weighted
average Re-Os model date of 2986 ± 98 Ma for very
course-grained arsenopyrite overlaps with the age of the
Tartoq Group of <3190–3012 Ma (Szilas et al. 2013a,
2014; Polat et al. 2016), whereas the Re-Os model dates
of 3136 ± 33 Ma and 3184 ± 42 Ma for medium-grained
arsenopyrite are compatible with its maximum age (Szilas
et al. 2013a, 2014).

At Tartoq, a group of serpentinites, which contain
conditions, water in equilibrium with arsenopyrite should have dissolved As concentrations at 0.01–0.10 ppm (Craw et al. 2003). These thermodynamic properties explain the stability of the ca. 2986 Myr-old massive arsenopyrite bodies, which is compatible with a relatively reduced Mesoarchaean ocean at the seafloor in spite of the presence of oxygenated near-shore shallow-marine environments at the interface with an overall reduced Mesoarchaean atmosphere (Heinrich 2015; Eickmann et al. 2018).

Collectively, the Re-Os data of pyrite (n = 6) yield, within uncertainty, an identical date (Re-Os isochron date of 2656 ± 83 [99] Ma; 2σ, Model 1 isochron, MSWD = 0.71, Osi ratio = 0.12 ± 0.02; Fig. 2c).

In connection with the tectonic-imbrication of short-lived and disrupted 'slabs' in an accretionary complex (Kisters et al. 2012; van Hinsberg et al. 2018) and the generation of TTG melts in thickened oceanic crust (Nagel et al. 2012; Hastie et al. 2016), the juxtaposition of greenstone belts and TTGs between ca. 3012 and 2824 Ma (Nutmans et al. 2004; Polat et al. 2016) may have caused deformation of competent massive arsenopyrite bodies in the oceanic crust, at amphibolite-facies conditions (van Hinsberg et al. 2018). Arsenopyrite bearing primary invisible gold remained chemically robust during amphibolite-facies metamorphism (Fougerouse et al. 2016) in the Nuuluk Greenstone Belt. Subsequently, the shear zones in the ECZ localized greenschist-facies retrograde metamorphism (Szilas et al. 2014; van Hinsberg et al. 2018). At the conditions indicated by tourmaline thermometry (van Hinsberg et al. 2018), the stoichiometric dissolution of pre-existing Mesoarchaean, gold-bearing arsenopyrite by small volumes of relatively low fS2, chlorine-bearing (~0.01M HCl) solutions may have occurred in the ECZ (Pokrovski et al. 2002; Fougerouse et al. 2016):

\[
\text{FeAsS} + 3\text{H}_2\text{O} + 2\text{H}^+ + 2\text{Cl}^- \rightarrow \text{FeCl}_2(\text{aq}) + \text{As(OH)}_3(\text{aq}) + \text{H}_2\text{S(aq)} + 1.5\text{H}_2\text{O}(\text{aq}) \quad (1);
\]

At ~380°C (tourmaline thermometry), significant sulphur isotope fractionation was hampered between the timing of arsenopyrite (\(\delta^{34}\text{S} = +1.6\) to +2.2‰) dissolution, resetting of its Re-Os geochronometer at 2608 ± 108 Ma, and, subsequent pyrite (\(\delta^{34}\text{S} = +1.8\)%s) precipitation at 2656 ± 89 Ma in the ECZ (Fig. 2c). With reduction of sulphur activity through pyrite precipitation, gold deposition may have occurred over distances of a few micrometres in the massive arsenopyrite bodies (on grain boundaries, in cracks of pre-existing arsenopyrite, or within newly formed pyrite), or, of several meters within quartz-pyrite veins that were later displaced during fuchsite precipitation.

In conclusion, a refined view of the ‘Mesoarchaean gold event’ is emerging: (i) a primary extraction of Au from the Mesoarchaean mantle at the time of basalt magmatism at the root of Mesoarchaean greenstone belts and their associated lower crustal harzburgite protoliths, (ii) hydrothermal cell circulation leaching As, Re and Os during secondary serpentinisation of those protoliths, (iii) magmatic-hydrothermal systems precipitating barren or Au-Os-bearing massive arsenopyrite bodies on the seafloor, (iv) metamorphic and structural upgrade of primary invisible gold in Mesoarchaean massive arsenopyrite into Neoarchaean lode gold mineralization.

Acknowledgements

This work was supported financially through a Swiss National Science Foundation Advanced Postdoc.Mobility
References


Tracing the S source reservoir of the Tropicana gold camp, Western Australia

Nicolas Thébaud, Steffen Hagemann and Laure Martin  
Centre for Exploration Targeting, School of Earth Sciences, The University of Western Australia

Stefano Caruso  
Australian Centre for Astrobiology, School of Biological, Earth and Environmental Sciences, University of New South Wales

Stanislav Ulrich  
Anglogold Ashanti, Perth

Douglas Allan  
Silverlake Resources, South Perth

Abstract. The Tropicana gold camp situated in the Albany Fraser Orogen on the edge of the Archean Yilgarn craton is associated with a number of gold deposits. The Madras deposit, situated 20 km S of the Tropicana mine exhibits a protracted hydrothermal history associated with the precipitation of successive sulfide species. Using in-situ multiple sulfur analysis, we investigated the structurally constrained sulfide paragenesis, and we show that the Madras deposit was associated with a dominantly magmatic reservoir that may have locally interacted with MIF-S Archean crustal reservoir at depth. Furthermore, we show that mineralised pyrites exhibit δ34S fractionation of up to +35.2‰. Such large fractionation is best interpreted as the product of the successive pyrite precipitation from a restricted S source reservoir.

1 Introduction

The undeveloped Madras gold deposit forms part of the greater Tropicana gold camp. The main mineralising event (D2) generated W-thrusting, decimetre (Madras North) to decametre-scale (Madras Shear Zone) shear zones that are compatible with the Tropicana pre-mineralisation D2 event and formed synchronous with a multi-phase hydrothermal system that was probably related to the thrusting of the Tropicana Zone over the Yamarna Terrane. The timing of mineralisation in the Tropicana gold camp has been proposed to be associated with the remobilisation (D2) of Archean gold mineralization? as proposed for the Tropicana deposit (Doyle et al., 2015). In order to further understand the mineralisation record of the Tropicana gold camp sulfur isotope analyses were conducted on the structurally constrained sulfide populations that were recognized in the Madras deposit.

In the past, isotopic investigations have focused on sulfur, oxygen and carbon isotopes to evaluate potential fluid reservoirs (e.g. McCuaig and Kerrich, 1998). Sulfur is a critical element commonly associated with sulfides coeval with gold mineralisation, and the δ34S isotopic variation has previously been used to delineate the source of sulfur (Alt et al., 1993). However, because δ34S is sensitive to physico-chemical processes occurring during hydrothermal circulation of fluids, depositional processes, and metamorphic re-equilibration, the original δ34S signatures from ore-related sulfides might not be representative of the sulfur reservoirs (Hodkiewicz et al., 2008). Recent development in the in-situ acquisition of multiple sulfur isotopes (e.g. LaFlamme et al., 2016) has the ability to fingerprint and monitor the ∆33S signature of sulfides precipitated from an auriferous fluid (LaFlamme et al., 2018). As ∆33S is a numeric quantification of dispersion from the mass dependent relationship δ33S = δ34S × 0.515 (Farquhar and Wing, 2003), large values are indicative of the mass independent fractionation of sulfur (MIF-S). In hydrothermal sulfides, this isotopic signature can indicate sourcing of sulfur from an unique MIF-S-bearing reservoir, the Archean sedimentary record (|∆33S| > ±0.2; Farquhar and Wing, 2003). MIF-S can be used as an isotopic tracer since it is chemically conservative and can only be modified by dilution. Recently, MIF-S has been identified in Archean orogenic gold deposits, demonstrating that some orogenic gold deposits source a portion of their sulfur from Archean sediments (Agangi et al., 2016; Selvaraja et al., 2017).

2 Geological framework

The Madras North prospect is located in the Tropicana Zone of the Albany-Fraser Orogen that encompasses the Neoarchean Tropicana Gneiss (Tropicana Domain of Doyle et al., 2013), Hercules Gneiss, and subordinate sanukitoid granites, which are locally overlain by barren basin sediments and intruded by Paleoproterozoic granites (Doyle et al., 2014; Occhipinti et al., 2014a; Spaggiari et al., 2009, 2014b). The Madras North prospect comprises an assemblage of massive to banded orthogneisses and paragneisses. These gneisses contain anatectic segregations, indicating up to granite facies metamorphism and that are generally subparallel to banding. The gneiss is overprinted in places by narrow (c. ≤1 m wide) shear bands that are defined by intensive brittle/ductile deformation and phyllosilicate-dominated...
alteration. Mineralisation is hosted within a sheared plagioclase-amphibole-pyroxene-garnet-leucoxene-quartz (mafic) gneiss. The main mineralisation (c. 1-10 ppm Au) is hosted within one metre-scale shear zones. The footwall K-feldspar-quartz ±plagioclase-biotite gneiss package is barren. Minor metre-scale basalt dykes, which are likely part of the ENE-trending c. 1210 Ma Gnowangerup-Fraser suite (Wingate et al., 2005), cross-cut both gneissosity and schistosity.

2.1 Madras structural evolution

The Madras structural evolution may be divided into three distinct deformation events. The first deformation event (D1) is associated with the peak granulite facies metamorphism dated between 2718-2554 Ma (Kirkland et al., 2014, 2015). Present over the whole region, D1 is associated with the development of a NE trending and SE dipping gneissic fabric development (Blenkinsop and Doyle, 2014). Although no gold endowment may be related to this event, the gneisses host either pre- to syn-D1 disseminated pyrrhotite-chalcopyrite assemblage (Po1) that are in textural equilibrium with the gneissic fabric.

D2 corresponds to the main Au mineralisation event and is associated with a progressive deformation process that developed in response to a NW-SE shortening event. D2w refers to the development of ductile reverse shear zones associated with a pronounced schistosity (S2w) that developed subparallel to the gneissic fabric. S2m shear fabric is defined by phyllosilicates including platy elongate biotite (± chloritised) and/or sericite. As deformation proceeded the S2a shear fabric is crenulated and transposed into a new cleavage (S2b). D2 is also associated with the development of a syn-foliation vein (V2a) set and shallow dipping extension quartz-carbonate vein (V2b) set compatible with WNW directed thrusting. An additional vein set (VUNK) that is moderately NNE-dipping and does not correlate with any structures in the Madras or Tropicana deposits. VUNK consists of quartz-carbonate-pyrite-pyrrhotite-chalcopyrite and is associated with gold mineralisation. Poorly constrained and rare over the Madras prospect, the exact timing of these veins is unconstrained.

D2 is associated with development of protracted hydrothermal activity. The early syn-D2 metasomatic event is associated with the replacement of the gneissic mineral assemblage by biotite-clinozoisite-chlorite assemblage with sulfides. Ongoing metasomatism is associated with the widespread, but non-systematic, overprinting of hydrothermal biotite by late-D2 chlorite and deposition of sulfides.

2.2 Sulfides populations

Two sulfide sets were recognized in the Madras deposit based on the structural context but also grain texture and optical petrography. The first sulfide set (Po1) is associated with disseminated and syn-Si sulfides that consists of traces of disseminated to blebby, anhedral pyrrhotite ± chalcopyrite within the gneiss fabric. These sulfides occur in textural equilibrium with the least-altered gneiss, often concentrated within anatectic segregations, and are either pre- or syn-D1. Grains are elongated and skeletal within the sheared gneiss and schist. The pyrrhotite is nickeliferous, locally exhibiting pentlandite exsolution lamellae.

The second sulfide set is hosted within D2 shear zone and related alteration halos, and can be subdivided into at least three sub-populations: (1) The first subpopulation consists of traces of coarse-grained, rectangular, disseminated to conjoined pyrite (Py1) within the Madras shear zone and S2 fabric. Pyrite growth early to syn-D2 is inferred because crystals exhibit pressure shadows and display a crystallographic preferred orientation, (sub)parallel to the foliation. (2) Traces of fine-grained, disseminated to conjoined, subhedral to euhedral pyrite±chalcopyrite (Py2) are heterogeneously-distributed throughout the intensely sheared mafic and felsic S2 fabric (i.e. proximal zone). Py2 represents the main gold bearing sulfide species. Py2 are inferred to have formed syn- to late-D2 because they lack pressure shadows and appear to be located within the D2-related crenulation cleavage. Py2 was observed as both inclusion-free and inclusion-rich grains. Additionally, subsets of Py2 also occur as inclusion-free, euhedral rims enclosing anhedral, inclusion-rich inherited cores. The third subpopulation (Py3) is related to poorly constrained VUNK veins and comprises minor pyrrhotite and chalcopyrite in the vein set.

3 Methods

In order to assess the sulfur reservoir involved in the formation of the Madras deposit, in-situ sulfur isotope techniques were conducted on the different sulfide populations. Characterisation of <500 µm sulfides by energy-dispersive X-ray spectroscopy, and identification of fractures, inclusions and zoning by backscatter electron (BSE) imaging was conducted using a FEI Verios 460 XHR SEM under conditions of 15 kV with a focused 6.0 nA beam at the Centre for Microscopy Characterisation and Analysis, University of Western Australia (CMCA-UWA). Multiple sulfur isotopic ratios were determined using a CAMECA IMS1280 large-geometry ion microprobe located at CMCA-UWA. Mounts (25 mm diameter) were made by coring pucks (3.2 mm in diameter) of rock and casted in epoxy. After polishing, mounts were coated with 30 nm of Au and loaded with a standard block into the sample chamber. A 3.7–4.6 nA focused Cs+ primary beam interacted with the sample at 20 keV. The beam, in Gaussian mode, bombarded the sample surface to create a 15 µm analytical pit. Isotopes 32S, 33S and 34S were simultaneously detected by three Faraday Cups using amplifiers with 1010 Ω (L’2), 1011 Ω (L1), and 1011 Ω (FC2 or H1) resistors. Data were collected over 123 s of acquisition time in 20 integration cycles. Measurements were interspersed with Sierra pyrite (δ34S = +2.17‰, Δ33S = −0.02‰) to correct for drift and monitor internal sample repeatability. In addition, analyses of matrix-matched reference material were used to calibrate isotope ratios following procedures in LaFlamme et al. (2016). Measurement error on δ34S is equal to about ~0.4‰ and on Δ33S is ~0.25‰.
4 Results

An early sulfide set located within the foliation (Po1) were analysed on two distinct samples. Chalcopyrite and pyrrhotite grains analysed returned homogeneous δ34S values that range from +2.3‰ to +3.5‰. Δ33S values acquired on the same samples returned contrasted values with Δ33S equal to -0.02 ± 0.06‰ and 0.97 ± 0.06‰, respectively.

Syn-D2 early sulfide populations (Py1) analysed on two distinct samples returned δ34S values that range from +6.0‰ to +15.8‰, and Δ33S ranging in value from 0.25± 0.06‰ and 0.56± 0.06‰.

Syn-D2 gold bearing sulfide populations (Py2) present distinctive core and rim textures indicative of the protracted growth of the pyrite. The core returned δ34S values that range from -0.8‰ to +5.2‰, and Δ33S values equal to 0.20± 0.06‰. Rims returned δ34S values that range from 7.9‰ to +35.2‰, and Δ33S values equal to 0.08± 0.06‰. Chalcopyrite from this sample returned δ34S values that range from +8.0‰ to +8.2‰, and Δ33S values equal to 0.13± 0.06‰.

Sulfide populations Py3 returned δ34S values that range from +1.7‰ to +3.6‰ and Δ33S values equal to 0.26± 0.06‰. Chalcopyrite analysed returned δ34S values that range from +2.2‰ to +3.6‰, and Δ33S values equal to 0.22± 0.06‰.

5 Discussion

Sulfide populations from the Madras deposit investigated as part of this study include: (1) disseminated chalcopyrite and pyrrhotite within the gneissic foliation (Po1); (2) one population of pyrite (Py1) developed during the early development of a D2 shear zone. (3) two syn-D2 and Au bearing sulfides assemblages Py2 and Py3.

Data obtained on Po1 show homogeneous δ34S values. Considering that δ34S is sensitive to physicochemical processes, the constant δ34S recorded by syn-Ss: sulfide grains may have been ‘homogenized’ during the granulite metamorphism that affected the host rocks. In contrast, Δ33S values associated with these early sulfides indicate very different signatures with samples returning both near nil ‰ values to slightly negative ‰ values, and positive values up to +0.97‰. A Δ33S of zero ‰ suggest the involvement of mantle derived sulfur source, whereas negative values are interpreted to represent the influence of sulfur derived from the Archean seawater sulfate reservoir. In contrast, Δ33S values acquired on some of the Po1 samples fingerprint the involvement of Archean supracrustal sulfur reservoir. Collectively these results suggest that the earlier phase of sulfides present prior to metamorphism (Archean) are derived from distinct sulfur reservoirs including magmatic and supracrustal sulfur source reservoirs.

In contrast with Po1, Py1 sulfide assemblage depicts δ34S variations of over 13‰. Sulfur isotope datasets from hydrothermal systems commonly report a spread in δ34S values (e.g., Hodkiewicz et al., 2008 and references therein) due to the sensitivity of δ34S to: (1) varying input of sulfur reservoirs, and (2) changing thermochemical fluid conditions at the time of sulfide precipitation. The range of Δ33S values recorded in Py1 (+0.25± 0.06‰ to +0.56± 0.06‰) attests to the involvement of Archean crustal sulfur reservoir in the early hydrothermal alteration and prior to gold mineralization, which was associated with D2 shear zones. As for other Archean hydrothermal systems in the nearby Yilgarn Craton, the range of Δ33S values measured on the Madras sulfides is much lower than that of recorded Archean sedimentary rocks comprised between +1.6‰ to +6.2‰, but dominantly between +1 and +2‰ (e.g. Bekker et al., 2009). The values recorded for early D2 sulfides, therefore imply that the sulfur source was homogenised with other non MIF-S-bearing (magmatic) reservoirs at depth.

Sulfides associated with the bulk of the Au endowment (Py2) display very complex textures and large isotopic variations. Locally, Py2 presents anhedral cores rich in inclusions surrounded by inclusion-free rims (Figure 1). The rim may display in cathodoluminescence light growth zone textures and various amount of mineral inclusions. Py2 also occurred as inclusion-free, euhedral crystal without core-rim zones. Collectively, these textural observations suggest that Py2 grew over multiple hydrothermal stages. Py2 displayed δ34S values ranging from -0.8‰ to +35.2‰. Py2 cores systematically show δ34S values that range from -0.8‰ to +5.2 (mean δ34S = +3.55‰), whereas Py2 rim and Ccp2 that grew at Py2 crystal margins return δ34S values spreading from +6.1‰ to +35.2‰ (Figure 2). Similarly, to the early sulfide population, this δ34S spread may be due to: (1) the variation of sulfur reservoirs tapped, and/or (2) changing thermochemical fluid conditions at the time of the sulfide precipitation (e.g. variation of redox conditions). Δ33S values obtained from Py2 exhibit Δ33S mean values of +0.14 ± 0.06‰ for the cores and +0.11 ± 0.06‰ for the rim. The overall constant Δ33S recorded suggests an homogeneous sulfur reservoir and, therefore indicates that the spread of δ34S values may be due to processes associated with the sulfide precipitation. Sulfur reduction

Figure 1. BSE photomicrograph of Py2 mineralised pyrite showing points analyses for δ34S vs Δ33S.
in a closed-system conditions may have led to early pyrite crystallisation (Py2-Core). Such a process would have fractionated the sulfur reservoir precipitating pyrite with −0.8‰ < δ34S < +5‰ values. Through this process, the remaining sulfur in the fluid may have resulted in its δ34S value to increase. In a second crystal growth stage pyrite would have crystallised from this 34S enriched fluid. This would have led to the precipitation of the outer crystal growth zones at the edge of gold rich pyrite cores which, in the Madreas deposit, is associated with δ34S values of up to +35.2‰.

Sulfide populations Py3 represent an atypical and poorly constrained style of mineralisation that was documented in Madras North. Pyrites analysed returned δ34S values that range from +1.7‰ to +3.6‰ comparable with the syn-ore sulfide population (cores). Δ33S values ranging from to +0.22± 0.13‰ to +0.33 ± 0.13‰ pointing towards the contribution of Archean crustal sulfur. The overall low Δ33S values recorded for Au bearing Py2 and Py3 points toward little to no MIF-S. Accordingly, we proposed that the sulfur source associated with gold mineralisation in the Madras deposit was associated with a dominantly mantle derived reservoir that may have locally interacted with MIF-S from an Archean crustal reservoir at depth.

The intense fractionation of δ34S recorded in mineralised pyrite appears to be closely associated with pyrite crystal growth processes deriving from a restricted S source reservoir through possible redox processes.

Acknowledgements
The authors wish to acknowledge AngloGold Ashanti for supporting this study.

References


LaFlamme, C., Fiorentini, M.L., Wing, B., Lindsay, M., Selvaraja, V., Caruso, S., Johnson, S., Bui, T.H., Occhipinti, S. (2018). Atmospheric sulfur is recycled to the crystalline continental crust during supercontinent formation, 9:4380


Abstract. U-Pb data for hydrothermal xenotime and monazite indicate that the Saattopora orogenic gold deposit with atypical (Au-Cu) metal association was formed by multiple hydrothermal events between 1.87 and 1.78 Ga. Stable (C, O, S, B) isotope data for carbonates, sulphides and tourmaline suggest that fluids of different origin and with different degrees of modification by interaction with host rocks participated in the hydrothermal processes. O and C isotope data for carbonates correlate with the Au and Cu grades of ore. The heterogeneous, low to high salinity aqueous-carbonic-sulphuric parent fluids contain traces of ethane and propane. This observation together with the negative $\delta^{34}S$ data indicate that one of the potential sources of hydrothermal fluids are the carbonaceous material rich metasediments in the CLGB.

1 Introduction

The majority of orogenic gold deposits contain only gold as the economically exploitable metal. However, base and semi metals, uranium or even rare-earth elements also have economically important enrichments in some of the deposits, classified as orogenic gold deposits with atypical metal associations (Groves et al. 2003). Intracratonic basins that have been turned into fold and thrust belts during orogenesis appear to be favorable places for the occurrence of this kind of gold deposit (Goldfarb et al. 2001). Alternatively, the high base or other metal content of an orogenic gold deposit could also be inherited from a proto-ore which was overprinted by the gold mineralization event during metamorphism (Groves et al. 2003). Sedimentary sequences with evaporates may also release high salinity fluids during metamorphism and these types of metamorphic fluids also have capacities to contribute base metals into orogenic gold systems (Yardley and Graham 2002).

The Central Lapland Greenstone Belt (CLGB) is the most important orogenic gold metallogenic province in Europe (Fig. 1). In the belt, the Kittilä Mine exploiting the gold-only Suurikuusikko deposit is currently the largest gold producer in the European Union (196 938 oz Au in 2017; http://agnicoeagle.fi/about-us/operation/).
2 Regional geology

The CLGB consists of a supracrustal sequence of mafic-ultramafic metavolcanic rocks, mafic dikes and sills, quartzites, phyllites and graphitic schists that were deposited between 2.40 and 1.95 Ga during the protracted rifting of the Archaean Karelian craton. Metamorphism and deformation of these rocks took place during the Svecofennian orogeny (1.93-1.80 Ga). Calc-alkaline intermediate-felsic volcanism and deposition of clastic sediments (Salila Group) was followed by accumulation of komatitic-tholeiitic volcanic rocks and terrestrial to shallow marine sedimentary units (Sodankylä Group) during the early stages of intracratonic rifting between 2.44 and ca. 2.2 Ga. Komatites-picrites and high-Mg basalts erupted and shallow to deep marine sediments were accumulated during the re-activation of rifting between ca. 2.2 – 2.05 Ga (Savukoski Group; Fig. 1). Continental break-up commenced at around 2.05 Ga and extensive komatitic and basaltic lavas, as well as carbonaceous material rich deep marine sediments (Kittilä Group; Fig. 1) were deposited in the oceanic basin(s). The closure of the oceanic basin(s) led to accretion of the Kola, Karelia and Norbotten micro-continent(s) between 1.92 and 1.87 Ga, followed by continental extension (from ca.1.88 to 1.85 Ga), continent-continent collision (1.85-1.80 Ga) and final orogenic collapse and stabilization between 1.80-1.77 Ga (Lahtinen et al. 2005). Syn-orogenic (Vuotso Complex, 1.91 Ga) and late/post-orogenic (Nattanen Suite, 1.81-1.77 Ga) granitoids intruded the northern part of the CLGB (Fig. 1). Other felsic complexes with less well known relationships to the orogenic stages also occur in the CLGB.

The main D1-2 ductile and D3 brittle-ductile deformation in the CLGB took place in conjunction with the SW-vergent thrusting of the Lapland Granulite Belt and northward-oriented thrusting along the Sirkka Shear zone (Figs. 1 and 2). The NE oriented major strike-slip fault zones were also formed during this accretional tectonic stage. However, the timing of D3 is a bit ambiguous and local tectonic features also support its placement into the late- to post-orogenic deformation stage. Ore mineralization is predominantly confined to brittle fractures cutting albitites and alteration halos around fractures. Fractures are filled by coarse grained, undeformed Fe-bearing dolomite, quartz and tourmaline. Pyrrhotite, chalcopyrite and pyrite are the most common ore minerals in these veins and surrounding disseminations. Sulphide minerals are late precipitations along grain boundaries and fractures of other vein filling minerals. Pentlandite, gersdorffite, cobaltite, arsenopyrite, tellurides and native gold are minor minerals that form inclusions within other sulphides. The abundance of Ni-Co bearing minerals appear to be elevated in some samples, but the average concentration of Ni is only 0.06 wt% and 0.11 wt% in the northern and southern orebodies, respectively.

3 General characteristics of the Au-Cu mineralization at Saattopora

The copper mineralization at Saattopora was discovered in 1970. Recognition of its similarity to the Bidjøvagge Au-Cu deposit, which is located in Norway along the northwestern continuation of CLGB, triggered re-investigation of mineralization and identification of gold grades in the mid-1980’s. Outokumpu Mining Ltd. extracted 2.24 Mt ore with 3.4 g/t Au and 0.31 wt% Cu average grades between 1988 and 1995 (Korkalo 2006). Since that time, the Saattopora mine has been closed.

The Saattopora Au-Cu deposit is located in the Sirkka Shear Zone (SSZ) in the western part of the CLGB (Fig. 1). In this area, the WNW-SSE oriented SSZ runs parallel with the thrustled and sheared contact zone between the Savukoski Group and Kittilä Suite. In this part of the CLGB, rocks of these units suffered mid-greenschist facies Svecofennian metamorphism.

The deposit consists of two major orebodies which are elongated parallel with the SSZ ((Niiranen et al. 2014; Fig. 2). The northern orebody is located between the tholeiitic metabasalt-graphitic tuffite assemblage of the Kittilä Suite and a metakomatiite (talc-chlorite schist) unit belonging to the Savukoski Group (Fig. 2). The southern orebody is mostly hosted by the micaschist and the graphitic phyllite units of the Savukoski Group.
average Co concentration is 0.02 wt% in both orebodies (Korkalo 2006). In some zones of the southern orebody, magnetite is also associated with the vein-filling sulphides. Pyrite is rather common in the veins of the southern orebody whereas it is rare in the northern orebody. The veins, which are from a few mm to up to tens of cm thick, typically have biotite alteration selvages. Their predominant orientation is N-S and E-W and appear to have formed in a conjugate set of brittle fractures within the competent albite units.

4 Results of current studies

4.1 U-Pb dating of hydrothermal processes

Previous attempts at determining the age of hydrothermal mineralization at Saattopora were based on bulk U-Pb and Pb-isotope analyses of mineral separates by TIMS (Mänttäri 1995). Those studies obtained 1894 ± 46 Ma Pb-Pb isochron age from sulphide and carbonate minerals and highly variable U-Pb ages between 1781 ± 18 and 1684 ± 5 Ma from monazite and rutile. The highly scattered nature of ages was explained by the hypothetical post-mineralization thermal effect of post-orogenic granitoid magmatism. In our current studies we dated individual monazite and xenotime grains of hydrothermal origin with known textural settings in polished thin sections by LA ICPMS. Results show distinct age groups in the northern and southern orebodies of the Saattopora deposit (Fig. 3).

In the northern orebody, the ~1.84 Ga xenotime and monazite are from the massive albite and its chalcopyrite rich carbonate-albite veins. In the southern orebody, the oldest monazite (1867 Ma) is also from a massive albite hosted vein. Younger ages, from ~1820 to ~1790 Ma, characterize monazite from the major carbonate-sulphide veins and their biotite alteration halos in both orebodies.

Multiple hydrothermal mineralization in the orogenic gold deposits of CLGB is a common feature (Molnár et al 2018). The most common ages for the formation of free gold bearing veins are between 1.81 and 1.76 Ga indicating the importance of late- to post orogenic re-activation of fault systems that were formed during the earlier stages of the Svecofennian tectonic evolution.

4.2 Stable (C, O, S, B) isotope data

Carbonate and oxygen isotope analyses of iron bearing dolomite from ore veins of both orebodies were completed by conventional carbonate mass spectroscopy. The range of the δ13C("PDB") values is from -4 to -9.5 ‰, whereas the δ18O("SMOW") data are between +11 and +13‰ (Fig. 4).

In the northern orebody, the ~1.84 Ga xenotime and monazite are from the massive albite and its chalcopyrite rich carbonate-albite veins. In the southern orebody, the oldest monazite (1867 Ma) is also from a massive albite hosted vein. Younger ages, from ~1820 to ~1790 Ma, characterize monazite from the major carbonate-sulphide veins and their biotite alteration halos in both orebodies.

Multiple hydrothermal mineralization in the orogenic gold deposits of CLGB is a common feature (Molnár et al 2018). The most common ages for the formation of free gold bearing veins are between 1.81 and 1.76 Ga indicating the importance of late- to post orogenic re-activation of fault systems that were formed during the earlier stages of the Svecofennian tectonic evolution.

The C- and O-isotope data correlate with the Au and Cu grade of ore. The high grade zones are characterized by relatively heavy C-isotope and relatively light O-isotope compositions compared to the low grade and barren zones. This variation probably reflects the effect of fluid/rock ratios on the isotope composition of carbonate because high grade zones are characterized by occurrences of a larger number and thicker carbonate-sulphide veins. The observed trends also suggest that ore forming fluids were mixed with fluids from local sources and spatial distribution of O- and C-isotope data may be used as a potential tool to predict high grade zones.

Sulphur isotope data in pyrite, chalcopyrite and pyrrhotite grains were determined by LA ICPMS (Fig. 5). In the veins dominated by pyrrhotite in the northern
orebody, the δ⁴⁴S data are between +5 and 0 ‰. In the southern orebody, where pyrite is more common and magnetite is also present in the veins, and the host rocks are mostly albitised metasediments and mafic dikes, the range of δ⁴⁴S data is from +18 to 0 ‰. The relatively heavy sulphur isotope compositions for vein filling sulphides reflect the primary source of sulphur from the metasedimentary units of the of the Savukoski group which are known to have heavy sulphur isotope compositions (Huhma and Hanski 2005).

δ¹¹B data for vein filling tourmaline were also determined by LA ICPMS. Tourmaline from a magnetite bearing vein in the southern orebody provided δ¹¹B values from -20.9 to -24.1 ‰. Tourmaline from magnetite absent sulphide veins is characterized by δ¹¹B values between -8.5 and -11.2 ‰ in both orebodies. These results reflect diverse sources of ore forming fluids because the observed differences cannot be explained by temperature dependent fluid/mineral fractionation of boron isotopes. The very light boron isotope composition may be indicative of metasediment-sourced boron, whereas the heavier compositions may reflect admixing of marine carbonate-evaporite-sourced heavy boron isotopes or a magmatic (granitoid) source of boron (Marschall and Jiang 2011).

4.3 Fluid inclusions

Fluid inclusion petrography supported by cathodoluminescence imaging and combined with microthermometry and Raman microspectroscopy revealed that aqueous-carbonic-sulphuric fluid inclusions with highly variable compositions are associated with sulphide grains along quartz fracture-fills in the sulphide bearing veins. The 10-15 vol% gas phase of the halite absent and halite- ± Fe-pyromalite) bearing aqueous phase rich inclusions always contain small amounts of CO₂, CH₄ and H₂S. Those inclusions associated with carbonic phase-rich fluid inclusions invariably contain traces of a low salinity aqueous phase. The composition of the carbonic phase in these inclusions is highly variable, ranging from almost pure CO₂ to CH₄-rich compositions. The CH₄-rich carbonic fluid inclusions also contain traces of ethane and propane together with H₂S. Observations support that the precipitation of ore minerals were triggered by phase separation in the aqueous-carbonic-sulphuric fluids. The variable salinities of aqueous phases may have resulted from the phase separation process. However, the presence of light hydrocarbons in the carbonic phase rich inclusions points towards the carbonaceous material-rich sedimentary units of the CLGB as potential sources of the ore forming fluids (Gaboury 2013).

5 Conclusions

The Saattopora orogenic Cu-Au (±Ni-Co) deposit was formed by multiple hydrothermal processes between 1.87 and 1.78 Ga. Stable isotope data for carbonates, sulphides and tourmaline, as well as compositions of fluid inclusions point towards various fluid sources including carbonaceous material rich metasedimentary rocks.

Acknowledgements

This work was supported by the Academy of Finland funded project #281670 "Mineral Systems and Mineral Prospectivity Mapping in Lapland".

References


Evolving the genetic model for the Cononish gold deposit, Scotland: from prospect to mine

Calum Lyell, Adrian J. Boyce, Darren F. Mark
Scottish Universities Environmental Research Centre, East Kilbride, UK

William McCarthy
University of St. Andrews, UK

Christopher J.S. Sangster, Peter Flindell, Maurits van den Berg
Scotgold Resources Limited, UK

Abstract. The Cononish deposit consists of a complex of fault-hosted, near vertically dipping, gold- and base-metal-bearing quartz-carbonate veins. Situated near Tyndrum, 70km north of Glasgow, it is on course to become Scotland’s first ever commercial gold mine. Extensive adit-mapping reveals two metallurgically distinct Au-bearing mineral assemblages that are spatially associated with discrete dilations along the Cononish fault. The first (X) constitutes much of the economic resource and is associated with: pyrite-tellurides ± chalcopyrite-galena, coincident with a quartz ± calcite-sericite-barite gangue. The second (Y) is composed of oxide-pyrite-pyrrhotite ± chalcopyrite, coincident with a quartz-carbonate-chlorite gangue. Mineralogical contrast reflects a marked change in composition and oxidation state of ore-fluids. Whilst Cononish displays broad commonality with the orogenic group of ore deposits, mineralization is temporally coincident with high-K Ba-Sr enriched, calc-alkaline magmatism. This observation is substantiated by δ34S analyses of coincident pyrite (~-1.5‰) and barite (~23.7‰) that mineralized at epithermal temperatures (~223°C), and geological observations in this study.

1 Introduction

Owned by Scotgold Resources Ltd, Cononish hosts an estimated JORC (2012) resource of 266koz Au and 1096koz Ag (Scotgold Resources, 2018).

Although classified as an orogenic deposit by Goldfarb et al. (2005), its genesis is debated. Significantly, the age of mineralization at 407 ± 1Ma (Ar/Ar; Rice et al. 2012) post-dates peak metamorphism of its Dalradian metasedimentary host (~470Ma (Stephenson et al. 2013)) – discounting an ore fluid sourced during devolatilization; the most accepted model for orogenic gold emplacement (Goldfarb et al. 1993; Pitcairn et al. 2015). However, whilst mineralization is coincident in time with peak Late Caledonian magmatism (Atherton and Ghani 2002; Neilson et al. 2009), the closest major plutonic body – the Etive Complex – is exposed over 15km away. A negative gravity anomaly around Cononish stimulates the debate (Pattrick et al. 1998).

As the mine opens in 2019, this timely study will analyze new in-adit exposure for the first time in >30 years and aims to develop a new genetic understanding of gold mineralization in the Scottish Caledonides. This paper documents new m- to µm-scale paragenetic observations – some of which may influence on-site processing methodology, preliminary δ34S data; and discusses the genetic implications of these observations.

2 Geological Setting

The Cononish deposit is located near the historic-mining town of Tyndrum, Scotland. The area comprises Neoproterozoic metasediment and metabasite of the Dalradian Supergroup that were subjected to lower-amphibolite grade metamorphism and deformation (D1-D4) during the Grampian Orogeny, ~470Ma (Stephenson et al. 2013).

The sequence is cut by major NE-SW trending structures such as the Tyndrum fault that saw >4km of dip-slip displacement (Treagus et al. 1999). These structures actively modulated the emplacement of Late Caledonian intrusions within the SW Grampian Highlands (Jacques and Reavy 1994).

The Cononish deposit is composed of a series of steeply dipping quartz-calcite veins up to 6m wide. Hosted by the NE-SW striking Cononish fault – a Riedel structure associated with the Tyndrum fault - it extends ~1km along strike (Tanner 2012). Veining cross cuts southerly dipping Grampian and lower-Appin Group metasediment, and lamprophyre sills of Late Caledonian affinity (Earls et al. 1992). These were deformed to a NE verging nappe structure, termed the Beinn Chuirn synformal-anticline, that formed during D2 Grampian deformation (Fig.1; Tanner and Thomas 2010). Deformation has juxtaposed metasedimentary-SEDEX horizons of the Easdale Subgroup below the stratigraphically-lower Appin Group along the Iltay Boundary Slide, a regional stratigraphic disconformity (Tanner and Thomas 2010). SEDEX units are enriched in Ba, Zn, Pb Cu, Fe, Cr and Ni around Tyndrum (Fortey and Smith, 1986) and are the lateral equivalents of mineralization at the Foss mine, Aberfeldy (Willan and Coleman, 1983).

The Cononish fault hosts two documented vein arrays. Au-Ag-Te (± Cu-Pb) mineralization occurs early in the
paragenesis and is coincident with K-feldspar alteration of wall-rock lithologies (Earls et al. 1992; Spence-Jones et al., 2018). Late, shallower-dipping Pb-Zn mineralized structures cross-cut early Au-bearing assemblages (Earls et al. 1992). Vein-sets are distinct: Au-mineralization displays massive crystalline textures, Pb-Zn mineralization is characterized by open-space textures.

Figure 1. Cross section through the Cononish area, including the hypothetical concealed granite. GG: Grampian Group, AG: Appin Group, EsG: Easdale subgroup with dark, SEDEX horizons, CsG: Crinan Grit subgroup.

3 Geological observations

Based on new geological mapping of the Cononish 400mL adit, samples were collected from the most texturally diverse exposures. From this, a paragenesis has been developed using a combination of standard petrography and SEM-CL. This builds on previous work by Earls et al. (1992) and Spence-Jones et al. (2018), and identifies three discrete gold-mineralizing episodes (Au1-Au3). Episodes are limited to specific structural dilations along the Cononish fault and display distinct mineralization styles.

3.1 System initiation

A spatially widespread series of sulfide-poor milky-quartz generations present throughout the adit, brecciated surrounding country rock and mark the onset of veining. These consist of 1.0-5.0cm veinlets, contain no Au and are characterized by massive, crystalline textures that show evidence of annealing. Silicification and, laterally, orthoclase alteration of wall-rock lithologies was pervasive and haloes extend ≤1.0-2.0m from veining. These generations form the medium that host many later Au-mineralizing episodes.

3.2 Ore zone one: assemblage X

Au1 is restricted to the footwall of the Cononish fault and is characterized by a calcite-sericite-barite gangue that forms <1.0cm veinlets - locally forming layered textures (Fig. 2a). Euhedral to subhedral pyrite aggregates up to 5.0cm long host a diverse gold-silver-telluride inclusion assemblage (≤150µm) displaying dissolution textures. A component of gold-ore here is refractory, present as petzite (Ag₃AuTe₂) in addition to electrum Au-Ag alloy (>80% Au). These are coincident with hessite (Ag₂Te), altaite (PbTe) and rare rucklidgeite (PbBi₂Te₄).

Figure 2. a) Layered sulfides typical of Au1 and Au2a, b) sulfide-mantled wall-rock clasts and sulfide ‘pods’ suspended in white quartz, c) Polished block of Au2 displaying multi-generational sulfide-gangue generations.

Au2 is a spatially extensive mineralizing event
coincident with a grey-quartz gangue generation that constitutes the main component of the Cononish ore resource. It can be subdivided into two episodes, a and b, that form a continuum and are often observed within the same hand specimen. Au2 is best observed as three distinct textures within the adit (Fig. 2): layered sulfides (much like in Au1), sulfide-coated wall-rock clasts suspended in white quartz that may be observed as sulfide ‘pods’ depending on disposition, and a multi-generational quartz breccia with spotted sulfides. Au2a is characterized by a pyrite ± galena sulfide assemblage, coincident with grey quartz and potassic alteration. Gold is only found as electrum (>80% Au), coincident with hessite and altaite, and is found as large inclusions (≤250µm) displaying dissolution textures within pyrite (Fig.3a). Au2b is the last gold-mineralizing event present in the main ore zone and is found in proximity to major faults. It marks a significant increase in base-metal mineralization (Cu-Pb) that cross cuts preexisting pyrite generations. Gold is present as Au-Ag alloy (≥70% Au) inclusions (≤250µm) by chalcopyrite, typically as fracture-fill in pyrite.

3.3 Ore zone two: assemblage Y

Ore zone two is separated from ore zone one by a late, cross-cutting dolerite dyke. Unique to this zone is the occurrence of a ~4.0m wide quartz-K-feldspar pegmatite bearing large acicular rutile rhomb’s (~1.0cm) and sparse pyrite mineralization. Au3 is coincident with a grey quartz, carbonate, Fe-chlorite gangue generation that dissects the Cononish pegmatite and locally alters country rock to chlorite. Oxide-dominated ore assemblages and rebrecciated gangue textures (± country rock clasts) are indicative of this zone. Gold is present as Au-Ag alloy (Au:Ag ≈ 1:1) and is coincident with native silver (≤1.0mm) and acanthite (Ag2S). Precious metals are hosted by an oxide-pyrite-pyrrhotite assemblage that displays replacement textures; Au-Ag alloy has a frayed texture and commonly occurs with a native-silver rim (Fig.3).

4 Sulfur isotope data

Table 1 displays 9 new preliminary S-isotope analyses of sulfides and sulfate from Cononish. Paragenetically constrained pyrite δ34S values range from -2.1 to +7.6‰; barite δ34S values mean ~23.7‰ (n=2). Pyrite-δ34S values from the Cononish pegmatite range from -3.0 to -1.4‰ - broadly overlapping the range of pyrite-δ34S values from Au1 (-2.1 to -0.9‰).

Although the small set of analyses introduces a degree of equivocality, the trend of increasing pyrite-δ34S over time is in good agreement with data from Hill et al. (2013) and Spence-Jones et al. (2018).

Table 1. Preliminary S-isotope data of Cononish. Tm: Temperature of mineralization, red: assemblage X, yellow: assemblage Y, blue: Cononish pegmatite.

<table>
<thead>
<tr>
<th></th>
<th>δ34S&lt;sub&gt;pyrite&lt;/sub&gt;</th>
<th>δ34S&lt;sub&gt;barite&lt;/sub&gt;</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au1</td>
<td>-0.9</td>
<td>21.6</td>
<td>256</td>
</tr>
<tr>
<td></td>
<td>-2.1</td>
<td>25.7</td>
<td>189</td>
</tr>
<tr>
<td>Au2a</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au2b</td>
<td>7.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au3</td>
<td>7.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cononish pegmatite</td>
<td>-1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-3.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5 Discussion

5.1 Sulfur Sources

Preliminary pyrite-δ34S data displays a marked change in sulfur isotope composition between paragenetic phases Au1-Au2b in assemblage X. This is interpreted as a temporal change in sulfur source and is congruent with the findings of Spence-Jones et al. (2018). Au1 pyrite-δ34S (~1.4‰) is within the range observed in pyrites from Cononish pegmatite (-1.4 to -3.0‰) and published δ34S data from Late Caledonian intrusions (Lowry et al. 2005), implying an early magmatic sulfur
input. Whilst local SEDEX horizons are barite bearing, average barite-$\delta^{34}S$ values from Foss (+36 ± 1.5‰; Moles et al. 2014) are significantly heavier than those in Au1 at Cononish (~23.7‰), suggesting no genetic affinity. Equilibrium mineralization temperature ($T_m$) estimates from cooccurring barite-pyrite (189-256°C) are within the expected range of an epithermal system (Hedenquist et al. 2000) which, given the association with the pegmatite, is consistent with a magmatic affinity.

Pyrite-$\delta^{34}S$ of Au2b (X) = Au3 (Y). This suggests the source of sulfur to both ore zones was homogenised by the end of the paragenesis, and that the late fluid sourced sulfur from surrounding metasediment, as outlined by Hill et al. (2013).

5.2 Interpretation of geological observations

Petrographic observations highlight the presence of a discrete set of calcite veinlets coincident with assemblage X. Their presence suggests the occurrence of a carbonaceous, CO$_2$-rich ore-forming fluid. Such fluids are characteristic of intrusion related deposits (Lang and Baker 2001) and given the $\delta^{34}S$ coincidence between Au1 and pegmatite suggests a genetic link exists.

Assemblage Y displays magnetite replacement textures; pyrite is typically present as frayed, linear vestiges. The oxidation of pyrite to magnetite, and occurrence of relatively large Au-Ag alloy inclusions within the magnetite suggests interaction with a surficial fluid modified the disposition of gold within assemblage Y.

6 Implications

The Cononish Au deposit formed from an early fluid with low-$\delta^{34}S$ (-1.5‰) and anomalously high Au-Ag-Te. Its spatial and isotopic association with the pegmatite suggests a concealed granite exists at depth (as indicated from gravity data). Oxidised, assemblage Y implies the occurrence of relatively-reduced assemblage X at depth and, significantly, the vertical continuation of ore-resource below present adit level.

References


Fortey NJ, Smith CG (1986) Stratabound mineralisation in the Earls G, Patterson RTG, Clifford JA, Meldrum AH (1992) The affinity. Equilibrium mineralization temperature ($T_m$) estimates from cooccurring barite-pyrite (189-256°C) are within the expected range of an epithermal system (Hedenquist et al. 2000) which, given the association with the pegmatite, is consistent with a magmatic affinity.

Pyrite-$\delta^{34}S$ of Au2b (X) = Au3 (Y). This suggests the source of sulfur to both ore zones was homogenised by the end of the paragenesis, and that the late fluid sourced sulfur from surrounding metasediment, as outlined by Hill et al. (2013).


Concepts and revised models for Phanerozoic orogenic gold deposits

Mortensen, J.K.
Camino Geoscience Inc., Canada

Craw, D. and MacKenzie, D.
University of Otago, New Zealand

Allan, M.
Teck Resources Ltd., Canada

Chapman, R.J.
University of Leeds, UK

Abstract. Most published orogenic gold deposit (OGD) models are based heavily on world-class Precambrian deposits, many of which are interpreted to have a spatial and genetic association with crustal-scale, commonly terrane-bounding, transpressive fault zones. Numerous examples of multi-million ounce Phanerozoic OGDs exist, however, and results of recent studies suggest that many (perhaps most) Phanerozoic OGDs are not directly associated with crustal scale faults, but rather represent a broader range of mineralization styles than is described in published models. We redefine Phanerozoic OGDs into several sub-types within a broad spectrum of deposit styles, which differ in terms of tectonic setting, host rock lithologies, metal sources, vein styles, and possibly grade/tonnage potential. The same range of processes was responsible for the formation of most or all of these sub-types; however, this more refined classification of Phanerozoic OGDs provides an improved framework with which to understand, rank and develop exploration strategies for such targets.

1 Introduction

Orogenic gold deposits (OGDs) are an increasingly attractive target for the mineral exploration industry, despite the fact that these are not a very well defined class of deposit. In addition, most published models for OGDs are based heavily on some of the very large “greenstone belt” type gold deposits hosted in Archean cratons in several parts of the world (particularly the Superior Province in central Canada, and the Yilgarn Block in western Australia). OGD models based on such deposits suggest that the deposits tend to be closely associated with crustal scale, commonly terrane-bounding, transpressive suture zones, and in fore-arc settings. Indeed, many of the Archean gold deposits do appear to fit these criteria. There are also many Phanerozoic examples of multi-million ounce OGDs, however, and many of these are not adequately described by published models for this class of deposit, but represent a considerably broader spectrum of deposit styles, in terms of local and regional tectonic setting, preferred host lithologies, metal sources, and possibly economic potential. We have developed a refined descriptive model specifically for OGDs of Phanerozoic age, based on investigations of a very large number of Phanerozoic deposits in various parts of the world. We redefine Phanerozoic OGDs into four main sub-types, based on structural controls and tectonic setting, associated lithologies (with implications for metal source(s) and trapping mechanism, and style of mineralization. These subdivisions are non-genetic; they are based mainly on descriptive features. Finally, we discuss the implications for economic ranking of the four main sub-types of deposit. Our classification scheme for Phanerozoic OGDs does not include all known deposits, and there are some world-class orogenic gold systems, such as the giant, Mesozoic-age Jiaodong gold district in eastern China, that have not yet been incorporated into the scheme. We suggest, however, that this more refined classification of Phanerozoic OGDs provides an improved framework with which to understand, rank and develop exploration strategies for such targets.

2 Sub-types of Phanerozoic OGDs

We recognize four main sub-types of Phanerozoic OGDs:

2.1 Sierra Nevada Foothills type

These are vein systems that are structurally related to major, crustal scale transpressive faults, and are similar in many respects to some of the larger Archean OGDs associated with the Kirkland-Cadillac and Destor-Porcupine fault zones in the Abitibi Belt in Ontario and the Boulder-Lefroy and other fault zones in the Yilgarn Block in western Australia. Phanerozoic examples include the Mother Lode and Alleghany/Grass Valley belts in California, the Bridge River-Bralorne belt in British Columbia, the Juneau belt in SE Alaska, the Caborca belt in Sonora, Mexico, and possibly the Valentine Lake shear zone in central Newfoundland. Gold-bearing quartz veins are commonly ribbon-banded, and the sources of metals and fluids are uncertain.
2.2 Klondike type

These are typically complex, late- to post-tectonic vein systems that formed within compressional orogens and are not obviously associated with any major fault structures. Veins are commonly low sulphide, single stage extensional veins that are usually localized in late stage brittle-ductile deformation zones. Metals are commonly derived from relatively local sources. Well studied examples include the Klondike and White Gold districts in western Yukon and the Cariboo Gold District in east-central British Columbia.

2.3 Otago type

This group of deposits occurs as dispersed vein arrays and mineralized shear zones in fore-arc accretionary wedges. Metals appear to be derived from prograde metamorphism in deeper structural levels of the accretionary complex. Examples include the Otago Schist Belt in South Island, New Zealand (including the >10 Moz Macraes deposit), and the Chugach Belt in southern Alaska.

2.4 Victoria type

This type of OGD comprises syn- and late-tectonic vein systems hosted by thick, deformed turbidite sequences. It includes early laminated veins along bedding plane faults, as well as later saddle reefs, spur reefs, and discordant fissure veins and vein breccias, commonly localized in fold hinge regions. This sub-type includes deposits in the Victoria and Meguma gold districts. In some instances, such as in several recently discovered zones in the Meguma, and in the Sukhoi Log gold belt in southern Russia and the Spanish Mountain area in the western part of the Cariboo gold district in east-central British Columbia, broad zones of disseminated gold mineralization are spatially associated with the more typical sediment-hosted veins and vein breccias.

3 Implications for ranking Phanerozoic OGD targets

A preliminary ranking of the economic potential of the various sub-types of Phanerozoic OGDs discussed above has been undertaken. This is based on studies of grade/tonnage relationships of many Phanerozoic deposits. These are briefly summarized below.

Klondike-type are likely to be relatively small and mostly uneconomic unless they have locally gold-enriched sources (e.g., Au-rich VMS as at Lone Star Ridge, Klondike).

The Sierra Nevada Foothills-type deposits appear to provide the best opportunity for multiple, possibly large deposits, because they have experienced prolonged fluid flow, with potential for access to multiple metal sources from different crustal levels and reservoirs.

Otago-type deposits form in fore-arc tectonic settings that are commonly not well preserved; they are expected to comprise widely scattered, small and uneconomic vein occurrences unless a major fluid conduit such as at Macraes is present.

Victoria-type OGDs are controlled by relatively local structures, and Pb isotopes suggest metals are mainly from relatively local sources. Such deposits are therefore likely to be small unless a major focusing structure is present (e.g., Fosterville; Globe-Progress shear zone at Reefton).
Abstract. Palaeozoic basin sediments host orogenic gold in the Harlech Dome in Wales and in the Truchas Synform in Spain. New data acquired from both areas, combined with the extensive published data, enable the testing of old and more recent models for the deposition of gold from hydrothermal fluids in orogenic settings where metapelites occur. Metamorphic grade is greenschist in both areas, with minor igneous activity but no major intrusions. P-T conditions are mezozonal. The quartz veins/breccias contain typical mineral parageneses associated with orogenic gold, with early non-auriferous sulphide phases characterised by Fe/As/Co while free Au occurs within later phases characterised by Cu/Pb/Zn sulphides. Cross-fault systems between major faults have been the typical hosts of the mineralisation in the Harlech Dome and this was observed outside the Welsh gold belt in this study and also in Spain. However, in Spain, the highest levels of Au mineralisation were found where quartz veins occur in quartzite near to the contact with the metapelites. Extensional faulting appears to be a strong control over this mineralisation, with a weaker signature where there has been mineralisation associated with movement on major regional faults.

1 A comparative study

The comparative study of apparently similar instances of scientific phenomena is a useful scientific methodology, directing the researcher immediately to areas of difference, where new insights may be available. The Harlech Dome in NW Wales and the Truchas Synform in NW Spain (Fig. 1) provide this opportunity.

Table 1. Summary of data, sources as in references above. Data for Wales refers to the Clogau and Gwynfynydd mines

<table>
<thead>
<tr>
<th>Metamorphic grade</th>
<th>Wales</th>
<th>Spain</th>
</tr>
</thead>
<tbody>
<tr>
<td>epizone, with some areas of high anchizone</td>
<td>Greenschists, epizone</td>
<td></td>
</tr>
<tr>
<td>White mica</td>
<td>White mica</td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td>Chlorite</td>
<td></td>
</tr>
<tr>
<td>±Quartz</td>
<td>±Quartz</td>
<td></td>
</tr>
<tr>
<td>±Albite</td>
<td>±Albite</td>
<td></td>
</tr>
<tr>
<td>Organic carbon content</td>
<td>C = 0.69%</td>
<td>C = 0.24%</td>
</tr>
<tr>
<td>Vein Type</td>
<td>Quartz</td>
<td>Quartz</td>
</tr>
<tr>
<td>±fault breccia</td>
<td>fault breccia</td>
<td></td>
</tr>
<tr>
<td>Phase 1 (As and Fe)</td>
<td>T = 300-390 °C</td>
<td>T = 300-390 °C</td>
</tr>
<tr>
<td>P = 200-220 MPa</td>
<td>P = 200-220 MPa</td>
<td></td>
</tr>
<tr>
<td>Phase 2 (Au, Cu, Pb, Zn)</td>
<td>T = 300 °C</td>
<td>T = 180-310 °C</td>
</tr>
<tr>
<td>P = 180 MPa</td>
<td>P = &lt;200 MPa</td>
<td></td>
</tr>
<tr>
<td>δ34S levels</td>
<td>50% S from wallrock equilibrated with host rocks</td>
<td></td>
</tr>
</tbody>
</table>

These features place the study areas within the remit of models for orogenic gold in low grade metapelite belts (Keppie et al. 1986, Jahoda et al. 1989, Cox et al. 1995, Bierlein et al. 2001, Pitcairn et al. 2006; Large et al. 2011; Hu et al. 2017). Note that the organic carbon contents are very low compared with the "black shales" of Vine and Tourtelot, (1970) which contain 3%.

2 The Harlech dome

The broad dome structure (Fig. 2) (with the local Caerdon Syncline) is traversed by long-lived "meridional" faults. The eastern (Fig. 2, Area B) and southern outcrop (Fig. 2, Area C) of the metapelite Clogau Formation hosts most of the gold mines (Hall 1990), with some in the overlying Maentwrog Formation. Cross-faults on these major faults host the mineralisation. Au has not been reported from the other pelitic horizon, the Dolgellau Member. A key study of the mineralisation and the role of
Life with Ore Deposits on Earth – 15th SGA Biennial Meeting 2019, Volume 2

Wall rock alteration by Gilbey (1968) was followed by extensive studies during the UK government Mineral Reconnaissance Programme (Allen et al. 1979, Cooper et al. 1985). A number of papers emerged from this work, including a study of the role of CH₄ and CO₂ in gold deposition (Naden and Shepherd 1989). As summarised in Shepherd and Bottrell (1993), chemical interaction of an externally derived auriferous hydrothermal fluid with C from the host black shales resulted in gold precipitation.

3 The Truchas synform

The Luarca Formation, a Middle Ordovician black metapelite (Gómez-Fernández et. al. 2009), similar to the Clogau Shale, outcrops round the structure of the Truchas Synform (Fig. 3) and succeeds the Lower Ordovician Armorican Quartzite stratigraphically. However D1 isoclinal folding with axes running ESE-WNW preceded the formation of the syncline by more modest D3 folding on the 110º regional trend. The dominant fault trend is circa 110º with a conjugate set at 170º-250º.

4 New data from Wales

Samples were collected from quartz veins across the NW Harlech Dome where very little mining has taken place (Fig.2, Area A). Quartz veins breccias on the "meridional" trend were included, and veins which cross-cut this trend. Stratigraphically, the samples are from the Gamlan, the Clogau Shale and the Maentwrog Formation. The results from optical, SEM and EMPA studies were supportive of the mineral paragenesis indicated in Table 1, with Phase 1 mineral assemblages including cobaltite, as well as arsenopyrite and pyrite. Of the 4 localities which provided Au values above 0.02 ppm in fire assay, one was in the Clogau Shale, two in the Gamlan and one in the overlying Maentwrog Formation. All were in cross-faults to the major meridional faults.

5 New data from Spain

Samples were collected from fault breccia at Pombriego and from quartz veins at Manzaneda and Cunas (Fig. 3). The samples from Pombriego and Manzaneda were both hosted by Armorican quartzite, while Luarca Shale hosted the Cunas samples.

At Manzaneda, samples were taken from a set of N-S trending extensional quartz veins, similar to those at La Casarina. An auriferous sample contained the complete suite of minerals from Table 1, including two phases of arsenopyrite, as reported from Llamas de Cabrera (Gómez-Fernández et al. 2005, 2012a). At Pombriego, the samples were taken from fault breccia on the regional trend of 110º and returned Au levels by fire assay generally lower than Llamas de Cabrera, but higher than all other sites. The mineral paragenesis was dominated by sphalerite and galena, with country rock inclusions.

At Cunas, there was no evidence of the mineral paragenesis as in Table 1, with only pyrite present in the quartz. The vein is highly irregular, and shows none of the features implying structural control over mineralisation seen at auriferous localities. The Luarca Formation is graphitic (Rodríguez Sastre and González Menéndez 2011) and hence favourable conditions for Au mineralisation occur, with a role for C, as in Wales (Shepherd and Bottrell 1993). In a separate study (González Menéndez et al. in press), we have conducted modelling with the objective of explaining the P-T-XCO₂ conditions of hydrothermal fluids and host rocks (volcanic and metapelite), and their relation to the Au precipitation.

6 Discussion and conclusions

In both Wales and Spain, in new and old data, highest Au
levels occur in minor cross-fault systems, rather than major regional faults. However, major faults may channelize other late hydrothermal fluids that re-dissolve Au. In Spain, the minor cross-fault systems are in (brittle) quartzites, near to the metapelites. Hence a structural control over the mineralisation is favoured by this study. The proximity of the mineralisation to the Luarca make both old (Shepherd and Bottrell 1993) and newer models (e.g. Gaboury 2013) relevant, but the organic C levels in both Wales and Spain metapelites are very low, compared with average "black shales". The models propose that C has been leached from the metapelites and transferred to CO2 and CH4 in the hydrothermal fluids (and later to carbonates) related to Au deposition. Perhaps this could occur on a regional scale during metamorphic devolatilisation and hence explain the low organic C levels. However recent studies suggest C associated with this type of Au mineralisation may be co-deposited during mineralisation, rather than sourced from "carbonaceous" wall-rocks (Hu et al. 2017). Finally the Luarca in our study area contains frambooidal pyrite. The model of Large et al. (2011), involving the capture of Au and associated elements in anoxic/euxinic basin sediments, with subsequent concentration during low-grade metamorphism is therefore interesting. Our current work seeks to evaluate this model.

Acknowledgements

This project was partially funded by Project 0284_ESMIMET_3_E, belonging to the INTERREG V-A Spain-Portugal Cooperation Programme (2014-2020). The support of Gavin Birkenheger of GreenOre Gold is gratefully acknowledged. JKC acknowledges the assistance given in Spain by Javier Fernández-Lozano and Miguel Fernández-Morán.

References


Orogenic gold deposits in the Variscan belt in northwestern Iberia

MacKenzie, D. and Craw, D.
University of Otago, New Zealand

Mortensen, J.K.
Camino Geoscience Inc., Canada

Abstract. Orogenic gold deposits (OGDs) produced most of the gold that was mined during Roman times in the Variscan Belt in NW Iberia, and continue to be the focus of active exploration activity. OGDs in this region appear to post-date most collisional tectonism and oroclinal bending that affected the area, but pre-date the emplacement of scattered post-tectonic intrusive rocks that are locally associated with intrusion-related gold mineralization. Based on our own field observations, ongoing geochronological studies and an extensive literature review, the NW Iberian OGDs can be grouped into a variety of styles, including sheeted gold-quartz veins, slate-belt type deposits, shear zone hosted veins and replacement type deposits in reactive host rocks (esp. ironstones).

1 Introduction

Gold and related deposits are widely distributed throughout the Late Paleozoic Variscan Belt in western Europe, and the portion of the Variscan Belt in NW Iberia was the most important single source of gold for the entire Roman Empire during the first and second centuries. Most of this gold was derived from lode rather than alluvial deposits, which included both orogenic and intrusion-related deposits. Distinguishing between intrusion-related and orogenic deposits, and between the various styles of orogenic deposits present, is critical for designing effective gold exploration models for the region. Our work thus far has focused mainly in central and northern Portugal, and parts of northwestern Spain, where we have mapped and sampled many of the known regional vein systems, gold occurrences and historic gold deposits (Fig. 1).

2 Regional setting

NW Iberia is underlain predominantly by deformed and metamorphosed clastic and rare carbonate and volcanic rocks of Neoproterozoic to early Carboniferous age that made up the west-facing (present-day coordinates) northern margin of Gondwana (e.g. Bastida et al. 2010; Fernández et al. 2013). These strata were affected by east-verging compressional tectonism during the Variscan Orogeny, resulting in the development of mainly east-verging nappe structures and thrust faults and eastward transport of structurally higher units. Metamorphic grade and intensity of penetrative deformation increases from the eastern Cantabrian Zone (CZ), which comprises the foreland of the Variscan Belt, to the Western Asturian-Leonese Zone (WALZ) and finally to the Central Iberian Zone (CIZ). The structurally highest transported rock units make up the Galicia-Trás-os-Montes Zone (GTMZ), which represents oceanic rocks that are interpreted to have been part of the Rheic Ocean. This episode of crustal thickening was associated with the widespread emplacement of syntectonic, 320-305 Ma intrusive rocks (e.g. Fernández-Suárez et al. 2000, 2011). The resulting tectonic geometry has been complicated by the development of two oroclines (e.g., Gutiérrez-Alonso et al. 2012; Shaw and Johnston 2015), the very tight Cantabrian orocline in NW Spain and the more open Central Iberian orocline in west-central Spain central and northern Portugal, at ~308 Ma (Gutiérrez-Alonso et al. 2015). Formation of these oroclines appears

Figure 1. Regional geology of northwestern Iberia, showing locations of intrusion-related and orogenic gold deposits referred to in the text: 1 - Rio Narcea belt (El Valle/Carlés); 2 - Linares; 3 - Salave; 4 - Corcoesto; 5 - Portas; 6 - Vilaflor district; 7 - Franca; 8 - Três Minas; 9 - Jales/Gralheira; 10 - Limarinho; 11 - Valongo Belt; 12 - Castromil; 13 - Bigorne. Major late sinistral faults: RVF - Régua-Vérin fault zone; VF - Vilaraçã fault zone. Oroclinal bends: CO -
to have triggered a lithospheric delamination event, and emplacement of a second, more limited pulse of mainly post-tectonic, crustally derived intrusions, at ~298-290 Ma (Gutiérrez-Alonso et al. 2011; Mortensen et al. 2014). Major NNE-striking sinistral strike-slip fault zones, including the Régua-Verín and Vilarica faults (e.g. Marquesa et al. 2002), are relatively late features that cut across the deformed metasedimentary and intrusive rocks, but locally appear to be contemporaneous with, and to some extent localized the emplacement of some of the post-tectonic intrusions.

### 3 Gold deposits in NW Iberia

Numerous gold deposits in NW Spain, including those in the Rio Narcea belt, the Vilalba district and at Salave, are spatially, temporally and probably genetically associated with post-tectonic, 298-290 Ma, intermediate and felsic intrusions (Mortensen et al. 2014; Rodríguez-Terente et al. 2018). A distinctive feature of the Variscan Belt in NW Iberia is the presence of very extensive NE, N and NW trending, barren quartz veins 10s of m in width with up to 20 km mappable strike lengths. Emplacement of these veins appears to have pre-dated most of the post-tectonic granites, but may be broadly related to regional strike-slip faulting. Although the veins represent a very significant regional hydrothermal event, they appear to be completely unmineralized. We interpret most lode gold deposits in NW Iberia to be orogenic rather than intrusion-related, and their timing and the specific structural and possible lithological controls on their origin are not completely understood. Gold-bearing orogenic vein deposits in the region are mainly late-tectonic with respect to most of the structures in the region, but for the most part pre-date emplacement of the post-tectonic granites. Several broad sub-types of orogenic gold deposits and occurrences can be distinguished in NW Iberia:

- Sets of uni-directional, N to NE-trending, gold-bearing quartz arsenopyrite veins are widely distributed throughout northern Portugal and northwestern Spain, and include Corcoesto, Grovelas, Boticas and Penedono. Previous fluid chemistry studies indicate that these vein systems formed from both metamorphic and meteoric fluids, but gold was mainly introduced during a late influx of meteoric fluids (Noronha et al. 1992; Boiron et al. 2003; Vallance et al. 2003).
- “Slate-belt type” deposits, including saddle reefs, bedding-parallel veins and discordant veins and vein breccias occur locally (e.g., Banjas in the Valongo Belt of northern Portugal; da Silva 2014).
- Shear zone related veins and vein systems are associated with regional scale strike slip faults, such as the sinistral Régua-Verín and Vilarica fault zones; examples include Jales/Gralheira, and possibly Boticas and Bigorne.
- “Homestake-type” replacement of ironstones and volcanic rocks, where reactive host rocks are intersected by late structures that were local conduits for gold-bearing hydrothermal fluid flow (e.g., Portas; Cepedal et al. 2018).
- A variety of other discrete quartz vein systems are also present; these are mainly structurally controlled isolated gold- (±Sb, base metal) bearing veins. These veins include both isolated veins and vein sets, or areas where pre-existing regional structures have been reactivated during local extension or normal faulting (e.g., Castromil in the Valongo Belt).

Antimony is associated with gold in many of the orogenic occurrences in NW Iberia. In some cases, the Sb appears to reflect deposition either late in the mineralizing process and/or at shallower depths than much of the gold. In addition to structure, there are important lithological controls on orogenic mineralization in the region. The Lower Ordovician Armorican quartzite unit, for example, is an important regional gold metatellotect throughout the Variscan Belt in NW Iberia, where it either hosts or is closely spatially associated with a large number of orogenic gold deposits.

### 4 Conclusions

The Variscan Belt in NW Iberia hosts a variety of orogenic gold deposits that generally post-date regional collisional tectonism and oroclinal bending and pre-date post-tectonic intrusion events. When exploring for these types of deposits, it is important to distinguish OGDs from the typically later intrusion-related deposits and to discriminate between the different styles of orogenic deposits. In NW Iberia, four main sub-types of OGDs are distinguishable. These include sheeted vein systems, ‘slate-belt type’ deposits, shear zone-hosted vein systems and structurally controlled replacement type deposits in reactive host rocks.

### Acknowledgements

Work presented here was funded in part by Medgold Resources Corp. and Hunter Dickinson Inc. Discussions with Prof. A Lima at the University of Porto helped clarify some of our interpretations.

### References


Cepedal A, Fuertes-Fuente M, Martin-Izard A, Arias D, Aragón D...


Topology as a tool to characterize gold stockworks

François Turlin, Michel Jébrak, Stéphane De Souza
Université du Québec à Montréal, Département des Sciences de la Terre et de l'Atmosphère, Montréal, QC, Canada

Jordi Turcotte
Sirios Resources, Canada

Abstract. The Archean Cheechoo auriferous hydrothermal system is hosted by a granodioritic to tonalitic intrusion in the Eeyou Istchee James Bay (Quebec, Canada) area in the Superior Province. It comprises quartz (Qtz) veinlets and quartz-feldspar-diopside (Qtz-Fsp-Di) veins that underwent amphibolite facies metamorphism. These veins were followed by pegmatites and by late-chlorite (Chl) veins. The geometrical analytical approach (vein thickness, shape, size, spacing, fractal distribution, etc.) to characterize the vein networks is not reliable because of vein deformation, modification of their shapes and relative positions, and/or of limited observations due to drill core thickness. To the opposite, the number of auriferous veins per length unit and the topology are the most reliable tools to characterize vein arrays that underwent high-grade metamorphism. Application of these methods in the gold-bearing Cheechoo system shows that the gold mineralization is controlled by the number and associated connectivity of the Qtz veinlets, and to a minor extent of the Qtz-Fsp-Di veins. To the opposite, pegmatites and Chl veins only locally remobilize the gold mineralization.

1 Introduction

Stockworks are commonly observed in hydrothermal ore deposits. For example, they can form part of (i) porphyry Cu-, Mo- and epithermal Sn- and Au-Ag deposits in association with disseminated mineralization (Sillitoe 2010), of (ii) Iron Oxide Copper Gold deposits, commonly associated with hematite- and magnetite-rich ore zones (Corriveau et al. 2010), of (iii) the epigenetic root zone of Volcanic-Hosted Massive Sulfide deposits or (iv) vein networks in orogenic gold deposits.

The structural characterization of these objects is challenging due to the superposition of multiple vein networks and to the presence of deformation and metamorphism that can modify original vein geometry and mineralogy. Two main methods have been proposed for the characterization of a vein or fracture network: (i) the geometrical approach dealing with parameters such as vein thickness, shape, size, spacing, fractal distribution, etc. (e.g. Gillespie et al. 1999; Marrett et al. 2018) and (ii) a new topological approach that allows the quantification of the connectivity of a vein network based on vein or fracture relationships (Sanderson and Nixon 2015). This second approach has the advantage of being based on parameters that are not modified by deformation and metamorphism and allows discussion of vein network permeability. Both methods have been essentially developed and used with a focus on petroleum geoscience and characterization of simple hydrothermal and fracture systems emplaced in a brittle medium (e.g. Narr and Suppe 1991; Gillespie et al. 1999).

To the opposite, a large proportion of hydrothermal metallic deposits, especially gold deposits, commonly show complex vein systems with multiple vein generations hosted in metamorphosed and ductly deformed rocks. They are generally formed through successive fracturing events and/or show an alteration/metamorphic overprint. Therefore, several questions arise, (i) are the geometric and topologic approaches used to characterize fracture and vein arrays useful in the case of a natural gold deposit that underwent high-grade metamorphism, and (ii) can they be used as an exploration tool to target stockwork-hosted gold occurrences?

This study focuses on the Archean gold-rich Cheechoo granodioritic to tonalitic intrusion located close to the contact between the Opinaca and La Grande subprovinces in the Eeyou Istchee James Bay area (Quebec, Canada, Fig. 1). It consists of a ca. 500 m thick sill intruded into wacke and showing variable degrees of hydrothermal alteration (Fontaine et al. 2018). It was cut by several vein generations with poorly understood geometry and distribution, but for which vein density has been inferred to control gold grade (Fontaine et al. 2018).

This contribution presents a paragenetic interpretation of the Cheechoo vein network and its characterization using the topologic approach of Sanderson and Nixon (2015) on drill core samples. It allows to discuss the structural specificity of the gold mineralization, and if the geometric and topologic approaches are adapted to characterize and explore such networks in amphibolite facies metamorphic rocks.

2 Geologic framework

The Cheechoo intrusion is located in the La Grande Subprovince close to the contact with the Opinaca Subprovince (Fig. 1, Fontaine et al., 2018). The area recorded four phases of deformation. D1 corresponds to NW-directed thrusts and F1 folds refolded by F2 folds around 2710-2697 Ma (Moukhisl et al. 2003; Ravenelle et al. 2010). D2 is the main phase of deformation, associated with the transposition of S1 into the E-W-trending S2 foliation (Bandyayera et al. 2010). It lasted until ca. 2603 Ma and was associated with amphibolite facies metamorphism (Bandyayera et al. 2010; Dubé et al. 2011; Ravenelle et al. 2010; Fontaine et al. 2018). D3 is associated with SW-NE-trending F3 folds, with a dome-and-basin structure and an S3 foliation (Fig. 1,
Bandyayera et al. 2010; Ravenelle et al. 2010). D_4 is recognized as E-W to NW-SE subvertical faults and high strain zones (Fig. 1, Morfin et al. 2013; Fontaine et al. 2018).

The Cheechoo intrusion is inferred to be emplaced syn- to late-D_2 at ca. 2612 Ma (U-Pb TIMS on zircon, Fontaine et al. 2015). It is granodioritic to tonalitic and of metaluminous and reduced composition (Fontaine et al. 2018). It underwent hydrothermal alteration including pervasive albitisation, local chloritization, and zones of calc-silicate alteration composed of plagioclase, quartz, phlogopite, diopside ± titanite porphyroblasts.

### 3 Vein types

Several vein types have been recognized in the Cheechoo intrusion by Fontaine et al. (2018) but only four show spatial associations with the gold mineralization. Based on crosscutting relationships they were emplaced in the following order.

1. Quartz (Qtz) only veinlets are ubiquitous, millimetric and folded (Fig. 2a) to locally transposed into the S2 foliation. They locally contain sulfides (pyrite, arsenopyrite, pyrrhotite) and visible gold.

2. Quartz-feldspar-diopside (Qtz-Fsp-Di) veins differ from the Qtz veinlets by their mineralogical composition (Fig. 2b) and are found in textural continuity of one another. Accordingly, both are early- to syn-D_2.

3. Pegmatitic veins are centimetric to decimetric granitic in composition and laterally evolve into metric pegmatites (Fig. 2c) with accessory biotite ± tourmaline ± apatite. Mineralization occurs as sulfide aggregates in pegmatites emplaced into the main intrusion. Both pegmatic veins and pegmatites are folded and may be partially transposed into the S_2 foliation but do not show evidence for solid state deformation, suggesting their syn-D_2 to early-D_3 emplacement.

4. Chlorite (Chl) veins are straight thin chlorite-coated fractures that crosscut previous vein generations and structures (Fig. 2c), pointing to their emplacement under brittle conditions. They rarely contain sulfides and visible gold particles that are generally in association with pyrite (Fontaine et al. 2018).

### 4 Reliability of the geometric approach

The classical geometric approaches to characterize vein networks consists in calculating aspect ratios (thickness/length) and spacing (e.g. Gillespie et al., 1999). The Qtz veinlets and Qtz-Fsp-Di veins are emplaced early- to syn-D_2 and recorded subsequent metamorphism and deformation leading to their folding, transposition and shape modification. Hence, these veins have lengths, thicknesses and orientations relative to the investigated scanline that do not reflect emplacement processes. Moreover, pegmatites and Chl veins are too thick and too long, respectively, compared to the drill core width to allow reliable measurement of length, thickness and orientation. Accordingly, the classical geometric approaches cannot be carried out on vein arrays from crustal segments that underwent such high-grade metamorphism and deformation.

### 5 Number of veins and gold grade

The number of veins, that is independent on features discussed above, has been investigated per length unit (ca. 1.5 m) along drill core sections for each vein generation and has been compared to the gold grade. It reveals that the number of Qtz veinlets, and to a minor extent of Qtz-Fsp-Di veins, is correlated to the gold grade (Fig. 3b-c). To the opposite, the pegmatites and Chl veins do not show similar correlations (Fig. 3b-c).
6 Topology and connectivity of the networks

We used the topological approach of Sanderson and Nixon (2015) on each vein array to decipher the relationships between veins and the respective network connectivity. It is based on counting and classifying the nodes of each vein termination or intersection into isolated tips (I), abutments or splays (Y) or crosscutting intersections (X). They are linked to an average connection per branch (C_B) that represents a quantification of the vein network connectivity (C_B <1 for unconnected networks and C_B >1 for connected networks; Sanderson and Nixon 2015).

The Qtz veinlets, Qtz-Fsp-Di veins and pegmatites show an I-Y dominated network with an X-node proportion generally below 10% (Fig. 4a). To the opposite, Chl veins show a more important proportion of X-nodes that can reach up to 50% of the node types (Fig. 4a).

The C_B parameter calculated for Qtz veinlets, and to a minor extent for Qtz-Fsp-Di veins, show strong correlations with the gold grade (Fig. 3b, d), i.e. when these networks are connected (C_B>1), the gold grade reaches values above 0.30 g/t. To the contrary, similar relationships cannot be outlined for pegmatites or Chl veins.

7 Discussion

This study allows to discuss the use of the geometric and topologic approaches and their application in the study of a natural gold deposit hosted in high-grade metamorphic rocks.

The Cheechoo intrusion is cut by several generations of veins that evolved from Qtz veinlets ± visible gold, to Qtz-Fsp-Di veins ± sulfides, to pegmatitic veins and pegmatites, and to late retrogressive Chl veins. Due to the deformation and folding of the two first vein generations, the geometric approach is not reliable and cannot be used to discuss stockwork formation and evolution.

To the opposite, the number of veins per length unit remains a useful and reliable parameter to be correlated to the metal grade, as shown by the strong correlation between the number of Qtz veinlets and, to a minor extent, of the Qtz-Fsp-Di veins, and their C_B. Abbreviations: Chl = chlorite; Di = diopside; Fsp = feldspar; Qtz = quartz.
Moreover, this study provides topological evidence that the connectivity of the Qtz veinlets and of the Qtz-Fsp-Di veins significantly influences the gold concentration. Indeed, gold grades that are higher than 0.30 g/t are associated with Qtz veinlets and Qtz-Fsp-Di vein arrays with CB over 1. This approach deals with vein relationships and types of connections and is therefore not influenced by subsequent deformation or metamorphism if it did not lead to obliteration of the vein terminations.

8 Conclusions

This study shows that complex and polyphased natural vein and fracture systems such as hydrothermal ore deposits that underwent high-grade metamorphism cannot be characterized using classic geometric approaches. To the opposite, the number of veins per length unit correlated to a metal grade and the topologic approach are reliable tools to decipher structural controls on the mineralization. The relative proportion of X, Y and I vein nodes allows to recognize individual vein networks within a polyphased hydrothermal system. Moreover, these parameters can be used as exploration tools.

Acknowledgements

The authors are grateful to Sirios Resources for allowing access to drill core samples, to Technomine for technical support and to Zofia Leroux (Université du Québec à Montréal, QC, Canada) for her help during data acquisition. This study was funded by the MITACS Accélération program in partnership with Sirios Resources (no. IT11826).

References


Figure 4. Link between gold mineralization and topologies of the vein networks. a: density of node types for each vein network. Quartz veinlets' connectivity is associated with gold grade values above 0.30 g/t; b and c: schematic representation of a barren I-dominated network and of a mineralized Y-dominated network, respectively. Note that I and Y nodes usually belong to the same vein system whereas X note indicate sub-perpendicular crosscutting relationships, implying a polyphased system.
Linking fluid flow to gold mineralization in the Senoufo Greenstone belt, northern Côte d’Ivoire

Lynnette Greyling, Johann Diener, Chris Harris, Tshepiso Bopape
Department of Geological Science, University of Cape Town, South Africa

Joe Holliday
Barrick Gold Corporation, Canada

Abstract. Gold mineralization in the Senoufo Greenstone belt, northern Côte d’Ivoire, West Africa, is associated with hydrothermal fluids that were derived from metamorphic devolatilization at the transition of greenschist to lower amphibolite facies metamorphic grades during prograde metamorphism. The presence of locally-derived metamorphic fluids is documented in high gold grade quartz assemblages associated with chlorite-epidote alteration. The bulk of gold mineralization occurred during post-peak retrograde metamorphism where hydrothermal fluids were channeled and trapped by pre-existing structures that were active during long-lived Eburnean orogenesis.

1 Introduction

Gold mineralization is hosted in the Palaeoproterozoic NNE trending Birimian Senoufo Greenstone belt in Côte d’Ivoire in West Africa (Fig. 1). Major gold mineralization is found in Birimian metavolcanic rocks at geological contacts with intrusions, in second or third order structures, and with subordinate occurrences hosted in metasedimentary rocks (Ledru et al. 1991, Milési et al. 1992). Mineralization in the Senoufo greenstone belt is generally viewed as orogenic in type (Greyling, et al. 2013) and also as skarn type (Lawrence et al., 2017)

The Senoufo greenstone belt hosts the 98 Mt Tongon gold deposit operated by Barrick Gold, which has been classified as skarn type mineralization (Lawrence et al., 2017). The Tongon mine is the country’s largest gold mine producing 3.2 Moz at 2.7 g/t Au. Whereas several gold occurrences are found within the ± 400km strike extent of the greenstone belt, the presence of a multitude of lower gold grade targets necessitates the ranking of individual targets in order to focus exploration resources on targets with higher gold hosting potential. This ranking may be applied to other exploration targets in other regions.

This study aims to provide a basis for such a ranking mechanism by evaluating and understanding the gold endowment potential of gold occurrences along the belt.

2 Palaeofluid reconstruction

2.1 Alteration assemblages and thermometry

Gold mineralisation in the Senoufo greenstone belt (excluding the Tongon deposit) is associated with chlorite, epidote, quartz, biotite, pyrite and arsenopyrite, and minor occurrences of pyrrhotite. Host rocks are metamorphosed basalts, tuffs, carbonaceous shales, argillites, volcanic ash breccias, phyllites, basaltic andesitic tuffs and pyroclastic flows. The intrusion of granodiorite and dioritic plutonic bodies predate main mineralization events. Host rock sequences in the immediate hanging- and footwall units to gold targets include medium- to fine-grained equigranular assemblages of hornblende, actinolite, epidote, chlorite albite, quartz, micas, and sphene/titanite.

Chlorite thermometry on quartz-chlorite-epidote assemblages associated with mineralization estimates temperatures between 275 - 347°C.

Figure 1. The Senoufo greenstone belt is located in northern Côte d’Ivoire in West Africa (image from Lawrence et al. 2017).

2.2 Metamorphic devolatilization

Unmineralized footwall and hangingwall samples from three sites in the south and north of the greenstone belt were used to model devolatilization and mobilization of hydrous and carbonaceous fluids during metamorphism. Quantitative mineral equilibrium modelling of greenstone rocks using THERMOCALC 3.45 in the system NCKFMASHTO were used to illustrate the metamorphic conditions, mineral assemblages, and fluid evolution. Calculated P-T pseudosections of samples containing medium- to fine grained equigranular assemblages of hornblende, actinolite, epidote, chlorite, albite, quartz, micas, and sphene/titanite show that 3–7 moles of fluid per mole of rock is produced during prograde
metamorphism between 450 and 500°C during the transition from greenschist to amphibolite facies metamorphism. Fluid production occurs primarily through the breakdown of chlorite, and equates to the focused release of 30–60% of the entire fluid budget of these rocks.

2.3 Stable isotopes

Oxygen isotope data were obtained by both conventional and laser fluorination methods at the University of Cape Town. The δ¹⁸O values of auriferous quartz were between 12.8 and 17.7 ‰, which equates to a fluid δ¹⁸O value between 6.0 and 11.7 ‰, using the oxygen fractionation between quartz and water equation of Zhang et al. (1989). The δ¹⁸O values of quartz veins decrease to the northeast to 10.0–14.1 ‰ (δ¹⁸O fluid 3.2–9.5 ‰), and generally increase with increasing gold grades.

2.4 Fluid inclusions

Minimum fluid trapping temperatures obtained from fluid inclusion homogenisation measurements are between 180–340 °C for samples with gold grades between 5.5 and 27.1 g/t Au. Samples with higher gold grades correspondingly show salinities <6 wt.% equiv. NaCl (Fig. 2). Aqueous and aqueous-carbonic CO₂ fluids are dominant, with minor occurrences of CH₄-rich fluids. Aqueous fluid compositions are inferred from eutectic melting temperatures as H₂O-NaCl- ± MgCl₂±KCl mixtures.

Figure 2. Gold grades and salinity plot for selected fluid inclusions in samples from the Senoufo belt show a decreasing salinity at increased Au grades.

3 Results

Senoufo samples show that (a) large quantities of fluid are generated from the host greenstones during prograde metamorphism at the greenschist- to amphibolite facies transition between 450 and 500°C; (b) gold mineralisation is associated with quartz and chlorite at lower minimum trapping temperatures around 340°C; (c) gold mineralization is associated with aqueous and aqueous-carbonic fluids with δ¹⁸O values of 6.0–11.7 ‰ for the fluid δ¹⁸O. These fluid compositions are similar to what has been documented for other orogenic gold deposits (Goldfarb et al. 2001).

4 Conclusions

This research suggests that voluminous and focused hydrothermal fluids may be produced during prograde metamorphism of metabasic greenstone belt rocks during regional deformation linked to the Eburnean orogeny. Sufficient fluid quantities are generated to mobilize gold from the surrounding rocks and transport it along dilational structures formed by active deformation. The residence time of these internally derived hydrothermal fluids may be long lived. Gold mineralization occurred at lower temperatures after fluid focusing along pre-existing structures. Exploration targets with calculated higher fluid flow can be assigned higher values on a ranking system in addition to considering the gold values of said targets. This additional criterion may aide in the reclassification of targets already ranked solely on gold values.

Acknowledgements

This study was supported by Randgold Resources and the National Research Foundation of South Africa. Barrick Gold/ Randgold Resources geologists Dioumacor Senghor, Sarah Quick, Celin Gronayes, Hilaire Niamke and Chris Millson are thanked for the contribution to the geological interpretation of the belt. Fayrooza Rawoot is thanked for sample preparation on the stable isotope line. Dawid Wilson is thanked for sample preparation of double polished wafers, and John Lanham is thanked for facilitating the stable isotope mass spectrometry.

References


Ore-bearing fluids of the Blagodatnoye gold deposit (Yenisei ridge, Russia): fluid inclusions data

Elena O. Shaparenko, Taras A. Bul'bak, Margarita O. Khomenko, Maria A. Ryabukha
V. S. Sobolev Institute of Geology and Mineralogy

Anatoly M. Sazonov
Institute of Geology and Geotechnology, Siberian Federal University

Abstract. The characteristics of gold-bearing fluids at the Blagodatnoye deposit are discussed. Currently, the Blagodatnoye deposit is of great interest for study, as it is one of the largest in the Russian gold mining industry. It’s located in the zone of influence of the Ishimbinsky deep fault on the Yenisei Ridge. Gold-bearing associations are confined to the quartz-vein zone in which quartz forms veins, lenses, and veinlets. Fluid inclusions from two ore bodies with gold content from 0.2 to 31 g/t have been studied. The types of fluids that took part in the formation and alteration of quartz veins of the Blagodatnoe deposit and their thermobarogeochemical characteristics have been established.

1 Blagodatnoye deposit

The large gold deposit Blagodatnoye is located in the Krasnoyarsk Territory (Fig.1), in the Zaangar part of the Yenisei Ridge. The Ishimbinsky deep fault is one of the main ore-controlling structures of gold mineralization in the area under consideration. There are many ore deposits in the zone of its dynamic influence, including Blagodatnoye. At present, the deposit is of great interest for study as it is one of the largest in the Russian gold mining industry with gold reserves of more than 220 tons and an average grade of 2.5 g/t in the ore.

Gold-bearing associations (early - quartz ± pyrite ± pyrrhotite ± arsenopyrite and late - quartz-sphalerite-chalcopyrite ± galena) are concentrated in the quartz-vein zone with a capacity of up to 150 m, a length of 2.5 km and a vertical amplitude of mineralization of more than 250 m. Quartz is the main mineral that forms veins, lenses, nodules, and veinlets.

2 Methods applied

In order to establish the thermobarogeochemical characteristics of the fluids of the Blagodatnoye gold deposit, fluid inclusions in quartz thin sections were analyzed. The gold content in the samples varies from 0.2 to 31 g/t. Primary, pseudo-secondary and secondary inclusions were studied using microthermometry, Raman spectroscopy and gas chromatography–mass spectrometry (GC-MS). The following inclusions types were analyzed (Fig.2): single-phase (LCO₂, GC₀₂, LCO₂+CH₄+N₂, GC₀₂+CH₄+N₂), two-phase (LH₂O+G) and three-phase (LH₂O+LCO₂+G, LH₂O+G+crystal).

3 Fluid temperature and pressure

The homogenization temperature of primary and pseudo-secondary inclusions, which was considered as the minimum temperature of the mineral formation, is in the range from 200 to 360 °C (Fig. 3). Homogenization temperature of secondary inclusions is 140-260 °C.

The pressure of the ore-forming fluid in the inclusions varies from 0.2 to 2.6 kbar (Table 1). Moreover, there is a noticeable difference in the value of fluid pressure in
quartz with high and low gold content: 1.8-2.6 kbar and 0.2-0.5 kbar, respectively (Fig. 3).

Figure 3. Pressure and homogenization temperature in fluid inclusions from quartz veins with different Au content

4 Salinity

Three types of fluid can be distinguished by salinity: low-, medium- and high-saline. Low saline fluid is conserved in secondary substantially aqueous (LH₂O+G) inclusions. Salinity in them varied mainly in the range from 0.5 to 5.0 wt.%, NaCl-eq. Medium saline fluid is captured in primary and primary secondary aqueous and aqua-carbon dioxide inclusions, in which the salinity varied in the range from 9.0 to 23.5 wt.%, NaCl-eq. Highly saline fluid (> 40 wt.%) is determined in secondary aqua-salt inclusions.

5 Gaseous phases composition

Carbon dioxide, methane, and nitrogen were identified in the gas phase of fluid inclusions. It was indicated by the melting points of liquefied gas in inclusions, which vary in the range from -145 to -56.6 °C, and in some cases below -170 °C. Raman spectroscopy analysis of the gas phase in individual inclusions showed the presence of CO₂, CH₄, and N₂ (Fig. 4).

Table 1. Fluid inclusion characteristics from the samples with a the different gold content

<table>
<thead>
<tr>
<th>Au, g/t</th>
<th>Tₘ, °C</th>
<th>P, kbar</th>
<th>Salinity, wt.%, NaCl-eq</th>
<th>CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9-31.5</td>
<td>250-360</td>
<td>1.8+2.6</td>
<td>10+23.5</td>
<td>0.01+0.13</td>
</tr>
<tr>
<td>0.2-1.7</td>
<td>200-280</td>
<td>0.2+0.5</td>
<td>9+22</td>
<td>31.33+81.50</td>
</tr>
</tbody>
</table>

Figure 4. Oxidized and reduced fluids according to the Raman spectroscopy data

Samples with high gold content have a high methane content. The difference in the percentage ratio of the content of volatile elements indicates a change in oxidation-reduction conditions in the process of ore formation (Gize et al 1993, Gize 1999).

6 Results of GC-MS

Eight samples have been analyzed by gas chromatography-mass spectrometry. The analysis has proved the presence of CO₂, CH₄, and N₂ in the mineralizing fluids. Apart from them, a wide range of compounds of subordinate quantities have been identified such as aliphatic, cyclic, oxygenated hydrocarbons, heterocyclic, nitrogenated, sulfonated, and inorganic compounds (in total, more than 160 species).

7 Implications

Table 1 represents a summary of primary and pseudo-secondary fluid inclusions characteristics in quartz from the Blagodatnoye gold deposit. The formation of quartz veins at the deposit took place with the participation of aqua-salt fluid containing CO₂, N₂, CH₄ and other compounds in the temperature range from 200 to 360 °C. Fluid salinity varied from 9.0 to 23.5 wt. %. Fluid pressure varied in the range from 0.2 to 2.6 kbar.

In the process of ore formation of high gold content, the reduced fluid played a leading role, as evidenced by high concentrations of CH₄ in fluid inclusions.

Highly saline fluid (up to 43 wt. %) and low saline (0.5-5.0 wt. %) were superimposed on already existing veins at temperatures from 140 to 260 °C.

Acknowledgements

The authors would like to thank Analoly A. Tomilenko and Nadezhda A. Gibsher for their support and sharing their ideas.
References

Exceptionally Au-rich mid-crustal fluids from the Kola super deep borehole

Prokofiev Vsevolod Yu.¹, Banks David A.², Lobanov Konstantin V.¹, Selektor Sofiya L.³, Milichko Valentin A.⁴, Akinfiev Nikolay N.¹, Borovikov Andrey A.⁵, Lüders Volker⁶, Chicherov Mikhail V.¹
¹Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, RAS, Moscow, Russia
²School of Earth and Environment, University of Leeds, Leeds, UK
³A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, Moscow, Russia
⁴The ITMO University, Department of Nano-Photonics & Metamaterials, Russia
⁵Sobolev V.S. Institute of Geology and Mineralogy SB RAS; Novosibirsk, Russia
⁶GFZ German Research Centre for Geosciences, Germany

Abstract. In the drillcore of the Kola super-deep borehole (SG-3, 12262 m depth) gold bearing rocks of Archaean age have been located at depths of 9500 to 11000 m. Quartz veins, between 9052 and 10744 m, within this gold zone, contain fluid inclusions with exceptional concentrations of gold, which are present as nanoparticles. There are 4 types of fluid inclusions (1) gas inclusions of dense CO₂, (2) liquid-vapour two-phase aqueous inclusions, (3) three-phase inclusions with NaCl daughter crystals, and (4) CO₂-aqueous inclusions. In all inclusion types, there are extremely high concentrations of Au. In the high salinity FIs the average concentration is c. 750 ppm and may be as high as 6000 ppm. We suggest these fluids could be a precursor of ”Orogenic gold fluids” which, at the Au concentrations determined, would reduce the requirements for large volumes of metamorphic fluids to form orogenic ore deposits. The gold is currently present as colloids and indicates that in this form it is possible to transport greater amounts of gold than in true solution.

1 Introduction

We first discovered fluids with the high gold concentrations during the study of the gold mineralization in deep zones of the Baltic Shield. Mineralization was discovered in the deepest man-made hole on Earth, the Kola Superdeep drillhole (SG-3, 12262 m), drilled to provide information about rocks and processes in the deep zones of the continental crust of the Baltic Shield (Kola, 1998). The borehole was drilled in the Pechenga ore district of the Russian Federation where there is a greenstone belt of Proterozoic age with gold mineralization at the present day surface (Sundblad, 2003). In drillcore from 9500-11000 m, a gold-bearing region with a vertical extension of about 1500 m was found, in which the gold concentration varied from 0.01 to 6.7 ppm (INAA analyses). Gold, with up to 26 % Ag, is present as small flakes (up to 10 microns) and irregularly shaped grains located in biotite, hornblende, plagioclase, and quartz.

These rocks were overprinted by Proterozoic regional metamorphism that reached amphibolite facies at temperatures of 520-650 °C and pressures of 3-4 kbar (Kola, 1998). Zones of greenschist facies metamorphism are also established in the Archaean section of the borehole. Gold mineralization at the present-day surface in Pechenga district and at a depth of 9.5-11.0 km in the borehole, is spatially associated with the zones of regressive transformations (1760-1700 Ma). The study of the deep structure of this area shows that the gold mineralization on the modern surface and at depth are controlled by a single system of faults associated with the tectonic activity during the Svecofennian orogen at 1760 Ma (Lobanov et al., 2013). Taking into account the erosion, which cuts out about 7 km, from the actual depth of occurrence, the gold-bearing zone in the borehole corresponds to depths of 16.6-18 km during the Proterozoic, i.e., we are dealing with hydrothermal mineralization at the depth of the middle crust.

2 Fluid inclusion studies

2.1 Fluid inclusion petrography

Fluid inclusions found in quartz veins between 9052 to 10744 m (sample numbers correspond to their depth) can be divided into four types (Figure 1): type 1) gas inclusions of dense CO₂, type 2) vapor-liquid two-phase aqueous inclusions, 3) three-phase inclusions with NaCl daughter crystals, and type 4) CO₂-aqueous inclusions.
2.2 Microthermometry and Raman analyses

Type 1 are CO₂ gas enriched inclusions with a small amount of water with Thlq from +30.8 to -45.0 °C. TmCO₂ is from -56.7 to -60.3 °C, with densities from 0.37 to 1.14 g/cm³. Salinity is between 3.4 and 4.1 wt.% eqv. NaCl (from the clathrate melt temperature). Raman spectroscopy shows the composition is 99.7-98.7 mol. % CO₂ and 1.3-0.3 mol. % N₂.

Type 2 inclusions, with Te from -74 to -55 °C, are brines containing Na and Ca. In these Fls Tmice is from -20.7 to -63 °C, corresponding to salinities of 21.6 to 30.2 wt. % eq. CaCl₂, Th is between 137 and 228 °C. Only low-density N₂ (100 mol %) was detected in the gas phase.

Type 3 L-V-S inclusions have Tₜ halite between 123-381 °C, and Tᵥ of the vapour between 137 and 264 °C. Low Te of -64 °C indicates Na and Ca chlorides, with salinities from 25.9 to 45.4 wt.% eq. NaCl. Only low-density N₂ (100 mol. %) was detected in the gas phase.

Type 4 CO₂-aqueous inclusions have Tₜ from 203 to 356 °C and salinities from 3.6 to 18.8 wt.% eq. NaCl. The composition of the gas phase is very similar to type 1, with CO₂ (99.6-98.1 mol. %) and N₂ (1.9-0.4 mol. %).

2.3 LA-ICP-MS analyses

The LA-ICP-MS data, revealed the presence of high concentrations of gold in individual fluid inclusions from all 4 types between depths of 9500 and 11000 m (Figure 2). Gold concentration in type 1 fluid inclusions varies from 0.7 to 326 ppm (average 56 ppm, n=64), in type 2 from 4.8 to 691 ppm (average 261 ppm, n=15), in type 3 from 3.0 to 6483 ppm (average 754 ppm, n=57), and in type 4 inclusions from 5 to 8081 ppm (average 919 ppm, n=38).

The ablation profile, for number of fluid inclusions in quartz (Figure 2), shows that the appearance of the gold signal during the ablation coincides with the appearance of the K and Na signals from the inclusion fluids. The presence of gold was not detected during the ablation of quartz around type 1 to 3 fluid inclusions, which indicates that gold is located only inside the fluid inclusions. The gold signal is not the continuous smooth asymmetric shape from elements in solution, but is a series of spikes indicative of particles.

Type 4 CO₂-aqueous inclusions are an exception as no significant signal for Na or K is present. During ablation of the enclosing quartz, gold was found in concentrations ranging from 4 to 52200 ppm. However, no gold particles were detected in this quartz, either by optical microscope or by SEM.

2.4 UV-Visible spectroscopy

The spikey gold signal indicates the occurrence of gold in the fluid as ultra-fine particles. Oblique illumination of the fluid inclusions by a laser beam shows intense scattering of the light in type 3 L-V-S inclusions (Figure 3a), while in aqueous only inclusions the laser beam is only scattered at interfaces (Figure 3c). This clearly indicates dispersed particles in these systems (Prokofiev et al., 2017), which can be attributed to the presence of gold nanoparticles in the inclusions.

The definitive proof of the presence of gold nanoparticles in the fluid inclusions was obtained from recording the confocal UV-Vis absorption spectra in different areas of fluid inclusions. For the type 3 and 4 inclusions, spectra recorded near the bubble/solution interface exhibit a pronounced band in the region of about 500 nm.
Thus, we have discovered for the first time extremely gold-rich deep fluids, containing gold in the form of ultra-fine particles (nanoparticles).

3 Discussion

The question arises as to what processes in nature can cause the formation of fluids containing gold nanoparticles.

Different types of fluid inclusions have different vertical distributions within the area of gold mineralization. Dense CO₂ inclusions (type 1) were found in almost all the samples studied (9052-10744 m). Two and three-phase inclusions of brines (types 2 and 3) are predominantly concentrated at depths in the center of the gold bearing zone (9907-10583 m). CO₂-water inclusions (type 4) are located at the top part of studied interval at depths from 9052 m to 10330 m.

Gas inclusions of dense CO₂ (type 1) are found across the whole depth interval where gold mineralization occurs, including the sample from the greatest depth which is beneath the depth at which the other types of inclusions occur. Therefore, it is unlikely that this dense gas fluid could be formed from phase separation of a hypothetical carbon dioxide-aqueous fluid. Apparently, it was a high-temperature gas fluid, essentially enriched by carbon dioxide, which ascended from much deeper. The density of carbon dioxide in the gas inclusions (type 1) varies from 0.37 to 1.14 g/cm³ over the sample interval. However, the minimum densities occur at the depth of 10583 m.

Raman spectroscopy measurements of CO₂ inclusions show a consistent composition of the gas phase throughout the studied depth interval: 98.1-99.7 mol. % of CO₂ and 0.3-1.9 mol. % of N₂. The carbon isotope values of these inclusions, δ¹³CO₂ values of -5.3 to -5.4, corresponds to values that would be consistent with a juvenile source of CO₂ (Hoefs, 2009). Therefore, we envisage the presence of a stream of juvenile, predominantly CO₂ fluid rising from deep in the earth.

Such a fluid, like all juvenile fluids (Yudovskaya et al., 2006.), could carry finely dispersed gold particles suspended in the gas phase. This is consistent with the discovery of gold in gas inclusions in quartz from the deepest sample 10744 in concentrations from 1 to 281 ppm.

We have also found aqueous salt solutions, with gold nanoparticles (colloidal gold solution?), formed at elevated temperatures and pressures. The simplest scenario for the formation of such a fluid is mixing of an aqueous solution with CO₂ gas transporting the gold nanoparticles (Prokofiev et al., 2016). L-V and L-V-S chloride brine inclusions are present in quartz veins from 9269 to 10179 m. These contain nitrogen in the gas phase without any trace of CO₂. Since the gas phase here was separated from the brines upon cooling, the absence of CO₂ can be due to its low solubility in brines. Therefore, it can be assumed that the CO₂ gas phase (type 1 inclusions) and the brines (type 2 and 3 inclusions) have different sources. Due to the limited availability of these unique samples (there is only one drillcore at these
depths) we can only surmise, there was a horizon of formational brines. However, the formation of such brines during metamorphism was shown by Yardley and Graham (2002).

The occurrence of interaction between the deep carbon dioxide stream and the horizon of pore waters is confirmed by the presence of a minimum of the carbon dioxide density at a depth of 10205.8 m, i.e., in the lower part of the assumed horizon of pore brines. The thermodynamic modeling of the process of mixing of carbon dioxide and a chloride aqueous solution has shown (Prokofiev et al., 2016) that upon this interaction part of the carbon dioxide dissolves in an aqueous solution, while some part of the water passes into the carbon dioxide gas-phase, which leads to an increase of the chloride concentration in the aqueous phase.

The process of interaction between gas and liquid is accompanied by the formation of a large number of gas bubbles, that is, the appearance of a large-area gas-liquid interface per unit volume of the system. This in turn leads to the initiation of various kinds of surface phenomena with high coefficients of phase-to-phase energy and matter transfer. Such interphase interaction could cause the transition of gold (and probably other metals) from the gaseous carbon dioxide phase into the aqueous fluid and its accumulation there in the form of nanoparticles.

The data obtained indicate that fluids exceptionally rich in gold can occur under conditions of the mid-crust depths. According to modern concepts (e.g. Saunders et al. 2014), such an amount of gold cannot be dissolved in the form of the true solutions in hydrothermal fluids at the homogenization temperatures of the fluid inclusions. The thermodynamic modeling of the process of mixing of carbon dioxide and a chloride aqueous solution has shown (Prokofiev et al., 2016) that upon this interaction part of the carbon dioxide dissolves in an aqueous solution, while some part of the water passes into the carbon dioxide gas-phase, which leads to an increase of the chloride concentration in the aqueous phase.

The occurrence of interaction between the deep carbon dioxide stream and the horizon of pore waters is confirmed by the presence of a minimum of the carbon dioxide density at a depth of 10205.8 m, i.e., in the lower part of the assumed horizon of pore brines. The thermodynamic modeling of the process of mixing of carbon dioxide and a chloride aqueous solution has shown (Prokofiev et al., 2016) that upon this interaction part of the carbon dioxide dissolves in an aqueous solution, while some part of the water passes into the carbon dioxide gas-phase, which leads to an increase of the chloride concentration in the aqueous phase.

The data obtained indicate that fluids exceptionally rich in gold can occur under conditions of the mid-crust depths. According to modern concepts (e.g. Saunders et al. 2014), such an amount of gold cannot be dissolved in the form of the true solutions in hydrothermal fluids at the homogenization temperatures of the fluid inclusions. The thermodynamic modeling of the process of mixing of carbon dioxide and a chloride aqueous solution has shown (Prokofiev et al., 2016) that upon this interaction part of the carbon dioxide dissolves in an aqueous solution, while some part of the water passes into the carbon dioxide gas-phase, which leads to an increase of the chloride concentration in the aqueous phase.

The data obtained indicate that fluids exceptionally rich in gold can occur under conditions of the mid-crust depths. According to modern concepts (e.g. Saunders et al. 2014), such an amount of gold cannot be dissolved in the form of the true solutions in hydrothermal fluids at the homogenization temperatures of the fluid inclusions. The thermodynamic modeling of the process of mixing of carbon dioxide and a chloride aqueous solution has shown (Prokofiev et al., 2016) that upon this interaction part of the carbon dioxide dissolves in an aqueous solution, while some part of the water passes into the carbon dioxide gas-phase, which leads to an increase of the chloride concentration in the aqueous phase.

The data obtained indicate that fluids exceptionally rich in gold can occur under conditions of the mid-crust depths. According to modern concepts (e.g. Saunders et al. 2014), such an amount of gold cannot be dissolved in the form of the true solutions in hydrothermal fluids at the homogenization temperatures of the fluid inclusions. The thermodynamic modeling of the process of mixing of carbon dioxide and a chloride aqueous solution has shown (Prokofiev et al., 2016) that upon this interaction part of the carbon dioxide dissolves in an aqueous solution, while some part of the water passes into the carbon dioxide gas-phase, which leads to an increase of the chloride concentration in the aqueous phase.

The data obtained indicate that fluids exceptionally rich in gold can occur under conditions of the mid-crust depths. According to modern concepts (e.g. Saunders et al. 2014), such an amount of gold cannot be dissolved in the form of the true solutions in hydrothermal fluids at the homogenization temperatures of the fluid inclusions. The thermodynamic modeling of the process of mixing of carbon dioxide and a chloride aqueous solution has shown (Prokofiev et al., 2016) that upon this interaction part of the carbon dioxide dissolves in an aqueous solution, while some part of the water passes into the carbon dioxide gas-phase, which leads to an increase of the chloride concentration in the aqueous phase.

4 Conclusions

The area of the earth's crust under consideration corresponds to the depths of the middle crust. This depth is the level at which mobilization of fluids forming orogenic gold deposits occurs (Goldfarb et al., 2015). Current estimates of gold concentration in orogenic deposits are 0.5-5 ppm (Garofalo et al., 2014). This is approximately 2-3 orders of magnitude lower than the maximum concentration of gold in the fluids from the Kola superdeep borehole. Therefore, the data from this study increases our understanding of the processes of transport and accumulation of gold by hydrothermal fluids at mid-crustal depths. The discovery of gold nanoparticles in such fluids at high concentrations, requires a new look at the scale of the migration of gold and the ratio of the mass of the fluid relative to the metal carried by it. The further study of these newly discovered fluids will expand our understanding of the gold behavior in deep fluid systems and mechanism of its accumulation in ore-deposits close to the present day surface.

Acknowledgements

This work was financially supported by Russian Foundation for Basic Research (Grant number 18-05-70001).

References


New constraints on fluid composition of the Neoarchaean Black Reef, South Africa

Hunadi K. Maselela*, Glen T. Nwaila, Grant M. Bybee, Raymond J. Durrheim
School of Geosciences, University of the Witwatersrand, South Africa

Jeremie Lehmann
Department of Geology, University of Johannesburg, South Africa

Abstract. The conglomerate-hosted Black Reef Formation gold deposit is located at the base of the Neoarchaean to Palaeoproterozoic Transvaal Supergroup. It has been subjected to several post-depositional alteration events. Compositions of ore-forming fluids were studied using fluid inclusion petrography and microthermometry. Results from this study show that two fluid pulse events (i.e. quartz-pyrite and quartz-hydrocarbon) played a major role in Au remobilisation. Inclusions developed in ore-bearing fractured quartz pebbles are of two types: liquid-rich inclusions (type I) and mono-phase inclusions (type II). Microthermometric data were inconclusive for type II inclusions as no phase change could be observed. Type I inclusions showed homogenisation temperatures between 113.9 °C – 269.7 °C and salinities ranging from 0.5 wt% NaCl to 19.0 wt% NaCl. Based on microthermometry, fluids in the Black Reef deposit are of H2O-CO2-H2S-CH4 type. The H2S indicates that Au was transported as AuHS(aq) - or Au(HS)2– complexes. The predominance of CO2 in carbonic fluids shows that hydrocarbons played a role during post-depositional alteration.

1 Introduction and geological background

The Neoarchaean Black Reef Formation (BRF) is a thin and laterally extensive lithostratigraphic unit of the Transvaal Supergroup, South Africa (Fig. 1). It contains sediment-hosted gold deposits and is classified as Witwatersrand-type gold deposits (Frimmel 2005). The BRF shares certain similarities with the underlying Witwatersrand Supergroup, including similar rock types and mineral assemblages. A distinct feature of the BRF is the high abundance of carbonaceous material. It consists of carbonaceous shale, quartz arenite, and conglomerate.

Although the BRF contains economic Au concentration, the amount of Au is far less when compared to the Witwatersrand Supergroup. Much of the BRF gold mining has occurred adjacent or alongside the Witwatersrand auriferous conglomerates. A recent study by Nwaila et al. (2019) proposed that gold was introduced into the BRF by mechanical recycling of underlying Witwatersrand reefs, followed by short-range (mm to cm scale) remobilisation during post-depositional alteration.

In addition, a study by Fuchs et al. (2016) suggested that post-depositional ore-forming fluids including hydrocarbons have contributed immensely to Au mineralisation in the BRF. In their study, Fuchs et al. (2016) found that some of the Au in the BRF is a product of a chemically triggered precipitation from hydrothermal fluids.

Although secondary processes are thought to have concentrated some of the Au in the BRF, the basal conglomerate unit is the primary control. The conglomerate unit of the BRF is characterised by milky, rounded quartz pebbles, supported by a carbonaceous matrix and massive pyrite. In the Witwatersrand reefs, the presence of pyrite and carbon seams has been used as indicators for Au mineralisation (Frimmel 2005) - similar features are present in the BR.

The aim of this current research is to characterise the nature and composition of ore-forming fluids responsible for Au remobilisation in the BRF gold deposit.

Figure 1. Kaapvaal Craton showing the distribution of Archaean to Proterozoic stratigraphic units. BRF is indicated by a blue line. Sample location is indicated by a red star (modified from Frimmel 2005).

2 Samples and analytical procedure

2.1 Optical microscopy

Ten conglomerate samples were used for optical microscopy to obtain mineralogical and textural details. Uncovered thin sections (4 cm x 25 cm) were prepared
and analysed under transmitted and reflected light using the Olympus BX63 petrographic microscope at the Microscopy and Microanalysis Unit, University of the Witwatersrand. The mineral assemblages and microstructures were analysed at low to medium magnifications (4x to 40x). Fluid inclusions were located using higher magnifications (50x to 100x) using the Olympus BX51 petrographic microscope from the School of Geosciences, University of the Witwatersrand. Images from the optical microscope were captured by a normal light-sensitive camera in order to generate photomicrographs.

2.2 Fluid inclusion microthermometry and raman spectroscopy

A total of ten samples underwent fluid inclusion analysis using the LINKAM MDS 600 cooling microscope. The samples are transparent quartz pebbles with sporadic microfractures. Most of these quartz pebbles are surrounded by both primary and secondary pyrite grains. Doubly polished (150 µm) sections were made into wafers and placed on a cooling stage connected to a liquid N₂ feeder. The LINKSYS32 program was used to operate the heating and cooling of the fluid inclusions and to also control the cooling and heating rates to at most 5 °C/min and to 1 °C/min when close to a phase transition. The freezing point temperatures (Tm) and homogenisation temperatures (T hom) were recorded when heating and cooling. Images of the fluid inclusions were captured by a digital camera attached to the microscope.

Raman spectra were acquired using the 514.5 nm line of an argon ion laser and a Horiba LabRAM HR Raman spectrometer equipped with an Olympus BX41 microscope. The incident laser beam was focused onto the sample using a 100x objective and the backscattered light was dispersed via a 600 lines/mm grating onto a liquid nitrogen cooled CCD detector. The signal was acquired and processed by LabSpec v5 software. The laser beam spot diameter was approximately 1 um. The spectral resolution for this configuration is about 1.5 cm⁻¹. The HOKIEFLINCS_H2O-NACL excel programme was used to calculate the salinity and density of these fluid inclusions.

3 Results

3.1 Fluid inclusion petrography

Petrography shows that the majority of the quartz pebbles are rounded while some show overgrowth features. Some of the pebbles are highly elongated. Phyllosilicate group minerals and carbonaceous material are the main constituents in the matrix of the BRF conglomerates. Opaque minerals are aligned along quartz pebble boundaries and also form aggregates. Various morphologies of pyrite including detrital and hydrothermal types were observed. Digenetic pyrite has overgrowth along grain boundaries.

Quartz pebbles have multiple intergranular microfractures filled with secondary minerals. Most of the cracks have matrix material (Fig. 2B (ii)) and at places, they contain pyrobitumen as the carbon phase. Some of the gold occurs in the cracks of quartz and along fracture zones (Fig. 2 A and B (iii)).

Using high magnification, fluid inclusions were located in quartz pebbles. At room temperature (25 °C) these inclusions are two-phased consisting mostly of a higher percentage of liquid than vapour (~3:1 and 3:2 ratio) and have been classified as type I. Type II inclusions were identified as mono-phase fluid inclusions but no conclusive microthermometry measurements were obtained. This is because phase changes could not be observed. Type II inclusions are not as abundant as type I inclusions.

In the quartz pebbles, away from quartz fractures, the
Fluid inclusions are occasionally randomly orientated and more commonly aligned as trails (Fig. 3D). Near quartz fractures, they occur as trails sub-parallel to the fracture orientation (Fig. 3B) and also at an angle obtuse to the microfractures (Fig. 3C). Fluid inclusions that are in close proximity (<10.0 µm) to pyrite are smaller than 4 µm (Fig. 3A). However, the average width of the fluid inclusions in the studied samples is 9.2 µm (σ = 4.8).

### 3.2 Microthermometry

Most of the studied quartz pebbles for microthermometry were in close proximity to pyrite mineralisation and along quartz microfractures. Microthermometric results are represented in Figure 4 as histograms of homogenisation temperature and salinity. The results reveal a large range of homogenisation temperatures from 113.9 °C to 269.7 °C (x = 171.0 σ = 31.6) (Fig. 4A) and a constrained range in the freezing point temperature from -15.5 °C to -0.3 °C (x = -4.9 σ = 3.6). Salinities of the fluid inclusions range from 0.5 wt% NaCl to 19.0 wt% NaCl (x = 7.4 σ = 4.7) (Fig. 4B) while the density of the fluid inclusions range from 0.792 g/cm³ to 1.060 g/cm³ (x = 0.956 σ = 0.052).

![Figure 4. Frequency histograms of a. homogenization temperatures in °C and b. salinities in wt% NaCl for fluid inclusions from the Black Reef Formation.](image)

### 3.3 Raman spectroscopy

Raman data was obtained at room temperature of 25 °C. Raman spectroscopy of vapour phases (Fig. 5A) showed peaks at 1340 – 1380 cm⁻¹ corresponding to CO₂, 1560 – 1620 cm⁻¹ corresponding to H₂O vapour, 2670 – 2730 cm⁻¹ corresponding to H₂S and two peaks for CH₄ from 2930 to 3260 cm⁻¹. The liquid phases of the inclusions (Fig. 5B) showed peaks at 2890 – 3620 cm⁻¹ corresponding to a broad H₂O band.

![Figure 5. Raman spectroscopy graphs for different phases of the fluid inclusions. a. Raman spectra for the vapour phase of a two-phase fluid inclusion. The major species is CO₂ followed by H₂O, H₂S and CH₄. b. Raman spectra for the liquid phase of a two-phase fluid inclusion. The major species in this phase is H₂O.](image)

### 4 Discussion

#### 4.1 Characteristics of the ore forming fluids

The results show that quartz pebbles from the BRF conglomerates contain fluid inclusions that are two-phase inclusions dominated by a liquid-phase with a minor vapour phase. This confirms a nearly homogeneous state of fluid during fluids capture (Lai et al. 2015). The microthermometric results (Figs 4 and 6) indicate a wide range of homogenisation temperatures and medium to low salinities. This large range of salinity from 0.5 wt% NaCl to 19.0 wt% NaCl indicates a wide variety of source fluids that may have mixed with a low salinity fluid (Lai et al. 2015). This low salinity fluid may have had a different composition to that of the main mineralising fluid and locally buffered the salinity of the mineralising fluid to result with an average salinity of 7.4 wt% NaCl. The homogenisation temperature data indicate that ore-forming fluids were of low to moderate temperatures (Yang et al. 2013).

![Figure 6. Correlation between homogenization temperature and salinities of fluid inclusions in the quartz pebbles of the Black Reef Formation. Pink circles represent BRF fluid inclusions. Fields used are obtained from Yang et al. 2013.](image)
The vapour phase composition of the fluid inclusions is mainly composed of CO₂ with lesser amounts of CH₄, H₂O and H₂S. The CO₂ is the abundant phase whereby the carbon is oxidised and exceeds the reduced species (CH₄ - the carbon is reduced). This suggests that the ore-forming fluid evolved in an oxidising environment (Yang et al. 2013). The liquid-phase composition of the fluid inclusion is mainly composed of pure H₂O.

The quartz pebbles of conglomerates from the BRF have fluid inclusions that are hydrocarbon-rich with minor components of hydrogen sulphide. This implies that hydrocarbon fluids were an integral part in the remobilisation and mineralisation of Au in the BRF. These fluids could have been internally derived within the Transvaal Basin. A study by Hallbauer and Kable (1982), focusing on quartz pebbles of conglomerates from the BRF, Ventersdorp Contact Reef and the Vaal reefs, found a range of homogenisation temperatures (~110 °C to 180 °C). Drennan et al. (1999) also obtained intermediate homogenisation temperatures (between 150 °C and 210 °C) for fluid inclusions in the Carletonville goldfield. These temperatures alongside homogenisation temperatures obtained in this study have been used to classify the hydrocarbon and sulphur-rich fluids as post-depositional.

The preservation of hydrocarbons in fluid inclusions led Drennan et al. (1999) to conclude that fluid hydrocarbons migration was a strong factor in the Witwatersrand Basin and had the potential to transport large concentrations of gold. This is also effective for the BRF whereby remobilisation of carbon, gold and pyrite occurred in millimeter to centimeter scale. Metal transportation within oils and brines in hydrothermal systems has been focused on strongly by William-Jones et al. (2009) on Witwatersrand reefs and they found that metals such as V, Ni, Cr, Mn, As, Hg, U, Fe and Au are transported in crude oil around 100 °C. These hydrocarbon fluids contain sulphur which aids in increasing the solubility of metals such as Fe, Cu, Ni and Co (Woods 2017). Sulphur complexes metals such as Au, Hg and Ag to make them slightly soluble in hydrocarbon fluids (William-Jones et al., 2009). Carbon nodules have also been attributed to being effective at remobilising elements since they are isolated from the carbon seams (Woods 2017). The nodules are minute and contain higher concentration of REEs than the seams. In the seams the REEs would be dispersed. Therefore, carbon nodules exhibit the ability for a hydrocarbon-rich fluid to remobilise elements that are considered immobile (Woods 2017).

Previous studies (e.g. Gartz and Frimmel 1999; Fuchs et al. 2016) suggested that bisulphide complex (Au(HS)₂⁻) acted as transport mechanism for dissolved Au and the presence of H₂S in figure 5A compliments theirs. The presence of H₂S in the Witwatersrand Basin has been interpreted by Frimmel (2005) and Heinrich (2015) as an indicator for magmatic water in the ore-forming fluid. In the absence of O-H isotopes, this may not be conclusive, however, figure 6 shows it may be magmatic water. A recent study by Nwaila et al. (2019) showed that some of Black Reef gold is found in fractured quartz pebbles alongside pervasive fluids. The results show that ore-forming fluids in BRF was a H₂O-CO₂-H₂S-CH₄ fluid. This is similar to the hydrothermal fluid systems obtained by Drennan et al. (1999) which were classified as aqueous, H₂O-CO₂-rich, H₂O-CH₄-CO₂-rich and CH₄-N₂-rich fluids.

The graph of homogenisation temperature versus salinity (Fig. 6) shows that in hydrothermal fluids, the fluid inclusions from the Black Reef cluster in a field where secondary magmatic fluid mixed with meteoric fluid. This suggests that a large amount of meteoric fluid diluted the secondary magmatic component (Yang et al. 2013).

5 Conclusion

This study emphasises the role of fluid chemistry as a transport medium for dissolved Au and subsequent short-range Au remobilisation in the BRF. Classifying the chemistry of the Au mineralising and mobilising fluids is important for studying similar Witwatersrand-type deposits outside the Kaapvaal Craton. This will assist in delineating the chemistry of the fluids as an important constituent for gold mineralisation.

Acknowledgements

I would like to thank DST NRF CIMERA for sponsoring this project. Gratitude is sent to Prof. Rudolph Erasmus from the School of Physics, University of the Witwatersrand, for assistance and interpretation of the Raman spectra.

References

Hallbauer DK, Kable EJD (1982) Fluid inclusion and trace element content of quartz and pyrite pebbles from the Witwatersrand conglomerates: their significance with respect to the genesis of primary deposits. Ore Genesis, 2:742-752

Gold from Orogenesis to Alluvial 755
Fluid inclusion analysis and isotopic investigation of two structurally constrained gold mineralized reefs in the Fairview mining district, Barberton, South Africa

Christina M. Comuso, Bjorn P. von der Heyden
University of Stellenbosch, South Africa

Matthew Severs
Stockton University, USA

Chris Harris
University of Cape Town, South Africa

Abstract: The Barberton Greenstone Belt (BGB) in South Africa hosts numerous lode gold deposits in several lithologies and structural settings. The goal of this project is to characterize and understand the nature/source of the gold-transporting fluids in the Sheba/Fairview mining district. To achieve this, a comprehensive fluid inclusion (FI) and δ18O investigation of black quartz veins present within the Hope Reef (HR) and Main Reef Complex (MRC) at the Fairview mine is being conducted. The formation of both orebodies is related to progressive phases of horizontal NW-SE directed shortening correlative to D3 deformation. Preliminary petrographic work shows that the samples contain primary and secondary FI assemblages containing liquid and vapor phases. Fluid inclusions revealed freezing temperatures between -55° to -56°C, indicating a CO2 rich fluid. Clathrate melting temperatures ranged from 8° to 18.9°C suggesting a thin liquid or vapor film may exist within the FI and the fluids are a H2O-CO2 mixture. Finally, homogenization temperatures ranged between 202°C to 231.6°C, suggesting the mineralizing fluids to be similar in composition and in P-T conditions. Further geochemical analytical work, based on a structurally constrained and larger sample set, will better characterize the fluids responsible for Au mineralization in the HR and the MRC.

1 Introduction

There is a lack of understanding on the dominant factors that lead to gold mineralization in the Barberton Greenstone Belt. The global accepted generic models of orogenic gold systems remain unanswered; however, the consensus is that metamorphic fluids are responsible for most of the world’s orogenic gold deposits (Groves et al. 2018). What is agreed however, is that structural kinematics provide the necessary features to facilitate fluid flow, and the siting of gold mineralization commonly depends heavily on fluid interaction with the surrounding wall rock. Models produced by Colvime, (1989) and Groves et al. (1998) suggest transport distances are extensive, coming from great depths, allowing hydrothermal fluids to interact with surrounding wall rock before being halted at more crustal depths. At the Sheba/Fairview mining district in the BGB, one of the oldest running gold mines in the world, over 345t of Au have been produced since 1883 (Dirks et al., 2009). The current values of gold production could be much higher with a better understanding of the geochemistry of the mineralizing fluids to target exploration.

2 Regional geology

The BGB is a NE trending synclinal belt bounded by 3.5-3.1 Ga Tonalite-Trondjhemite-Granodiorite (TTG) and granites centralized to the east of the Kaapvaal Craton (Anhaeusser, C.R et al. 1981; De Ronde et al. 1992; Lowe and Byerly 1999; Lowe & Byerly 2007; Gloyn-Jones & Kisters 2018). The Sheba/Fairview mining district, situated in the BGB, is dominated by the Eureka and Ulundi reclined synforms. Multiple phases of deformation (D1-D4) including accretion, shortening, regional folding, and extension have affected the regional geology of the BGB.

Three main stratigraphic units make up the BGB, which include, starting with the base and moving upward: (1) The Onverwacht Group (ca. 3.57 – 3.30 Ga), composed of mostly mafic and ultramafic volcanic lithologies, interbedded with thinly layered chert and felsic volcanics; (2) the Fig Tree Group (3.259-3.298 Ga), consisting of turbiditic greywackes, chert, mudstone, shale, banded iron formations and some volcaniclastic rocks; and (3) the Moodies Group (3.226 -3.16 Ga), mainly clastic sedimentary rocks, sub greywacke, quartzose, and feldspathic sandstones (De Ronde et al. 1992; Lowe and Byerly 1999; Lowe & Byerly 2007). Along the central-southern part of the Eureka and Ulundi Synclines sits the Fairview Mine as seen in Figure 1 (Otto et al. 2007). Over time the Eureka and Ulundi Synclines were refolded leading to the multitude of quartz-carbonate veins seen throughout the mine (Dziggel et al. 2007). The increase in structural porosity through these less competent rocks allowed for Au to be hosted in these numerous veins within the Fairview mine (Hofmann and Harris 2008; Altigani et al. 2016). The Sheba Fault, which acts as a catalyst for most deformational events within the Fairview mining district is made up of various sheared and reformed serpentinites, talc- carbonate schists and...
cherts all found within the Weltevreden Formation fixed between both the Ulundi and Eureka synforms (Ramsay 1963; Byerly et al. 1996; Lowe and Byerly 1999; Gloyn-Jones & Kisters 2018). The formation of the HR and the MRC orebodies is predominantly linked to progressive phases of horizontal NW-SE direct shortening which has been correlated to late D₃ deformation (Gloyn-Jones & Kisters 2018).

Figure 1. Regional map of the Barberton Greenstone Belt illustrating gold mine localities, stratigraphic lithologic groups and surrounding intrusive bodies (Anhaeusser et al. 1981; Dirks et al. 2013; Agangi et al. 2014; Gloyn-Jones & Kisters 2018).

3 Mineralizing reef complexes

3.1 Hope reef complex (HR)

There are two main mineralized shear zones within the HR that are characterized as high-angled sets brittle ductile regions. First being a shallow ESE dipping, slightly undululated NNE trending reef, and several moderate to steeply dipping NW and NE trending structures (Gloyn-Jones & Kisters, 2018). The more imperative portion of the HR where mineralization and this study is focused is within the shallow reef. Structural analysis from Gloyn-Jones & Kisters (2018) was done within the Fairview Mine of the Hope Reef complex at level 58. This level of the mine is the shallow portion of the reef and shows high grade mineralization with associated quartz veining, sulphide mineralization, and fuchsite/sericite rich alteration, all bounded by a SE shallow dipping brittle-ductile shear zone system (Gloyn-Jones & Kisters 2018). The Hope Reef is situated in the lower portion of the Sheba Formation above the Sheba fault and Main Reef Complex, composed of mostly a greywacke package (Gloyn-Jones & Kisters 2018). The entirety of the Hope Reef is made up of both shallow and steeply dipping mineralized zones that are confined to the greywacke units of the Fig Tree Group (Gloyn-Jones& Kisters 2018).

3.2 Main reef complex (MRC)

The MRC is moderately- to steeply- SE-plunging orebody governed by a jog-like corridor characterized by a severely mis-oriented brittle-ductile shear zone confined to the immediate hanging wall greywacke and shale units along the Sheba fault zone (Gloyn-Jones & Kisters 2019). In the MRC of the Fairview mine, higher gold grades are spatially associated with shale units of the metasediments in the lower Fig Tree mine and gradually terminates along strike (Gloyn-Jones & Kisters 2019). There are two distinct forms of mineralization within the MRC; sulphide mineralization that is associated with blackish-grey quartz carbonate veins, and mineralization of similar sulphides dominantly in the surrounding shale wall-rocks (Gloyn-Jones & Kisters 2019). Samples were collected from level 25/27 for this study.

4 Preliminary data

4.1 δ¹⁸O stable isotope data

Figure 2. δ¹⁸O stable isotope data of samples from this study collected at Sheba/Fairview mines MRC and HR compared to other isotopic data collected in similar localities. The data range between 12-14.5 for all studies show similar metamorphic signatures for fluid source. For this study the purple points represent MRC samples, light blue is from HR and dark blue are samples analyzed from Sheba mine.

Black quartz grains from both HR and MRC were crushed and isolated at 4g per sample to be analyzed for oxygen isotopes at the stable isotope laboratory of the Department of Geological Sciences, University of Cape Town utilizing the laser fluorination method of Harris and Vogeli 2010. A total of twelve samples were tested for δ¹⁸O signatures, ten samples from Fairview mine (both of HR and MRC) and two from Sheba were analyzed. Figure 2 shows the samples from this study have similar isotopic compositions compared with others in literature at similar deposit types such as K. Farber et al. 2016; De Ronde et al. 1992 study at the Barberton Greenstone Belt, and Beaudoin & Pitre 2005 at the Val-
4.2 Microthermometric analyses

Microthermometric analyses were performed on samples containing viewable fluid inclusion assemblages. Freezing and homogenization measurements were done using an Olympus BH-2 microscope equipped with a Linkam THM600/HFS600 temperature-controlled stage with a T95 system controller. Calibration was set using H2O/CO2 inclusions in quartz against the melting point of CO2. The results suggest an H2O-CO2 dominated composition that homogenized between 202-231.6°C.

4.3 Raman spectroscopy

In order to better understand the composition of the liquid and vapor phases for selected fluid inclusions, the Raman spectrometer (Witwatersrand University, School of Physics) was used. Representative samples of viewable fluid inclusions from both HRC and MRC were analyzing using a Horiba LabRAM-HR Raman spectrometer, mounted to an Olympus BX-41 microscope with a Lexel Model 95 SHG Argon ion laser. Preliminary results suggested the presence of graphite, methane, water and carbon dioxide within the inclusions.

5 Discussion

The variable amounts of gold mineralization in the BGB represents the multiple fluid pulses, the differences in structural kinematics, and the fluid to wall rock interactions that can be seen in both Sheba and Fairview Mines (Bierlein and Maher 2001; Altigani et al. 2016). Combining the geochemical data from this study to the structural studies done by Gloyn-Jones & Kisters in 2018 and 2019 it is evident that both the MRC and HR vary, structurally, lithologically and temporally. These differences, however, do not reflect the fluid phases that have flowed through both the HR and MRC. Utilizing the structural kinematics from Gloyn-Jones & Kisters 2018 and 2019 for sample collecting in this study and running preliminary fluid inclusion and isotope analysis it is more plausible that the fluids that mineralized both the HR and MRC at Fairview mine originated from a similar source. After the F3 folding event of the Ulundi Syncline, the “fluid valve” that percolated fluid to HR was closed off. The presence of the Sheba Fault allowed fluid flow to be centralized up the fault through the MRC. The clustering of isotopic data and microthermometric data supports the idea that fluids that mineralized both the MRC and HR could be similar in origin. It is essential to understand the role the wall rock and ligands play when interacted with fluid phases. Whether gold mineralization is sourced from fluid transport or as a result of precipitation remains enigmatic. More geochemical analytical work is being done at both mineralizing reefs at Fairview mine to further support the theory that mineralizing fluids could have originated from the same or very similar sources.

Acknowledgements

This study was made possible through support from NRF grant 106006 with additional funding from DST-NRF CIMERA and the Society of Economic Geologist. Thank you, Mark Evans at Central Connecticut State University,
for allowing me to run preliminary microthermometry experiments. Rudolph Erasmus at the University of Witwatersrand for Raman spectroscopy analysis and the CAF lab at University of Stellenbosch for assistance with SEM-CL analytical data.

References


Shearing and fluid evolution of Porto Nacional orogenic gold district, Transbrasiliano-Kandi shear system, Brazil

Maria Jose Mesquita, Jefferson Picanço,
Geosciences Institute, Campinas University, Brazil

Iain Samson
University of Windsor, Canada

Leo Hartman, Marcia Boscato Gomes
Institute of Geosciences, Federal University of Rio Grande do Sul, Brazil

Abstract. The Porto Nacional gold district, in the Tocantins Province, Brazil, is an orogenic gold district hosted in the crustal-scale Transbrasiliano-Kandi Shear System. First-order shear zones, namely CSZ, MSZ, and CoSZ have been recognized. The CSZ marks the contact between two different geotectonic units, with the development of hydrothermal staurolite, garnet, and graphite in phyllonites. The crystallinity of carbonaceous material (CM) and graphite indicates median Ts of 488°C and 617°C, respectively. The MSZ and CoSZ comprise second-order shear zones, with carbonate-chlorite phyllonites. All zones host quartz-gold veins and quartz-carbonate veinlets. Chlorite and carbonate geothermometry indicate Ts of 355-400°C for mylonites-phyllonites and pre-ore veinlets, and 300°C for post-ore veinlets. Three types of fluid inclusion assemblages have been found in quartz-gold veins: carbonic dominant-aqueous (CA), with median homogenization Th ~355°C and low salinity (< 5.7 eq. wt.% NaCl); aqueous dominant-carbonic (AC), with Th ~290°C, and salinity 2.2-15 eq. wt.% NaCl; and aqueous (A) with Th ~230°C, and up to 17 eq. wt.% NaCl. The δ13C of graphite (-26 to -28‰) from phyllonite indicate biogenic carbon sources, whereas the δ13C (δ13C = -6 to -7‰) of carbonate from veinlets indicate a magmatic/metamorphic source. The δ18O (9 to 11‰) of quartz from veinlets and veins also indicate a magmatic/metamorphic source, with the heaviest values (up to 16‰) in CSZ. Mixing of fluids from different sources was likely responsible for gold precipitation.

1 Introduction

South America hosts a major NE-SW continental-scale tectonic corridor called the Transbrasiliano-Kandi Shear System (TKSS), which extends through Brazil, Paraguay, Argentina, and West Africa (Fairhead and Maus, 2003). It represents a Neoproterozoic continent–continent collision involving the conjoined Amazon and West African cratons against the São Francisco-Congo and Saharan cratons (Cordani et al., 2013). Besides its magnitude, a few gold deposits have been described along the TKSS, namely the Príncipe orogenic Au deposit and the Natividade Au deposit. In central Brazil, the TKSS hosts the Porto Nacional gold district (PNGD), which provides a unique opportunity to study the structural and hydrothermal evolution of this important shear system, and to understand gold mineralization within the framework of that evolution. The PNGD is also important for understanding the evolution of the Brasiliano-Pan African orogeny, because this gold district occurs in a wedge of Paleoproterozoic rocks within the Neoproterozoic orogen.

To achieve this, we have carried out extensive field work and used that as a basis for an integrated study combining microstructural quartz mapping, microthermometric and Raman spectroscopic data on fluid inclusions in quartz and graphite, and stable (O and/or C) isotopic analysis of quartz, carbonate, and graphite. We also discuss the applicability of the orogenic gold model to these deposits based on their characteristics, including their tectonic and structural environment and the composition and source of the fluids (cf. Goldfarb et al. 2015 and Groves et al., 2018), in order to obtain a better understanding of this district and its relationship to the development of the TKSS. Assessing the orogenic gold model for the Porto Nacional deposits will be important in the exploration for new targets in the region and along the entire TKSS.

2 Geology

The Porto Nacional gold district is in Tocantins Province, which consists of a series of Archean-Paleoproterozoic terranes that are surrounded by Neoproterozoic Goias magmatic arcs, and supracrustal orogenic belts (Araguaia, Paraguay, and Brasilia belts).

In the most northern part of Tocantins Province, particularly in the PNGD, Paleoproterozoic units are dominant, represented by the Porto Nacional Complex (PNC), the Manduca Suite (MS), granites of the Ipueira suites (IS), shelf metasedimentary rocks of the Natividade group, and the Morro do Açúles formation. First-order shear zones, namely the Cachimbo Shear Zone (CSZ), the Mutum Shear Zone (MSZ), and the Conceição Shear Zone (CoSZ) are related to the TKTS, and hosts more than fifty artisanal mines (garimpos), some of which are actively mined.

2.1 The Ore System

The CSZ is the wider zone, and marks the contact...
between granulites of the PNC and upper-amphibolite granite-gneisses of the MS. It is the only zone with staurolite, garnet, and tourmaline, and where graphite phyllonite hosts shear quartz-gold veins.

MSZ and CoSZ are narrower shear zones inside the MS and IS. Both comprise second-order shear zones, mainly with biotite-chlorite-carbonate phyllonites, which host shear quartz-gold veins. Five types of veinlets are present: type-1 quartz-feldspar veinlets, type-2 quartz-carbonate veinlets, type-3 carbonate-sulphite-gold veinlets, and type-4 and -5 carbonate-quartz veinlets.

3 Methods

Microthermometry was performed using a Linkam THM-600 freezing-heating stage attached to an optical microscope, in the Fluid Inclusion Laboratory of the University of Windsor, Canada, and in the Research Microscopy Laboratory of Campinas University. Microthermometric data was processed using the software packages FLUIDS (Bakker, 2003) and CLATHRATES (Bakker, 1997). Raman spectra were collected using a Ramanan U-1000, attached to a Spectra Physics Ar ion laser (514.5 nm line) and a microscope Nachet (80x objective). Raman microscopy of graphite was performed at the University of Windsor, Canada. The isotopic data was collected using a dual-inlet VG Optima stable isotope ratio mass-spectrometer at the Laboratory for Stable Isotope Science (LSIS) at Western University. The isotopic data are reported in δ notation relative to VSMOW for oxygen and VPDB for carbon (Coplen, 1996). Microprobe data were obtained using a JEOL JXA-8600 superprobe electron microprobe at Western University, Canada.

4 Microstructural domains of quartz and fluid inclusion assemblage

Fluid inclusion and microstructural analyses were performed on the same samples from the shear quartz-gold veins from the CSZ, MSZ and CoSZ. Three types of fluid inclusion assemblages (FIA) have been distinguished: carbonic-dominant (CA) and aqueous-dominant (AC) carbonic-aqueous inclusions, and aqueous inclusions (A).

These three FIAs are distributed in six microstructural domains in quartz from the veins. The aim was to characterize the domains in order to place the FIAs in a deformation chronology for the variably deformed quartz.

Microstructural domain 1 occurs in old porphyroclast quartz from the CSZ and MSZ, which contains preserved primary CA FIAs (Fig.1A). Secondary AC FIAs are also common in domain 1. Domain 2 occurs in subgrain-new grain microstructures. Domain 3 is the recrystallized quartz matrix that wraps around old porphyroclasts (Fig. 1A). Fluid inclusions in domains 2 and 3 are too small to be measured. Domain 4 is a new generation of vug-fill quartz associated with sulphide, which hosts AC FIAs (Fig. 1B).

AC and A FIA occur in domain 5, healing intra- and intergranular fractures in all shear zones, and A FIA are the only type in healed intergranular fractures of domain 6, mainly in the CoSZ.

CA FIAs contain an aqueous liquid phase and one or two carbonic phases, with CO₂ and CH₄. The median homogenization temperature (Th) is 355°C with density from 0.6 to 0.9 g/cm³, and low salinity (< 5.7 eq. wt.% NaCl). AC FIAs comprise an aqueous liquid phase and one or two carbonic phases with pure CO₂. The median Th is 290°C, salinity from 2.2 - 15 eq. wt.% NaCl, and density from 0.7 to 1.0 g/cm³. A FIAs contains two phase, liquid-rich, liquid-vapor inclusions. The median Th is 230°C, with the highest salinities (9.9 -17 eq. wt.% NaCl) and densities (0.90 – 1.0 g/cm³).

5 Geothermometry

Together with Th of fluid inclusions from quartz-gold veins, the crystallinity of graphite from phyllonites, and the chemical composition of carbonate and chlorite from mylonites/phyllonites and veinlets were used for geothermometry. Graphite-phyllonite of the CSZ shows two types of epigenetic carbonaceous material (CM): type-1 graphite, elongated along the foliation, and type-2 CM with no preferred orientation. After Beyssac et al. (2002), crystallinity indicates temperatures of 617°C for type-1 graphite and 488°C for Type-2 CM.
Chlorite (Inoue et al., 2009) and carbonate (Powell et al. 1984) geothermometers indicate: 1) Ts for mylonites of the MSZ (400°C), 2) similar T for phyllonites, type-2 and -3 veinlets of the MSZ, as well as Ts for veinlets of the CSZ between 355° to 365°C, and 3) Ts for type-4 veinlets of MSZ close to 300°C.

6 Stable isotopes

Isotopic compositions were determined for quartz (O) from veins and veinlets, for calcite and dolomite (O, C) from veinlets, both from the three shear zones, and for graphite (C) from quartz veins and graphitic phyllonite in the CCZ.

The majority of quartz from veins and carbonate from veins and veinlets from the three shear zones show a narrow range of $\delta^{18}$O, from 8 to 11‰ (Fig. 2A). CSZ quartz veins and a few carbonate-quartz veinlets show heavier $\delta^{18}$O values, from 12 to up to 16‰. Carbonate (calcite and dolomite) samples from veinlets also show a narrow range of $\delta^{13}$C, from -7.7 to -9.1‰, whereas carbonates from later type-4 veinlets have slightly heavier $\delta^{13}$C values, from -5.1 to -7.1 ‰, (Fig. 2B). Graphite samples from phyllonites and veins from the CSZ show a $\delta^{13}$C range from -26.0 to -28.3 ‰, in the range indicative of biogenic carbon.

7 Discussion and conclusions

The combined data from mylonite, phyllonite, quartz-carbonate veinlets and quartz-gold veins of the PNGD suggests fault-valve behavior throughout the evolution of the mineralized shear zones, as discussed below.

The formation of mylonites, phyllonites, type-2 veinlets, and microstructural domains 1 to 3 in quartz-gold veins are considered to represent pre-ore events. According to garnet-staurolite thermometry, the mylonites and phyllonites in the CSZ were developed at conditions similar to amphibolite facies (staurolite zone) metamorphism, between 550° and 610°C (Mesquita et al. 2006). Consistent with that, type-1 graphite, which is oriented parallel to the phyllonitic foliation, crystallized at a median T of 617°C, and CA-FIA isochores in quartz veins suggest P from 3.7 to 6.8 kbar (Fig. 3A).

Type-2 CM, which filled pressure shadows around garnet and staurolite, together with sulphides, and in the quartz-gold veins, induces a median T of 488°C, and pressures from 2.8 to 4.8 kbar. These data could suggest that the CSZ was activated during the metamorphic peak of the host Manduca Suite (Mesquita et al 2006); only the host rock ages are known as circa 2.09 Ga (Mesquita et al., in press).

Chlorite and carbonate geothermometers suggest lower temperatures for MSZ activation, however, no other T index mineral was found in the MSZ. Chlorite from earlier mylonites reveals a median T of 400°C, and CA-FIA isochores in quartz veins suggest P between 2.3 and 3.8 kbar (Fig. 3B), and a low fluid pressure gradient.

Chlorite from type-2 veinlets of the CSZ and MSZ, indicate Ts of ~360°C, and CA- and AC-FIA isochores in quartz-gold veins of domain 1 suggest P from ~1.5 to 3.0 kbar (Fig. 3A, B). Both veinlet types indicate periods of supralithostatic pressure regimes in the host phyllonites, where fluid pressure higher than shear stress was responsible for the development of fractures.
and shortening caused folding and boudinage of the type-2 veinlets along with the phyllonitic foliation.

The $T_h$ of CA-FIA of domain 1 (~355°C) marks the minimum $T$ of formation of the quartz-gold veins. Later episodic periods of high shear stress and shortening are recognized in structural domain 2, where the quartz porphyroclasts underwent recrystallization by subgrain rotation (SGR), which is thermally activated around ~400°C when the rate of diffusion is higher than dislocation production (Stipp et al., 2002). Structural domain 3 in the CSZ and MSZ is characterized by recrystallized matrix; which indicate bulging recrystallization (BGR) at lower $T$ (~280 to 380°C).

The main period of gold precipitation (syn-ore events) was related to open space episodes, which formed the type-3 ore veinlets and the vug-fill quartz (domain 4) in the quartz-gold veins of all shear zones. The type-3 veinlets have a median chlorite crystallization $T$ of 355°C, and AC-FIA isochors in quartz veins of domain 4 suggest $P$ from 1.5 to 4.0 kbar (Fig. 3C). The large pressure range may indicate pressure fluctuations and evidence from seismic-pumping fault valve processes for gold precipitation (Sibson et al. 1988).

After gold mineralization, chlorite and calcite-dolomite crystallized in the type-4 carbonate veinlets at a median $T$ of 307°C and $P$ between 0.6 and 1.4 kbar (Fig. 3D). The aqueous A-FIA healed later fracture planes at a median $T$ of 236°C.

The calculated isotope signature of the fluid that precipitated the graphite and CM indicates a carbon source that is heavier than expected from a biogenic reservoir, and also isotope disequilibrium between graphite and carbonate (Fig. 2B). The fluid $\delta^{13}C$ values in equilibrium with carbonate from the five types of veinlets are close, and coincide with average crustal values, but are also close to mantle fluids (Fig. 2B).

The fluid $\delta^{18}O$ values in equilibrium with quartz from the veinlets and from the veins of the MSZ are close, ranging from 3 to 6‰, whereas those for the veins of the CSZ are heavier (~8‰), and are lighter for veins from the CoSZ (~1‰), consistent with a mixture of magmatic/metamorphic and meteoric fluids or magmatic/metamorphic fluids and sea water (Fig. 2A).

The uniformity of the $\delta^{18}O$ and $\delta^{13}C$ fluid values could indicate high fluid/rock ratios along the shear zones (cf. Kerrich, 1987).

### Acknowledgements

This research has been supported by CNPq-Brazil. We are grateful to University of Windsor and UFRGS, Luiz Neto and Verena Mine for the support provided to the researchers.

### References


A unique (?) telescoped orogenic system: insights from the Fosterville gold deposit

C. R. Voisey, A. G. Tomkins, Y. Xing
School of Earth, Atmosphere and Environment, Monash University, Clayton, Australia

Abstract. The Fosterville Au deposit is hosted in the Bendigo Zone within the western Lachlan Orogen, south east Australia. The Fosterville deposit contains three distinct mineralization styles, (i) refractory Au locked into fine-grained arsenopyrite and pyrite disseminated throughout metasedimentary wall rocks; (ii) visible Au hosted in quartz-carbonate veins associated with stibnite mineralization; and (iii) vein-hosted native Au with no stibnite association. Refractory Au mineralization is found throughout the deposit, whereas visible Au +/- stibnite occurs deeper in the system (>800 m depth from surface). Thus, Fosterville provides a unique locality for studying a telescoped orogenic Au system that changes with depth. Microscopy, neutron tomography, nanoscale secondary ion mass spectrometry and field observations have been conducted to investigate mineralogical and structural controls on the various styles of Au mineralization. These results provide the foundation for equilibrium geochemical modelling using HCh software. Results are considered in the context of an evolving mineral system over the history of the deposit and relative timing of mineralization is inferred. A genesis of the Fosterville deposit itself is proposed and the mechanisms behind various Au-Sb-As relationships in orogenic Au systems are considered.

1 Introduction

Telescoped ore deposits refer to those in which early high-temperature mineralization and alteration are overprinted vertically by late low-temperature mineralization events and their characteristics. This term is often used to describe the juxtaposition of epithermal-type mineralization over porphyry-style deposits. There has been little consideration for telescoped orogenic-style deposits, although the mineralogy in these systems can differ with depth (Groves et al. 1998). This may be due to large distances separating the distinct mineralization styles/deposits, so they are considered individually, or if vertical zonation is local it may have been lost to erosion or re-working. Gold commonly has a bimodal distribution in orogenic Au systems, where Au occurs within sulfides as well as in quartz-carbonate veins, and metasedimentary-hosted orogenic depositsoften have an Au-Sb association (e.g., Hagemann & Lüders 2003). The Fosterville deposit hosts these three Au assemblages at distinct vertical extents, providing an ideal setting for investigating geochemical and structural controls that change with depth in a single deposit.

2 Regional and deposit geology

The Fosterville Gold Mine (FGM) is hosted by Ordovician turbidites of the Bendigo Zone within the western Lachlan Orogen (Gray et al. 2003) (Fig. 1). These sedimentary sequences have undergone greenschist facies metamorphism and were deformed into dominantly north-south trending chevron folds that are cut by thick-skinned thrust systems (VandenBerg et al. 2000). The majority of Au deposits in the Bendigo Zone contain visible Au mineralization hosted by quartz veins associated with saddle reefs and faulting. The Fosterville deposit differs in that it contains three distinct mineralization styles, (i) refractory Au locked into fine-grained arsenopyrite and pyrite disseminated throughout metasedimentary wall rocks; (ii) visible free Au hosted in quartz-carbonate veins associated with stibnite mineralization; and (iii) vein-hosted native Au with no stibnite association. Refractory Au mineralization is ubiquitous throughout the deposit, whereas visible Au +/- stibnite occurs deeper in the system (>800 m depth from surface) (Fig. 1).

Disseminated sulfide hosted ore is the dominant Au mineralization phase at FGM and averages grades of 5-10 g/t Au with individual assays of up to 60 g/t Au (Hitchman et al. 2018). This mineralization is structurally controlled by discordant bedding-faulting relationships and forms as a selvage to quartz-carbonate veining (Fig. 1) (Leader et al. 2012). Arsenopyrite is fine-grained (0.05-6 mm) acicular needles that occur either aligned with trending cleavage or with no preferred orientation. Auriferous pyrite crystals are pyritohedrons between 0.1-2 mm in size. Gold contents in arsenopyrite range from 100-1000 ppm and pyrite contains between 10-100 ppm Au (Roberts et al. 2003). Sulfide mineralization is variably overprinted by visible Au ± stibnite event(s) at depths greater than 800 m from the surface.

Visible gold found in the Eagle Zone and below (Fig. 1) averages grades of 15 g/t Au with individual assays over 1% Au and as high as 3% Au. Gold occurs as disseminated grains with sizes >1 mm and are loosely arranged in an orientation parallel to their host veins. In this zone, visible Au contributes ~40% of the contained Au ounces (Hitchman et al. 2018). Areas with stibnite mineralization may contain disseminated visible Au (<3 mm), although the grade is highly variable. This mineralization event can replace and infill earlier quartz-carbonate veins or occur as massive stibnite-quartz breccias along fault margins. Gold-stibnite mineralization can also be found hosted in variably sized vugs (1-5 cm) within quartz-carbonate veins.
Gold from Orogenesis to Alluvial

3 Methods

Samples were prepared as polished sections for optical and scanning electron microscopy (SEM). SEM imaging was conducted at the Monash Centre of Electron Microscopy using a JOEL 7001 FEG-SEM as a first order examination of Au distributions and vein textures.

To inspect episodic quartz growth with respect to Au distributions, catholuminescence (CL) and elemental mapping was conducted using a JOEL 8500F electron probe microanalyzer (EPMA) at the Commonwealth Scientific and Industrial Research Organization Microbeam Laboratory, Clayton.

Neutron tomography was conducted on Au-rich samples at Australian Centre for Neutron Scattering to map the 3D distribution of Au with respect to vein microstructures using the DINGO instrument. The data sets were reconstructed with the Octopus package, while ANU Vizlab’s Drishti software was used for visualization, analyses, and full three-dimensional image reconstruction.

High-resolution elemental mapping was carried out using the Camaca NanoSIMS 50L at the Centre for Microscopy Characterization and Analysis (CMCA) at The University of Western Australia. NanoSIMS measurements were performed with a Cs+ primary beam, with a spot size of approximately 100 nm, impact energy of 16 keV, and a beam current of 10 pA. The instrument was operated in multicollector mode, allowing for detection of seven ion species in tandem (34S, 54Fe32S, 60Ni32S, 75As32S, 123Sb, 130Te and 197Au).

Equilibrium geochemical modelling was conducted using the HCh software package. This package was developed for modelling fluid-rock systems at moderate to high temperatures (1000°C) and moderate pressures (<500 MPa) using a thermodynamic database (Unitherm). The system modelled here was Al-As-Au-Sb-Fe-Mg-Sb-S-Cl-Si-Na-Ca-C-H-O to best represent the bulk rock compositions found in the Victorian gold fields and depositional mineralogy. This model assumes a turbidite source rock with a composition of that reported by Pitcairn et al. 2006. Fluid derived from the source rock at greenschist-amphibolite boundary conditions is then migrated through a rock column with the same composition at a 5:1 fluid rock ratio through a modern geothermal gradient of 30°C per km. This process is repeated for 20 waves to best represent the fault valving nature of orogenic deposits, where large volumes of fluid are repeatedly flushed through relatively narrow interconnected fault/vein networks.

4 Results

4.1 Vein and ore textures

Underground exposures show that Sb mineralization is often on the margins of splay faults below the Phoenix level and exist as stibnite-quartz breccia and vuggy Au with variable Au content (Fig.2). Stibnite textures in fault veins is commonly dendritic. Microscopy reveals an intimate relationship between Au and stibnite (Figs.2 & 3). Some of the highest-grade Au samples from FGM (upwards of 1-3% Au) are mineralization of this type. Gold and stibnite are often intergrown in vuggy cavities within quartz-carbonate veins. Often, it appears that Au has grown onto stibnite crystals, as seen in Fig.2B. CL images of vein-hosted Au-Sb show that quartz has not be recrystallized or damaged post-crystallization and crystal zoning is preserved (Fig.2). NanoSIMS images of wallrock selvages next to Au-Sb-bearing fault veins show stibnite overprinting arsenopyrite and pyrite porphyroblasts (Fig.4). Stibnite mineralization is contained to fractures, porosity and pressure shadows with no obvious crystal-bound Sb within the grains.

4.2 Thermodynamic modelling of the FGM

Thermodynamic calculations using HCh software were implemented to replicate the ore and alteration mineralogy at FGM to gain insight into controls on mineralization. Preliminary results of this modelling are mimicking FGM assemblages (Fig.5). The top of Fig.5 shows that arsenopyrite is stable during early fluid influx waves at depths between 1.8 and 3.6 km and temperatures between 150 and 250°C. This is in fair agreement with fluid inclusion studies that describe the formation of auriferous arsenopyrite at Fosterville to be between 2.6 to 5.7 km depth and temperatures of 180 to 270°C (Mernagh 2001). After n=5 waves of fluid influx events, calcite becomes stable in this same depth range, likely representing the calcite-ankerite spotting at FGM. At 10 waves of fluid influx, stibnite has a narrow stability range that begins to overlap near the bottom of the earlier deposited arsenopyrite extent. Finally, at 20+ fluid influx events, the stability range for stibnite has
grown to encompass roughly 1/3 of the early arsenopyrite range at depths between 2-3 km and temperatures between 180 to 230°C. Pyrite is stable throughout the model, save the pyrite-pyrrhotite transitions at the greenschist-amphibolite boundary. Graphite has a wide stability but is lost during intermediate stages of fluid influx, and then returns in strong association with the stibnite field.

Figure 2. A) Underground exposure of stibnite-quartz breccia from the Swan fault at FGM. B) CL map of Au-Sb mineralization quartz vein. C) Elemental map of (B) highlighting Au-Sb mineralization

5 Discussion

Antimony is largely considered to be deposited at shallow crustal levels (Groves et al. 1998), which agrees with Au-Sb sample textures found at FGM (Figs.2&3). Structures and textures such as fault breccias, open cavities and vugs are indicative of shallow emplacement. At temperatures above 300°C, Sb is stable in hydrothermal fluids in many environmental conditions (Krupp1988) and require large changes in temperature to precipitate stibnite. At a pH of 5.5, a drop in temperature from 250°Cto 200 °C would decrease Sb solubility by one order of magnitude causing significant stibnite mineralization (Hagemann & Lüders 2003). Thermodynamic modelling of the FGM shows stibnite precipitation at temperatures between 180 to 230 °C, suggesting Sb saturation by temperature decrease(Fig. 5). Cooling of ore fluids can occur by fluid unmixing or decompression during fluid ascent. The fault-valve model from Sibson et al (1988) predicts dramatic pressure fluctuations during seismic events by an increase in fault permeability. Pressure reduction of ascending fluids promotes CH4, CO2, and H2S loss during immiscibility (Seward 1989; Hagemann & Lüders 2003). This unmixing would shift the ore fluid to lower temperatures and cause stibnite to precipitate.

In the Fe-Sb–S system, Au-Sb co-precipitation requires a decrease of the fluid pH (Williams-Jones and Normand 1997). Modelling of the FGM shows stibnite required not only a change in temperature, but also a fluid pH shift from 6 to 5.5 (Fig.5). This pH shift appears to be facilitated by CH4consumption and the onset of carbonate mineralization by CH4→Ca(CO)3+4H+. This explains the close association of the stibnite and carbonate stability fields (Fig. 6). If Sb is transported by theHSb2S4-ligand, reaction with free H+ ions from methane breakdown will occur by HSb2S4 +H→Sb2S3+H2O. A pH shift of 6 to 5.5 is also coincident with drop of Au solubility in HS and (HS)2-bearing hydrothermal solutions by an order of magnitude, from 10 ppb to 1

Figure 3. A) Neutron tomographic reconstruction of vein-hosted Au-Sb ore. B) Photograph of vugh-hosted Au-Sb ore within quartz-carbonate vein. C) Microphotograph of intergrown Au-Sb mineralization in quartz vein sample.

Figure 4. A) Photomicrograph of arsenopyrite crystals. Inlay is nanoSIMS elemental RGB map of the area highlighted by the red square. B) Photomicrograph of pyrite crystal. Inlay is nanoSIMS elemental RGB map of the area highlighted by the red square. C&D) Photomicrographs ofarsenopyrite crystals. Inlays are nanoSIMS elemental RGB map of the area highlighted by the red squares.
during early refractory Au mineralization event(s) at 420-

5.5 which is needed for stibnite

significant Au-As mineralization events and are found

wide-spread throughout central Victoria, and the third

event is considered to form ‘pyrite-arsenopyrite-stibnite’

Victoria occurred in three main events, at ca 450-435 Ma,

agrees with the interpretation that Au mineralization in

fluids to precipitate stibnite, and consequently, Au. This

wallrock for the second Au-Sb event.

mineralization, and that the first Au-As event “primed” the

a structural corridor that was able to adopt both styles of

in this way, it is suggested that Fosterville was situated in

crustal distribution and relationship to other gold deposit types. Ore geology reviews, 13(1-5):7-27.

Hagemann, S. G., & Lüders, V. (2003). PTX conditions of


ppb (William-Jones et al. 2009). The deposition of stibnite has been shown to reduce the ore-fluid H2S concentration, thereby destabilizing Au bisulfide complexes in solution, and causing Au-Sb assemblages (Hagemann & Lüders 2003).

These Au-Sb mineralization mechanisms is working in
tandem explain the intimate association of Au-Sb mineralization FGM. Considering that Au-Sb orebodies are within splay faults, shear veins and breccias that cross cut refractory mineralization, and that Sb mineralization is found in fractures, porosity and pressure shadows of wall rock sulfide porphyroblasts (Fig.4), the Au-Sb mineralizing event at FGM post-date refractory ore deposition. This is consistent with the need of wall rock carbonate alteration to buffer the pH of later ore-forming fluids to precipitate stibnite, and consequently, Au. This agrees with the interpretation that Au mineralization in Victoria occurred in three main events, at ca 450-435 Ma, 420-400 Ma, and ca 380-370 Ma (Vandenberg et al. 2000; Bierlein et al. 2001). Where the first two events are significant Au-As mineralization events and are found wide-spread throughout central Victoria, and the third event is considered to form ‘pyrite-arsenopyrite-stibnite’ type assemblages and can be found only in the Melbourne Zone and eastern parts of the Bendigo Zone. In this way, it is suggested that Fosterville was situated in a structural corridor that was able to adopt both styles of mineralization, and that the first Au-As event “primed” the wallrock for the second Au-Sb event.

6 Key points

-FGM is a (unique?) telescopic orogenic Au deposit. Aunferous sulfides are pervasive throughout the deposit, a narrow vertical extent of vein-hosted Au-Sb mineralization exists ~800 m from the surface, and vein-hosted Au-only mineralization at depth.

-Wall rocks at FGM were primed with carbonate alteration during early refractory Au mineralization event(s) at 420-

440 Ma.

-Gold-stibnite mineralization appears to be late (380 Ma) and overprints previous refractory Au events along spalying linkage faults (timing difference of ~40 Ma).

-pH buffering of fluid by altered wallrock via carbonatization is needed for stibnite precipitation.

-Stibnite mineralization active at low temperatures (< 250°C) and can influence Au solubility, driving co-precipitation of Au-Sb ore.

-Stibnite fault breccias, Au-stibnite vugs, and open cavities infer a shallow emplacement. Geochemical modelling and previous fluid inclusion studies agree with a shallow emplacement depth of 1.8 km to 3.6 km, placing FGM as an epizonal orogenic deposit.

-Differing Au mineralization assemblages with depth may be the result of a continuously evolving ore system or the serendipity of two ‘separate’ deposits emplaced in the same locality during different mineralization events.

References


Gold metallotects and mineralization styles of northwestern Abitibi greenstone belt, Canada

Sébastien Castonguay, Benoît Dubé, and Patrick Mercier-Langevin
Geological Survey of Canada

Abstract. The Detour Lake gold mine (~708.7 t Au) and Lower Detour zones (e.g. Zone 58N; ~15.1 t Au) are spatially associated with the Sunday Lake and Lower Detour deformation zones that delineate E-W oriented gold trends in the northwestern part of the Archean Abitibi greenstone belt. Gold is associated with quartz-carbonate±tourmaline veins, stockwork and disseminated to locally semi-massive sulphides in silicified, sericitized, chloritized or biotitized host rocks. These structurally controlled auriferous zones are hosted in tholeiitic and komatiitic sequences of the ca. 2734 to 2724 Ma Deloro assemblage and locally in small alkaline and sub-alkaline porphyritic intrusions and dykes near structural contacts with Porcupine-like turbidite of the ca. 2.70 Ga Caopatina assemblage. Strained Timiskaming-like polygenic conglomerate locally delineates these prospective regional-scale deformation zones. These relationships constitute gold metallotects that are analogous to parts of the southern Abitibi gold belt, such as in Timmins–Porcupine or Val-d’Or gold districts and to other Archean greenstone belts worldwide.

1 Introduction

The principal first-order metallotects of orogenic quartz-carbonate vein gold deposits, such as regional-scale long-lived fault zones, synorogenic polygenic conglomerate, intermediate to felsic, locally alkaline intrusions, tholeiitic and komatiitic basalt, and extensive iron-carbonate alteration have been documented in numerous Precambrian terrains, including the well-studied southern Abitibi greenstone belt (e.g. Robert et al., 2005). These metallotects also occur in the poorly exposed and underexplored northwestern Abitibi belt, most specifically along two regional-scale deformation corridors termed the Sunday Lake and Lower Detour deformation zones (Fig. 1; Ayer et al. 2009; Oliver et al. 2012; Faure 2015). The primary focus is to study the significance of these deformation zones, and their relationship with spatially related gold mineralized zones (Castonguay et al. 2019). Another objective is to compare these mineralized deformation corridors with those of the southern Abitibi, such as the Destor–Porcupine and Larder Lake–Cadillac deformation zones.

2 Geological setting

The northwestern Abitibi greenstone belt comprises the ca. 2734 to 2724 Ma Deloro volcanic assemblage and the younger than ca. 2700 Ma Caopatina turbiditic assemblage that forms an E-trending elongated sedimentary belt, similar to that of the Porcupine/Cadillac in the southern Abitibi (Fig. 1; Ayer et al. 2009). Synvolcanic to syntectonic, gabbroic to granodioritic complexes and plutons surround and intrude the volcanic and sedimentary assemblages.

In the Detour Lake area (Fig. 1), the Deloro assemblage, locally assigned to the Detour Lake Formation (Oliver et al. 2012), comprises ultramafic-dominated flows and intrusives, and mafic-dominated volcanic and volcanoclastic rocks, separated by the ca. 2725 Ma “Chert Marker Horizon” (CMH). The CMH is not a primary chert, but rather a fine-grained felsic to intermediate calc-alkaline volcanioclastic or dyke (Oliver et al. 2012). The Sunday Lake deformation zone (SLDZ; Fig. 1) juxtaposes the Deloro assemblage against the Caopatina assemblage (Ayer et al. 2009). The latter consists of <2697 Ma quartz wacke, argillaceous siltstone and mafic volcanioclastic units, cut by gabbroic rocks (Oliver et al. 2012).

The Lower Detour (e.g. Zone 58N) area lies 7 km south of the SLDZ, and the Caopatina belt in the structural hanging wall of the Lower Detour deformation zone (LDDZ; Fig. 1). The LDDZ juxtaposes the Deloro assemblage against deformed and locally Fe-carbonatized polygenic conglomerate beds along its structural footwall. Altered, sub alkaline to alkaline feldspar porphyritic dykes locally intrude both sequences.

In Quebec, the Deloro-correlative Manthet assemblage consists of massive, pillowed, and locally brecciated tholeiitic basalt, interlayered volcanioclastic and ultramafic volcanic rocks, and locally graphitic argillite (Fig. 1; Lacroix et al. 1990; Faure 2015). A lenticular, fault-bounded basin of polygenic conglomerate (Lac Casault basin; Faure 2015) occur along the SLDZ. The Caopatina-correlative Rivière Turgeon turbiditic assemblage lies to the south of the SLDZ. Southward, the LDDZ juxtaposes mafic volcanic rocks of the ca. 2729 Brouillan volcanic complex (Lacroix et al. 1990) against a band of magnetite banded iron formation and polygenic conglomerate.

Rock units of the study area have been polydeformed and metamorphosed (Oliver et al. 2012). The main regional fabric, S2, is generally steeply dipping and axial-planar to W-trending tight F2 folds. Displacement along the SLDZ is dominated by D2 reverse faulting, overprinted by strike slip motion. Broad SE-trending F3 folds, mostly occurring north of the SLDZ, clearly affect the contact with the Opatica subprovince (Fig. 1). In general, the metamorphic grade increases toward the contact with the Opatica subprovince. In the Detour Lake mine area, amphibolite facies assemblages in
Gold from Orogenesis to Alluvial

3. Sunday Lake ‘gold trend’

The Sunday Lake ‘gold trend’ is informally defined by gold deposits and mineralized zones occurring within the SLDZ and along its second-order structures in a broad (~4 km wide) corridor, including: The Detour Lake gold mine (~708.7 t Au; Detour Gold Corp. 2017), the Vortex zones, and the Martinière–Bug Lake deposits (16.8 t Au; Balmoral Resources 2018; Fig. 1).

3.1 Detour Lake gold mine

Auriferous zones of the Detour Lake gold deposit are hosted in lower amphibolite facies basaltic and altered ultramafic volcanic rocks, both as low-grade disseminated quartz-sulphide zones or as quartz±carbonate veins and silicified high-grade zones (Oliver et al. 2012; Detour Gold Corp. 2017). Ore zones are commonly oriented subparallel to a series of high-strain zones occurring coplanar and in the hanging wall (north) of the steep north-dipping SLDZ.

Previously mined high-grade zones focused on the CMH and included the hanging wall ‘Q-Veins’ and footwall ‘Talc Zone’ (Oliver et al. 2012; Detour Gold Corp. 2017). The mineralization associated with the CMH is hosted in silicified fine-grained intermediate intrusive rocks and silicified-sulphidized volcanic or volcaniclastic layers (Fig. 2a, b).

The Q-Veins are strongly deformed centimetric quartz±carbonate fault-fill veins and pyrrhotite-pyrite-chalcopyrite stringers hosted by biotite-rich mafic volcanic rocks. Gold associated with sulphides also occurs in the Talc Zone within strongly sheared, serpentinized ultramafic rocks adjacent to an intermediate intrusive body. Since 2012, open-pit mining...
has been concentrated in the low-grade (~1 g/t Au) Calcite Zone, which consists of steep W-trending zones comprising boudinaged quartz-calcite-pyrite-pyrrhotite veinlets in biotitized mafic volcanic rocks (Fig. 2c).

3.2 Vortex zones

The Vortex zones (Midland Exploration 2018) are located along an interpreted splay of the SLDZ, at the western tip of the Lac Casault conglomeratic basin (Fig. 1). They comprise several steep north-dipping auriferous high-strain zones in volcaniclastic rocks at the contact between tholeiitic and calc-alkaline volcanic units, and are locally spatially associated with redish, locally alkaline, porphyritic intrusions. The andesitic and lesser rhyolitic volcaniclastic rocks are tentatively correlated with the CMH occurring at the Detour Lake deposit (Faure 2015).

From north to south, there are several mineralized corridors: Zone 475 consists of deformed quartz-carbonate-sulphide veins in sheared mafic blocky tuff, locally with semi-massive pyrite (Fig. 3a). Zone 450 comprises quartz-carbonate-sericite veins and disseminated pyrite associated with a high-strained and brecciated contact zone between mafic volcaniclastic rocks and an albitized-sericitized reddish granodioritic dyke (Fig. 3b, c). Secondary zones 435 and 425 consist of quartz-carbonate veins and disseminated pyrite in strongly deformed, hematitized-sericitized lapilli tuff. In general, disseminated sulphides reach 5 to 7 vol.% in the high-grade zones. Quartz veins are boudinaged and folded, but some locally cut foliation, suggesting an overall early- to syn-deformation timing. The brecciation is late-main phase deformation as it affected a previously foliated rock and is spatially associated with crenulation fabric near mineralized zones (Fig. 3d).

3.3 Martiniere West-Bug Lake deposits

The Martiniere West and Bug Lake deposits (Martiniere property) are hosted in greenschist-grade basalt and intrusive rocks occurring a few km north of the SLDZ (Fig. 1; Balmoral Resources 2018).

The Martiniere West deposit comprises a series of 1 to 2 m thick silicified, carbonatized high-strain zones and breccia with multiple generations of quartz-dolomite-tourmaline veins and 1 to 5 vol.% pyrite-arsenopyrite (Fig. 4a). NE-trending mineralized zones are hosted in moderately foliated, sericitized, leucoxene-bearing quartz gabbro near, and subparallel to, the contact with mafic volcanic and sedimentary units.

The Bug North and Bug South deposits consist of en échelon, moderately to steeply eastward-dipping high-strain zones occurring along contacts of the NNE-trending Bug Lake porphyry dyke (BLP), which lies almost perpendicular to the layering of host rocks. The BLP is a buffy grey fine-grained subalkaline quartz porphyry with 2 vol.% disseminated pyrite. It is mostly massive to weakly foliated, with decametric brecciated margins. Gold is typically associated with fine-grained pyrite and occurs in several discrete altered and silicified high-strain zones in the hanging wall (‘Upper Bug’) and

footwall (‘Lower Bug’) of the BLP. At Bug North, mineralization in the hanging wall is characterized by brecciated silicified zones with pyrite stringer and minor quartz-carbonate veining hosted in sericite-calcrete-chlorite-altered mafic volcanic rocks. Auriferous zones in the footwall occur in silicified-sulphidized leucoxene-bearing quartz gabbro and quartz-dolomite-pyrite veins (Fig. 4b). The Bug South deposit is hosted in sericitized mafic volcanic rocks characterized by more abundant quartz-carbonate veins (Fig. 4c,d). In general, better grades are associated with increased silicification and pyrite content.

4 Lower Detour ‘gold trend’

The Lower Detour gold trend lies 7 km south of the SLDF, across the Caopatina belt (Fig. 1). It comprises gold mineralization spatially associated with the Massicotte
and Lower Detour deformation zones, including zones 58N and 75 (15.1 t Au; Detour Gold Corp. 2017) and several auriferous intersections to the East.

4.1 Zones 58N and 75

The Lower Detour area is underlain by volcanic units of the Deloro assemblage (Ayer et al. 2009). Gold mainly occurs in the steeply south-dipping zones 75 and 58N, in the structural hanging wall of the LDDZ. Zone 75 is hosted in a high-strain zone separating silicified and biotite-sericite altered tholeiitic and komatiitic mafic volcanic units and locally in a feldspar porphyritic intrusive (Fig. 5a). The mineralization comprises sulphide-rich zones reaching locally up to 20 vol.% (Fig. 5b). The much wider Zone 58N consists of discrete laminated quartz-tourmaline-carbonate veins and stockworks, hosted in a swarm of leucocratic feldspar porphyry dykes. The auriferous veins are associated with a dm-wide sericite-silica-biotite alteration zone (Fig. 5c). Sulphides vary between 1 and 5 vol.%, occurring as disseminated coarse pyrite within the veins or their immediate selvages, along with trace amounts of sphalerite and chalcopyrite. Structurally below Zone 58N, the host porphyry is intruded and brecciated by a melanocratic intermediate porphyry (Fig. 5d). The latter phase is mostly barren, except in high-strain zones.

![Figure 5. Lower Detour zones: a) Zone 75: silicified, sulphidized, and biotite-sericite-altered mafic volcanic units and feldspar quartz porphyry (core diameter is 47.6 mm). b) Zone 75: sulphide-rich zone in highly strained and altered mafic volcanic rocks. c) Typical zone 58 N: laminated quartz-tourmaline veins in silica-sericite-altered feldspar porphyry with coarse pyrite along contacts (interval is 35 g/t over 1 m). d) Ore-hosting leucocratic porphyry (IFP1) is brecciated by a melanocratic intermediate porphyry (IFP2).](image)

5 Discussion

The ongoing study on the geological setting of the Detour Lake gold mine and various deposits and prospects along what we informally refer to as the Sunday Lake and Lower Detour gold trends, suggest that gold is distributed along, and structurally controlled by high-strain zones commonly occurring at contacts between mafic and ultramafic volcanic units or with competent intrusive rocks. These mineralized zones occur within regional deformation/fault zones or their subsidiary splays, which are spatially related to a Porcupine/Cadillac-like sedimentary basin and Timiskaming-like polygenetic conglomerate. These deformation zones are also locally intruded by subalkaline to locally alkaline, intermediate to felsic, typically reddish, porphyritic dykes and plutons. Gold is associated with quartz-carbonate-tourmaline veins and/or silicified zones and disseminated to locally semi-massive sulphides in veins and stockwork or as replacement in sericitized, chloritized or biotitized wall rocks. These relationships constitute gold metalloquets that are analogous to various gold camps (e.g. Robert et al, 2005), such as those of the southern Abitibi gold belt.

Acknowledgements

This is a contribution to Natural Resources Canada’s Targeted Geoscience Initiative Program, Gold Project. Detour Gold Corporation, Midland Exploration, Balmoral Resources, Probe Metals, and SOQUEM are sincerely acknowledged for sharing knowledge and data sets.

References


Gold from Orogenesis to Alluvial 771
Au-and U-bearing conglomerates in the Bababudan Group, Dharwar Craton, India

Hartwig E. Frimmel
Bavarian Georesources Centre, Institute of Geography and Geology, University of Würzburg, Germany

Venkatraman S. Hegde
SDM College of Engineering and Technology, India

Wyatt E.L. Minter, Chris Harris
Department of Geological Sciences, University of Cape Town, South Africa

Abstract. Gold-and U-bearing oligomictic quartz pebble conglomerates at the base of the 2.96–2.72 Ga Bababudan Group (lower Dharwar Supergroup) in the western Dharwar Craton in the state of Karnataka, India, bear many sedimentological and petrological similarities to conglomerates in the 2.98–2.79 Ga Witwatersrand Supergroup, which are well known for representing the world’s largest concentration of gold. A sedimentological, geochemical and oxygen isotopic study of these conglomerates with the aim to assess their exploration potential revealed that in spite of the noted similarities there are a number of significant differences with regard to depositional setting and potential gold-concentrating mechanisms. These limit the potential of discovering new gold deposits in the Bababudan Group that are of comparable size to those in the Witwatersrand Basin.

1 Introduction

Conglomerates in the Mesoarchaean Witwatersrand Supergroup in the Kaapvaal Craton, South Africa, host(ed) the largest known concentration of gold in the Earth’s crust and, for decades, constituted the biggest source of gold in the world. The richest ore bodies are, however, mined out by now. In the light of continuously decreasing production by the South African gold mines, the question whether similar deposits can be discovered elsewhere in the world becomes more and more pertinent. Several conglomerate-hosted gold districts are known from almost all continents but, as currently understood, none of them comes close to the Witwatersrand gold province in terms of gold endowment recorded (Frimmel 2014). This might have genetic reasons and/or simply reflect a lack of knowledge of these other deposits. One of these gold districts/provinces is in southwestern India on the Western Dharwar Craton.

Since the early 1960s detrital pyrite-bearing quartz pebble conglomerates at the base of the Bababudan Group, lower Dharwar Supergroup, in the Bababudan Schist Belt (Fig. 1) have been known to contain elevated concentrations of gold and uranium (Rama Rao 1963). Apart from preliminary sedimentological (Srinivasan and Ojakangas 1986) and geochemical/ mineralogical studies (Viswanath et al. 1988), little information is available on the economic potential of these rocks. In the light of the petrological similarity of these conglomerates and the Au- and U-bearing conglomerates in the Witwatersrand Basin, we studied the sedimentology, mineralogy, and geochemistry of the conglomerates and associated quartzites, as well as oxygen isotopic composition of the pebbles and U-Pb age data of detrital zircon. Based on this we draw a comparison between the two provinces in order to better assess the exploration potential of the Bababudan Group.

Figure 1. Geological map showing the main tectonostatigraphic units of the Dharwar Craton in southern India, including the position of the Bababudan Group (modified after Orberger et al. 2012); 1–Bababudan Belt, 2–Western Ghat Belt, 3–Arbail in Shimoga Belt, 4–Chitradurga Belt, 5–Chikkanayakanahalli Belt, 6–Holenarsipur Belt, 7–Sigegudda Belt.

2 Geological setting

Rocks of the Dharwar Supergroup in the Western Dharwar Craton unconformably overlie 3.3 to 3.0 Ga basement. The basement consists of remnants of 3.5 Ga
protocrust onto which Mesoproterozoic schists, iron-formation and tholeiitic as well as komatiitic volcanic rocks of the 3.35-3.2 Ga Sargur Group were deposited. The latter group was intruded by voluminous tonalite-trondhjemite-granodiorite magmas, now present as Peninsular Gneiss Complex, which caused high-grade metamorphism in the Sargur Group between 3.13 and 2.96 Ga. The Dharwar Supergroup rocks were deposited, after a major hiatus, onto the widely penepalined basement between ca. 2.9 and 2.6 Ga. The supergroups divided into the lower Bababudan Group, largely comprising fluvial sedimentary and subaerial volcanic rocks, and the upper Chitradurga Group, a mix of marine clastic and chemical sedimentary as well as subaqueous volcanic rocks (Swami Nath and Ramakrishnan 1981). The rocks, which have experienced low-to-medium-grade metamorphism, are exposed in several schist belts in the Western Dharwar Craton (Fig. 1).

Terabaud Group starts with a conglomerate that is the focus of this study. This is followed by quartzite and a first sequence of predominantly mafic metavolcanic rocks, subordinately also metagabbro, altogether comprising the Kalasapura Formation. The maximum age of the Bababudan Group is given by the youngest age of metamorphism in the unconformably underlying basement, that is, ca. 2960 Ma, and a Sm-Nd whole rock age of 2911 ± 49 Ma for mafic metabasalt in the Kalasapura Formation (Kumar et al. 1996). A lower age limit is given by U-Pb zircon ages of 2720 ± 7 and 2718 ± 6 Ma obtained on tuff beds near the base of the Chitradurga Group (Trendall et al. 1997).

3 Sedimentology and petrography

The basal conglomerate of the Bababudan Group represents channels that were incised into a regolith derived from a gneissic tonalitic bedrock that also contains quartz veins (Peninsular Gneiss Complex). A typical profile displays a multi-channel sequence of pebbly quartz arenite lithofacies representing increments of massive gravel overlying scoured degradation surfaces and interbedded with trough cross-beded sand (Fig. 2). Planar cross-bedding becomes more abundant higher up in the stratigraphy. Measured orientations of the trough cross beds indicate a unimodal palaeocurrent direction between 130° and 170° with a dominance of southeasterly directions. Clast size in the overall oligomictic conglomerate beds and lenses, whose cumulative thickness is 3.20 to 3.75 m (32-34 % of exposed sequence), ranges from small pebble toas much as 15 cm in diameter with generally upwards fining trend. Size distribution is polymodal and sorting is poor. No imbrication is visible. The pebble-sized gravel is moderately-to well-rounded and comprises mainly quartz, ranging in colour from milky white, light blue, brown to grey, and subordinately of chert and quartzite. Clasts of the immediately underlying tonalitic gneiss basement are conspicuously absent. Other locally present detrital phases are microcline, plagioclase, and very little white mica. Detrital heavy minerals comprise sulfides (mainly pyrite, variably weathered to Fe-oxides, rarely chalcopyrite, arsenopyrite, pyrrhotite, and sphalerite), ilmenite, chromite, zircon, garnet, rutile, tourmaline, monazite, xenotime, uranium and gold. The dominantly siliceous matrix consists predominantly of sand-sized quartz and metamorphic white mica, commonly as pale green Cr-bearing fuchsite, rarely biotite, and abundant rutile (up to 6 vol%). Haematite and/or goethite occur as weathering product of pyrite, locally jarosite lines void spaces.

At the bottom of the sequence, the conglomerates are clast-supported, in contrast to single pebble lags and matrix-supported pebbly arenite higher up. Above a stratigraphic height of ca. 10.3 m, a 4.5 m-thick unit of argillite follows, in turn overlain by a sericitic quartzite, representing a quartz wacke.

Although largely oxidised due to lateritic weathering, pyrite is abundant, evident by widespread rusty Fe-staining or pseudomorphs of Fe-oxides after rounded pyrite. In several, less intensely weathered places, fine-grained, less commonly coarse-grained, pyrite concentrations can be observed within conglomerate layers and on winnowed surfaces. Overall four morphological types of pyrite can be distinguished: (i) compact rounded particles defining cross-bedding laminae; (ii) rounded porous, concentrically laminated particles; (iii) euhedral crystals; and (iv) pyrite veinlets. The former two types are interpreted as allogenic, with the compact rounded variety being detrital and the concentrically laminated type probably a product of syn-depositional growth, whereas the latter two are clearly related to post-depositional fluids.

Uraninite occurs as both rounded, muffin-shaped, pitted and fractured grains of most likely detrital nature and irregularly shaped to euhedral, fracture-free grains of post-depositional age. From one locality (Arbail), hydrocarbon granules enclosing uraninite have been reported (Viswanath et al. 1988). These are interpreted as pyrobitumen that formed by polymerization and cross-linking of liquid hydrocarbons around radioactive uraninite.

The exposed sequence is characteristic of braided
channel deposition. A high-energy flow regime is reflected by the large clast size, especially at the base, where cobbles of >10 cm diameter were observed. The subaerial depositional environment was dominated by unimodal fluvial transport in environments ranging from alluvial plains to braid deltas. Transport of sand-sized particles was dominated by trough cross-bedded dunes.

4 Geochemistry

The clast-supported conglomerates have SiO₂ contents exceeding 90 wt% and Al₂O₃ contents below 5 wt%, reflecting the high proportion of quartz. The matrix-supported conglomerates have higher Al₂O₃ (≤18 wt%) and K₂O contents (≤4 wt%), reflecting muscovite (in most places fuchsitic) in the matrix. Calculated CIA (Chemical Index of Alteration) values are between 71 and 99 (the higher values were, however, obtained on very mature conglomerates with low Al₂O₃ and thus are not reliable), on average 80, somewhat lower in the quartzites (on average 74).

Most of the trace elements analyzed for have concentrations significantly below average Archaean continental crust, particularly a strong depletion in Ba, Sr, V, Co, Ni, and Cu is noted. In contrast, the analyzed conglomerates are enriched in Cr (maximum of 1195 ppm, on average 583 ppm), which can be explained by the widespread occurrence of fuchsite or Cr-bearing muscovite. Detrital chromite is extremely rare.

The Th and U concentrations range from not detectable (<1 ppm Th, <0.2 ppm U) to 507 ppm Th and 216 ppm U. The original U contents were most likely higher but suffered from weathering-induced U-loss. In drill core, even higher concentrations were reported by Balakrishnan et al. (1988) who noted Th and U concentrations of as much as 2900 and 450 ppm, respectively, especially in the Western Ghat Belt and the Chitradurga Belt. Thorium and U concentrations in the quartzites are significantly lower and range from 4 to 63 ppm and from 1.4 to 14.4 ppm, respectively.

Gold contents of as much as 1.5 ppm have been mentioned for some of the conglomerates by Viswanath et al. (1988). Gold assays for our samples returned detectable (>1 ppb) concentrations in most conglomerates of all the various belts in which the lowermost Bababudan Group is exposed, with maximum values of 135 to 235 ppb in the Western Ghat Belt. In the quartzite samples, Au contents are below the lower limit of detection, except for those interbedded with conglomerate (3-42 ppb Au).

5 Provenance

A total of 43 quartz pebbles were analysed for their δ¹⁸O values. All of the results are within a very narrow range between 9.92 and 11.83‰ (relative to V-SMOW), with one exception, a pebble from Arbail, which yielded 14.16‰ (Fig. 3). The latter value is typical of hydrothermal vein quartz, whereas all the others are best explained by derivation from granitic, pegmatitic and/or high-grade metamorphic gneiss sources.

The δ¹⁸O values support a sediment derivation mainly from the underlying Peninsular Gneiss Complex, which is also supported by the abundance of detrital zircon. Preliminary U-Pb isotope data on detrital zircon grains revealed most concordant ages between 3087 and 3287 Ma. Archaean greenstone belts (as in the regional Sargur Group) evidently played only a subordinate role, hinted at by the very rare occurrence of detrital chromite. Chromium in the abundant fuchsite was introduced by metamorphic fluids of unknown origin.

6 Comparison with the Witwatersrand

Several reasons speak for the arenaceous basal units of the Bababudan Group being an excellent target for Witwatersrand-type palaeoplacer gold exploration:

(i) The sediments are very mature, mainly quartz arenites and oligomictic conglomerates, analogous to the Witwatersrand;

(ii) The sedimentary rocks are of similar Mesoarchaean age, which has been identified as a critical parameter for the endowment in gold (Frimmel 2018);

(iii) The sedimentary depositional environment was subaerial and dominated by unimodal fluvial transport in alluvial plain to braid delta environments under an oxygen-deficient atmosphere;

(iv) Sediment transport was dominated by trough cross-bedded dunes which are known to concentrate heavy mineral grains by selective entrainment from the sand fraction during the cut-and-fill process of bedform migration;

(v) The mineralogy of the 2.90–2.79 Ga Central Rand Group arenites reflects acidic conditions (lack of feldspar, high CIA between 72 and 95, on average 83), explained by deep chemical weathering of palaeo-surfaces under tropical conditions. The degree of chemical weathering reflected by the lowermost Bababudan Group sedimentary rocks is similar, except for the local presence of detrital feldspars;

(vi) The depository was extensive with a provenance extending from Chitradurga in the east to beyond the present west coast of India, an area encompassing at
least 72,000 km², approximating that of the Witwatersrand;

(vii) Maximum uranium concentrations are similar to those typically found in Witwatersrand deposits and the maximum gold tenor is equivalent to background gold content in pyritic Witwatersrand strata;

(viii) Considering that the extent of Witwatersrand goldfields (individual braid deltas) averages 400 km², considerable scope should exist to find any large targets that might be present in those areas of relatively continuous outcrop.

There are, however, several significant differences to the Witwatersrand deposits, all of which reduce the exploration potential of the Bababudan Group:

(i) the most fertile stratigraphic unit in the Witwatersrand is the Central Rand Group. It has a maximum thickness of ca. 2.8 km with auriferous conglomerates throughout the stratigraphy of the Central Rand Group. Potentially auriferous conglomerates in the Bababudan Group are restricted to the bottom 40 m of this group;

(ii) Sedimentary reworking of older conglomerates within the same group played an important role in upgrading gold content in younger conglomerates higher up in the stratigraphic sequence of the Central Rand Group. The Bababudan Group lacks the high number of intra-group unconformities;

(iii) Pre-concentration of gold by extensive microbial mats is considered a pivotal requirement for the exceptional gold endowment of the Central Rand Group (Frimmel 2014; 2018). Except for the local occurrence of some pyrobitumen, to date no evidence of microbial colonies has been found in the Bababudan rocks;

(iv) In the absence of gold-rich microbial mats as potential source of placer gold, other, geographically more limited point-sources would be required, such as greenstone-hosted gold-quartz veins. With one local exception, the oxygen isotope data speak against the majority of them was derived from granitic and/or pegmatitic sources.

7 Conclusions

Comparison between the conglomerates in the basal Bababudan Group (Dharwar Supergroup) in the western Dharwar Craton and those in the Central Rand Group (Witwatersrand Supergroup) in the Kaapvaal Craton revealed not only striking similarities in sedimentary facies, mineralogy, texture, CIA values, and potential ore components, but also significant differences with regards to setting and possibly age of the depositary, extent of sedimentary reworking along unconformities, and lack of remnants of auriferous and uraniferous microbial mats. All of these parameters are considered important for the overall gold endowment. Thus, we predict that the potential for discovering major goldfields comparable in golden endowment those in the Central Rand Group is low. This notwithstanding, the possibility of finding smaller, yet potentially workable, deposits exists.

Acknowledgements

Parts of this work are based on an exploration initiative by BHP Minerals in the 1990s under the leadership of R Goss. WELM thanks SA Pandit for field guidance and R. Heine for geochemical and petrological analyses. Financial support from the DFG to HEF (grant FR 2183/11-1) and from INSA and DAAD to VSH are gratefully acknowledged.

References


The geological characteristics of metasedimentary rock-hosted orogenic gold deposit in Awak Mas area, Indonesia

Ernowo Harjanto  
Geological Agency of Indonesia

Franz Michael Meyer  
RWTH Aachen University, Germany

Arifudin Idrus  
Gadjah Mada University, Indonesia

Abstract. The Awak Mas gold deposit is hosted by phyllites and schists. Indicated and inferred resources are around 38.4 Mt at 1.41 g/t Au, accounting for a total resource of 1.74 Moz gold. Hydrothermal alteration zones proximal to the gold-bearing veins, are characterized by the mineral assemblage albite-ankerite-pyrite and marked by elevated Na/Al ratios and depleted 3*K/Al ratios. These changes are manifested by the replacement of muscovite by albite, Ankerite and siderite formed simultaneously with albitization proximal to the veins. Distal alteration zones are characterized by chlorite-albite in phyllites, and albite-quartz in schists.

Two types of Au-mineralizing veins are quartz-albite-ankerite veins and quartz-ankerite-siderite veins. Gold occurs in pyrite as sub-microscopic inclusions and as fracture fillings with a gold fineness of 925 to 935 and Au/Ag ratios between 12:1 and 14:1.

The aqueous ore fluid was CO₂-poor and of low salinity with homogenization temperatures between 275 and 325 °C. Fluid inclusion leachates have Br/Cl ratios between 1.0 and 2.0 x 10⁻³ and I/Cl ratios of 5.6 to 18.3 x 10⁻⁵ suggesting that the ore fluids were derived from metamorphic dewatering of organic-rich marine sedimentary rocks. The Awak Mas deposit is an orogenic gold deposit.

1 Introduction

The Awak Mas gold exploration project is located in the Latimojong District, Luwu Regency, South Sulawesi Province, the Republic of Indonesia. Geologically, Awak Mas is situated within the Cretaceous Latimojong Metamorphic Complex (Archibald et al. 1996; Djuri et al. 1998; White et al. 2017). The region is underlain by phyllites, slates, basic to intermediate volcanics, limestones, and schists that represent a platform and/or fore arc trough flysch sequence intruded by granite, diorite, monzonite and/or syenite plugs and stocks (Djuri et al. 1998; White et al. 2017).

A total of 118,081.30 m drill core from more than 1,000 drill holes was collected from drilling activities since 1987 (Querubin and Walters 2012). The Awak Mas mineralized system contains three gold prospects, namely Salu Bulo, Tarra and Awak Mas. It was estimated to contain an indicated and inferred resource of 38.4 Mt at 1.41 g/t Au, which equals a total resource of 1.74 Moz gold (company report, 2017). This study is particularly focused on the Awak Mas prospect.

2 Methodology

Twenty-two polished sections were studied under the microscope as well as 35 polished thin sections to describe the petrography.

Major elements concentration of 32 samples were analyzed using X-Ray Fluorescence (XRF). Trace elements and REE analysis of 38 samples were conducted with Inductivity Coupled Plasma Mass Spectrometer (ICP-MS) and Instrumental Neutron Activation Analysis (INAA) analysis.

Microthermometry of the fluid inclusions from 16 doubly polished thin sections was analyzed enabling fluid compositions and temperature parameters to be calculated. The crush-leach analysis was carried out for 18 quartz vein samples using ion chromatography.

3 Geology of Awak Mas

The lithology of the Awak Mas prospect area is grouped into fault-bounded sequences of Basement, Top Decollement, Eastern Mafic, Western Grit and Cover Sequence (Archibald et al. 1996; Querubin and Walters 2012) (Fig. 1).

The Basement Sequence consists of gneiss, schists, diorites and ultramafic rocks. The Top Decollement Sequence is composed of highly deformed calcareous rocks, separating the Eastern Mafic sequence from the Cover Sequence. The Cover Sequence is the dominant outcropping rock in the Awak Mas area, consisting of meta-sediments and rare grits or conglomerates. The Western Grit Sequence is dominated by polymictic conglomerates with an uncertain relationship with the Cover Sequence. The Awak Mas prospect is transected by 3 major fault zones i.e. the NNE-SSW-trending Chinese Fault, the parallel to sub-parallel Garlic Fault and the sub-vertical Discovery Fault (Archibald et al. 1996; Querubin and Walters 2012).

The discussion on lithologies in this study is focused on the metasedimentary rocks of the Cover Sequence,
which are directly related to the gold mineralization (Fig. 2). Phyllites are characterized by shiny luster, highly cleaved, fine-grained with the dominant compositions of sericite, chlorite, plagioclase, and quartz. The dark phyllites are rich in organic matter, the green phyllites predominantly comprise chlorite and the red phyllites are characterized by the higher iron-oxide content. Schists are consists of an alternating thin layer of mica and quartz with schistosity features which bent into small folds.

Figure 1. Generalized geological map of the Awak Mas prospect area (Archibald et al. 1996 in Querubin and Walters 2012).

The chemical compositions of schists suggest that their parent lithologies were shales and phyllites which, in turn, were derived from Fe-shales to shales (after Herron, 1988). Shale and Fe-shale are metamorphosed to phyllites and schists which are mineralogically composed of muscovite, chlorite, quartz, albite, Fe-oxide, and biotite. Metamorphism is characterized by the replacement of clay minerals by white K-mica and chlorite. Chlorite thermometry (cf. Cathelineau, 1988; Jowett, 1991) indicates the temperature of metamorphism of 297° C to 350° C. Mineralogical compositions and the observed temperature range of the host-rock lithologies point to greenschist-facies metamorphic conditions (Bucher and Grapes, 2011).

4 Hydrothermal alteration

4.1 Phyllites

The hydrothermal alteration of phyllites hosting the gold mineralization is recognized in two distinct zones i.e. a distal albite-chlorite and a proximal albite-ankerite-pyrite alteration zone.

The distal albite-chlorite alteration in the phyllites exhibits a dark greenish grey color, due to the moderate chlorite content. The altered rocks are strongly foliated and cross-cut by thin quartz-calcite veins and veinlets. The mineralogical composition of the albite-chlorite alteration is predominantly albite, followed by chlorite, calcite, muscovite, and quartz. The main secondary minerals formed by hydrothermal alteration in this zone are albite, chlorite, and calcite, which are also present in the least altered phyllites to varying degrees. Chlorite and albite replace the matrix and detrital grains of muscovite along the foliation.

The proximal albite-ankerite-pyrite alteration in the phyllites exhibits a pale grey color, due to the dominant content of albite. The dominant secondary mineral is albite, which almost totally replaces muscovite and chlorite but maintaining the foliation texture. Disseminated pyrite replaces the Fe-bearing minerals (muscovite, chlorite, and ankerite) along the sheared foliation as well as porphyroblasts.

4.2 Schists

In the schist host-rocks, two styles of alteration zones adjacent to the quartz-ankerite-albite vein zone are recognized i.e. distal albite-quartz and proximal albite-ankerite-pyrite alteration zone.

A typical feature of the albite-quartz altered schists is a pervasive silicification and albitization with schistose (lepidoblastic) and mylonitic structures of quartz and crenulation texture of albite replacing muscovite along the sheared foliation. The secondary minerals are quartz, albite and chlorite. The silicification is characterized by 0.01-1 mm large, recrystallized grains of quartz. Chlorite and albite replaced muscovite in the matrix and in detrital grains of muscovite along the sheared foliation.

The albite-ankerite-pyrite altered schists show a pale brown color, due to the dominant presence of albite. This alteration zone is cross-cut by quartz-ankerite-albite veins which are both concordant and discordant to the foliation. Disseminated pyrite replaces the iron-bearing minerals along the foliation as well as porphyroblasts. The dominant secondary mineral albite also almost totally replaces muscovite and chlorite along foliation.

5 Gold mineralization

5.1 Mineralized quartz veins

Three styles of auriferous veins associated with gold mineralization are observed in Awak Mas including quartz-ankerite-albite veins, quartz-ankerite-albite
breccia, and quartz-ankerite±siderite veins and veinlets (Fig. 3).

The quartz-ankerite-albite veins cross cut the altered phyllite and schist wall-rocks in concordant (Fig. 7A) and discordant direction to the foliation (Fig. 7B). The veins vary in thickness between 0.5 and 20 cm. The hydrothermal breccia zone displays various widths ranging from 10 cm to 3 m. This zone typically consists of disintegrate altered wall-rocks in a hydrothermal matrix composed of quartz-ankerite-albite. Wall-rock breccia clasts (up to 3 cm across) are angular and variably rotated (Fig. 7C). Pyrite occurs in the altered phyllite and/or schist fragments. Rutile and apatite are also present as accessory phases within the quartz-ankerite-albite matrix.

The quartz-ankerite±siderite veins and veinlets are only a few mm to 1 cm thick and cross cut the altered wall-rocks (Fig. 7D).

5.2 Ore mineralogy

Ore mineralogy and ore paragenesis studies show that the mineral assemblages are identical in the albite-ankerite-pyrite alteration zone both of phyllite and schist wall-rocks. Two textural styles of sulfides are observed including (1) sulfides filling fractures in association with ankerite veinlets, and (2) disseminated sulfide in the albite matrix of altered wall-rocks. The distribution of sulfides in the altered schist wall-rocks is disseminated following the relicts of foliation. The sulfide mineral assemblage consists of pyrite, galena, chalcopyrite, as well as rare native gold.

Pyrite is the most abundant sulfide, present in fine grains with up to 1 mm in size, which tend to form scattered euhedral crystals both in phyllite, and schist altered wall-rocks. Inclusions of very fine-grained galena, chalcopyrite, and rutile are common within pyrite, and monazite is also rarely observed.

Gold grains are frequently observed in the mineralized albite-ankerite-pyrite alteration zone in the schist.

Fracture filling gold grains occurs within pyrite. Representative electron microprobe analyses yield gold contents of 89.9 to 92.3 wt. % Au and 6.2 to 7.5 wt. % Ag. The gold fineness is similar to that from other orogenic gold deposits, which have a typical gold fineness and bulk Au/Ag ratio of more than 900 and 5:1, respectively (Groves et al. 2003; Morrison et al. 1991). The assemblage of alteration minerals, the disseminated distribution of sulfide minerals, and gold fineness show typical characteristics of orogenic gold deposits (Groves et al. 1998; 2003; Morrison et al. 1991) formed under upper greenschist to lower-amphibolite facies conditions (Eilu et al. 1999).

6 Hydrothermal fluid characteristics

The character of hydrothermal ore fluids is recorded by the fluid inclusions from mineralized quartz-ankerite-albite veins. The mineralizing fluid has the dominant homogenization temperatures range from 275 to 325 °C. The mineralizing fluids are characterized by low salinity, predominately aqueous, minor CO2 and N2 solutions. The presence of low salinity aqueous fluids is commonly found in metamorphic terrains (Yardley and Graham 2002).

Fluid inclusions in samples from mineralized veins have Br/Cl ratios ranging from 1.0 to 2.0 x 10⁻³ and I/Cl values that vary from 5.6 to 18.3 x 10⁻⁵. I/Cl ratios of all samples are much higher than those of seawater and MORB. The distribution of halogen is mainly similar to sedimentary marine pore fluids with a number of samples overlap with magmatic fluids.

The high I/Cl ratio in the fluid inclusions of Awak Mas indicates a crustal fluid source from sediments, possibly enriched in organic material, and the absence of any evaporate-derived fluid. However, a number of mineralized vein samples are close to those of magmatic/mantle related fluid source.

The halogen composition indicates that the mineralizing fluids formed from mixture of metamorphic dewatering of original marine sediments with magmatic fluids derived from granitic crustal melts.

7 Conclusion

The phyllite and schist host-rocks to the gold mineralization at the Awak Mas are members of the Cover Sequence of the Cretaceous Latimojong Metamorphic Complex.

The distal alteration zones of phyllites and schists are characterized by secondary mineral assemblages of albite-chlorite and albite-quartz, respectively. The proximal alteration zones of both host-rocks are similar in terms of petrographic and geochemical compositions, which are characterized by replacement of muscovite by albite and chlorite by ankerite and pyrite. The enrichment of Na due to albitionization and the depletion of K is the key geochemical guide to ore zones.

The gold mineralization is associated with the occurrence of pyrite, which is distributed within the albite-ankerite-pyrite alteration halo (up to ~75 m width) in the
Gold from Orogenesis to Alluvial  779

phyllite and schist host-rocks. Pyrite also occurs filling fractures together within ankerite veins and veinlets. Gold healing fractures in pyrite are characterized by very high fineness (925 to 935) and Au/Ag ratios (12:1 to 14:1) which are typical of the orogenic gold type.

The mineralizing hydrothermal fluid is preserved as low salinity aqueous and CO₂-poor fluid inclusions with homogenization temperatures ranging from 275 to 325 °C. Halogen composition in fluid inclusions from mineralized veins indicates that the mineralizing fluid was derived from metamorphic devolatilization of organic-rich sedimentary rocks. However, magmatic-sourced fluids are found in fluid inclusions from non-mineralized veins.

The gold was transported as a reduced sulfur complex and deposited by the interaction of the weakly alkaline fluid (Na-rich) with Fe-rich wall-rocks under greenschist facies conditions. The fluid composition as indicated by halogen, as well as the temperature of entrapment and mineralization controlled by brittle deformation, suggest the gold deposit develop in transition between epizone and mesozone of an orogenic-gold type.

Acknowledgments

This research was supported by the Ministry of Energy and Mineral Resources, Republic Indonesia and fully facilitated by the Institute of Applied Mineralogy and Economic Geology, Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen University. Many thanks also to the management of Masminido Dwi Area Company for their permission to use their data and samples for this study. I also would like to thank Professor Walter Prochaska for allowing me to use his crush-leach analysis facility at the University of Leoben, Austria.

References


Gold in Irish coal: Palaeo-concentration from metalliferous groundwaters

Liam A. Bullock
*University of Southampton, UK*

John Parnell, Joseph G.T. Armstrong
*University of Aberdeen, UK*

Sam Spinks
*CSIRO Mineral Resources*

Erico M. M. Flores, Paola A. Mello
*Universidade Federal de Santa Maria*

Filipe S. Rondan, Marcia F. Mesko
*Universidade Federal de Pelotas*

Abstract. Gold grains, up to 10 microns in size and containing variable percentages of admixed platinum, have been identified in coals from Castlecomer, SE Ireland. Gold mineralization occurs in sideritic nodules in coals in association with pyrite and anomalous selenium content. Pyrite in the cores of nodules indicates fluid ingress. Mineralization here may have reflected very high heat flow in foreland basins north of the emerging Variscan orogenic front, responsible for gold occurrence in the South Wales Coalfield. At Castlecomer, gold-platinum is attributed to a mixture of fine-grained detrital matter and precipitation from groundwaters. The underlying Caledonian basement bedrock is mineralized by gold, and thus may provide a source for gold. The combination of the gold occurrences in coal in Castlecomer and in South Wales, proximal to the Variscan orogenic front, suggests that these coals along the front could comprise an exploration target for low-temperature concentrations of precious metals.

1 Introduction

Much of the world’s resources of gold and other precious metals occur in magmatic and metamorphic ‘basement’ rocks. The gold deposits may be located following detection of anomalies in stream sediment and water samples, especially in terrains where bedrock exposures can be very limited (Coker and Shilts 1991). However, the mobility of gold indicated by the water-borne anomalies implies that the gold is also susceptible to concentration in sedimentary geochemical or hydrodynamic traps, such as in coal-forming settings.

Coal-hosted gold mining first took place over a century ago in the USA (Jenney 1903), with a renewed interest in coals and associated derivatives taking place in recent years (Sorokin et al. 2009; Wang et al. 2010; Seredin and Dai 2014). There are numerous records of gold mineralization within coal (e.g. Chyi 1982; Arbuzov et al. 2006). These include enrichments of gold above upper crustal averages (1.5 ppb; Rudnick and Gao 2004), and discrete occurrences of gold-bearing minerals. Anomalous concentrations of gold in coal have a potential significance because large quantities of coal are converted to ash in power stations, and thereby concentrates of trace elements become available as a by-product (Seredin et al. 2013; Sahoo et al. 2016). This processing could yield economically viable gold (Seredin and Dai 2014; Wang et al. 2015).

In Britain, the discovery of gold in anthracitic coal in South Wales (Gayer and Rickard 1994), often spatially associated with sulfide and selenide minerals, was accompanied by widespread speculation about coal as a source of precious metals. More recently, speculation has been renewed by claims of new technology for the extraction of gold from coal in Russia (Rozhdestvina et al. 2011). Since 2016, interest in gold and platinum occurrences in SE Ireland has been rejuvenated thanks to their discovery in stream sediments by the Geological Survey of Ireland’s Tellus Programme.

In this study, microscopic observations and mineral associations (e.g. spatial and chemical relationships with pyrite and selenium) have been used to demonstrate the first known occurrence of platinum-rich gold particulates within Carboniferous coals at Castlecomer, SE Ireland (Fig. 1). We show that precious metal deposits in the Caledonian basement of SE Ireland are represented in mineralization of coal in the cover succession. Anomalous concentrations of gold and platinum in modern stream samples imply similar mineralizing groundwaters during the Carboniferous when the basement had been exhumed. This occurrence adds weight to nascent models for extracting precious metals as a by-product of coal ash. These observations also offer new prospects for exploration in SE Ireland, in coal-bearing strata and coal-hosted nodular mineralized zones.

2 Geological setting

An anthracitic (high rank) belt of coal extends from the South Wales Coalfield, Britain, to the Leinster Coalfield, Ireland, adjacent to the Variscan orogenic front (Fig. 2). These Upper Carboniferous coal deposits have a greater thermal maturity than other coal in Britain and Ireland.
Gold from Orogenesis to Alluvial (Clayton et al. 1989; Bevins et al. 1996). Samples from the Leinster Coalfield represent coals of the Westphalian and Namurian, deposited as basin sediments (Nevill 1956; Higgs and O’Connor 2005). The Leinster Coalfield is the largest onshore coalfield in Southern Ireland, located in NW Co. Carlow, NE Co. Kilkenny and SE Co. Laois. The Coal Measures of the Castlecomer Plateau (Leinster Coalfield) formed from plant material in a swamp environment atop a massive delta. The No. 2 horizon is the most economically important seam of the coalfield, historically worked in Castlecomer (Higgs and O’Connor 2005).

To the authors knowledge, no gold has been reported in these Irish coal deposits. Gold was recorded in South Wales coals, accompanied by selenide minerals, on fracture surfaces of anthracite (Gayer and Rickard 1994). The gold-selenium (Au-Se) mineralization is described as a localized expression of more widespread sulfide-rich mineralization in South Wales coal containing siderite nodules (Bevins and Mason 2010). The Westphalian section in the vicinity of Castlecomer is both pyritic and contains abundant siderite nodules (Nevill 1956). Therefore, we investigated the sideritic coal of Castlecomer for evidence of mineralization comparable to that in South Wales. Coal mining in Castlecomer has ceased, but coal detritus including sideritic nodules can be sampled from the River Dinin (Irish Grid Reference S 545730).

**3 Results**

Electron microscope studies of rough and polished surfaces of the sideritic coal showed that it is extensively mineralized by replacive pyrite (Fig. 3), and also by barite, xenotime, iron oxides and clay minerals. XRD of Castlecomer coal also reveals the presence of quartz, kaolinite and illite. Pyrite occurs particularly in siderite nodules, where it is part of the crack-fill septarian mineral assemblage. Gold occurs in both pyrite and the siderite matrix, up to 10 microns in size (Fig. 3).

Quantitative analyses of the gold show that it contains variable percentages (5.3-18.6%, mean 10.5%) of admixed platinum. No silver was detected, which thus cannot exceed 0.2%. The gold contains traces of copper (up to 0.3%). Measurements were made to test rigorously the genuine attribution of the gold to the Castlecomer samples, including:

(i) Gold was recorded in three distinct samples.
(ii) Gold was recorded on both polished and unpolished surfaces.
(iii) The composition of the gold is distinct from that of gold sputter coating used in the laboratory.
(iv) No other gold-bearing material was prepared at the same time.
(v) The context of trace element sulfur (S) in the gold is variable, suggesting that it is a natural precipitate rather than a man-made artefact.

Bulk ICP-MS analysis of the sideritic coal shows that it contains a mean Se content of 14.3 g/t (n=5, maximum value of 25.8 g/t; measured by CRC-ICP-MS; Henn et al. 2018). The mean Se content of British coal is 2.1 g/t (Bullock et al. 2018). Heavily pyritic siderite nodules contain up to 29.5% S (0.7% in the coal matrix).

4 Discussion

4.1 Conditions of mineralization

The mineralization at Castlecomer, as in several parts of the South Wales Coalfield, occurs in sideritic nodules in the coal. The development of sideritic nodules is a feature of diagenesis at depths down to a few hundred metres burial (Young 1993), in a non-marine environment where iron is deposited as the carbonate. Subsequent mineralization by pyrite occurs replacively and in septarian crack fills. Siderite nodules in coals and organic-rich shales elsewhere are consistently mineralized at their cores by pyrite, base metal sulfides, barite and petroleum (e.g. Alderton and Bevins 1996). These mineral occurrences indicate the ingress of fluid during burial, despite the low permeability of the nodules and their host rocks. Pyrite in the cores of the Castlecomer nodules indicates such fluid ingress, to which the Se enrichment can be attributed. Data from South Wales suggests that mineralization commenced at relatively low temperatures (<100⁰C) (Alderton et al. 2004), but at temperatures high enough (>60⁰C) to explain the incorporation of migrated hydrocarbons within cracks (Firth and Eglinton 1972).

Mineralization of these basins, rather than other coal basins in Britain and Ireland, may have reflected very high heat flow in foreland basins north of the emerging
Variscan orogenic front. In South Wales, the geothermal gradient was calculated to be 45°C km⁻¹ (Alderton et al. 2004). Northward-directed flow away from the orogen controlled the formation of high rank anthracite, and the distribution of mineralization (Gayer et al. 1998). The coal at Castlecomer is anthracitic as in the mineralized section of the South Wales Coalfield, and therefore had similar potential for mineralization.

Figure 3. SEM backscatter images of gold particulates in (a) pyrite and (b) siderite matrix (in close proximity to pyrite).

4.2 Gold and platinum source

Gold and platinum are both mobile in surface environments, especially in acidic groundwaters, and their enrichment in peat (Dissanayake and Kritsotakis 1984) are analogous to their concentration in coal. Gold in coal is attributed to a mixture of detrital matter and precipitation from groundwaters, and thus most likely to be found where gold ores occur in the bedrock source regions for the groundwaters. The same scenario could be envisioned for any platinum. Therefore, the occurrence of gold-platinum mineralization in coal in a region where stream sediment sampling has identified these elements in anomalous concentrations suggests that groundwaters were the source. Thus, the knowledge that the gold-mineralized Leinster Massif region had been exhumed in advance of coal deposition makes such a provenance likely. The lack of silver in the coal-hosted gold, while the nearby bedrock gold consistently contains silver, is indicative of authigenic gold precipitation from groundwaters rather than detrital gold (Santosh and Omana 1991), and is also compatible with gold precipitated from oxidizing chloride systems at redox fronts (Leake et al. 1991).

The Lower Palaeozoic rocks of SE Ireland are a known source of gold (O’Connor and Gallagher 1994), and related placer gold was the cause of a celebrated gold rush in 1795 (Alborn 2011). To the south-west, the Devono-Carboniferous Munster Basin also contains showings of gold in hydrothermal veins (Spinks et al. 2016), the source of which is not clear but indicates a protolith somewhere in the region. Provenance studies in the Devono-Carboniferous rocks of England and Ireland indicate that the Irish Caledonides were exposed and eroded into the sedimentary succession (Morton et al. 2015). Notably, the Devonian deposits of SW Ireland contain clasts of tourmalinite (Todd 2000), associated with gold mineralization in the Leinster Massif (McArdle et al. 1989). There was, therefore, gold in the surface environment at that time. Platinum is also found in stream sediments (see below).

The source for the gold in South Wales could also be in SE Ireland (no available data for platinum group elements) and in Pembroke (SW Wales), but palaeocurrent data for the South Wales Coalfield allows possible derivation from regions spanning Nova Scotia, Ireland, Wales and France (Diskin et al. 2011), all of which had been recently mineralized by gold (Romer and Kroner 2018). There was, therefore, a good chance of gold availability to coal-forming environments along the Variscan orogenic front. The occurrence reported here contributes to growing evidence for the mobility of gold in the sedimentary environment (e.g. Youngson and Craw 1996). A high proportion of gold in the northern hemisphere is in basement rocks (Caledonian basement and older), or in placer derivatives. Most of the coal is of Carboniferous-Permian age (Cleal and Thomas 2005), and the provenance of Carboniferous rocks is dominated by the basement (Morton et al. 2015). Thus, there is potential for concentrations of precious metals within coal and coal ash.

The purity of the coal-hosted gold is high, and contrasts with much epigenetic gold which contains a greater proportion of alloyed silver and other trace elements. Analyses of gold in the bedrock of SE Ireland show silver contents often in the range 5-10% (Chapman et al. 2006), over an order of magnitude more than in the coal-bearing gold. Such high purity is a feature of gold precipitated from oxidizing solutions at redox interfaces within sedimentary systems, in which precious metals remobilized by the dissolution of older high-temperature deposits become fractionated during re-precipitation. The precipitation of gold in sedimentary rocks is commonly redox-controlled, and occurs as a trace component of pyrite, among other minerals. The focus of pyrite precipitation in siderite nodules has made them a focus for gold precipitation.

Gold with platinum is a rare alloy in nature, but in this case reflects the elements available in the groundwaters. Although rare, platinum enrichments are recorded in coal where a source is available (Chyi 1982). As in the case of gold, the rocks of SE Ireland are anomalously rich in platinum, evidenced by stream sediment surveys, provisionally identified in placer sands worked during the gold rush (Mallet 1850), but this observation has not been replicated in modern studies (Moles and Chapman 2019). Tellus data for the 90th percentile of stream sediment compositions shows a Au/ Pt ratio of ~8, comparable to the ratio measured in the coal-hosted gold.
Acknowledgements

The project was supported by the NERC Security of Supply programme (grant NE/L001764/1).

References


Gold growth under low temperature conditions: a case study from the Amani Placer gold deposit, Tanzania

Stephan C. Dunn, Bjorn P. von der Heyden, Abraham Rozendaal
University of Stellenbosch, South Africa

Rikard Taljaard
Walkabout Resources Ltd

Abstract. The Amani Placer Gold Deposit (APGD) is located within a braided river valley in southwestern Tanzania. Gold nuggets from this deposit have anomalously fine macroscopic textural features with significant Ag-depletion in the nugget rims, making them ideal for studying the controls on low-temperature gold cycling. Geochemical investigation of the river channel revealed a strong redox gradient down-profile. This redox gradient together with observed oximorphic mottling textures in sediments and slumped river terraces, suggest redox conditions fluctuate as a function of seasonality and episodic fluvial incision events. These fluctuating physico-chemical conditions alter the stability of ambient gold bearing complexes (e.g. Au(S₂O₃)²⁻ and Au(HS)₂⁻), resulting in the precipitation of nanophase gold particles on clay minerals, organic matter and pre-existing gold nugget surfaces. This low-temperature diagenetic geochemical process promotes the formation of supergene-enriched gold nuggets with characteristic Ag-depleted rims (<6 wt.%) and delicate morphological textures.

1 Introduction

A growing body of scientific literature is highlighting that gold actively cycles in low temperature environments (Reith et al. 2006, 2007, 2013; Southam et al. 2009; Fairbrother et al. 2012; Shuster and Southam 2015; Craw et al. 2017; Kerr et al. 2017; Shuster and Reith 2018). Gold nuggets in placer deposits are classified into two groups based on their chemistry: hypogene gold occurring as coarse-grained Ag-rich alloys (5-50 wt% Ag) and supergene gold occurring as Ag-depleted overgrowth rims with Au concentrations approaching 100 wt% (Freyssinet et al. 1989; Groen et al. 1990; Hough et al. 2007; Rosell et al. 2018). Ag-depletion in nuggets have been linked to self-electrorefining processes (Groen et al. 1990) and deformation induced recrystallization during mechanical transportation in fluvial environments (Stewart et al. 2017).

Despite recent advancements in our understanding of the biogeochemical behavior of gold in placer environments (Shuster and Reith 2018), the effects of short-term post-depositional alteration on supergene gold mineralization, remain equivocal. These short-term changes are most pronounced in recent placer deposits, thus such deposits become useful for studying the effects of early diagenetic alteration and geomorphological changes on ambient gold growth. An example of a recent placer deposit is the APGD in Tanzania, where alluvial gold is mined from a ~3 m thick conglomerate horizon at the base of a ~27 m thick sediment column. Gold in this deposit occur as angular and irregular nuggets, often with multiple small bulbous protrusions extending from a longer central framework (Fig. 1). Here we present geochemical and morphological information related to early placer diagenesis associated with shallow burial and interaction with groundwater having fluctuating physico-chemistry. Our results highlight the importance of early diagenesis and seasonality in the evolution of placer gold deposits.

2 General setting

The APGD is located within the Upangwa terrane of the Paleoproterozoic Ubendian Belt. Geographically, this deposit is located within the Njombe Region, 50 km east of Lake Malawi and 125 km south from the town of Njombe. The region has a hot tropical climate and is drained by the Amani River and several ephemeral streams.

3 Gold nugget morphology and chemistry

Gold nuggets found in this deposit range in size from 0.2-17.5 cm. Apart from their angularity, the gold nuggets exhibit extensive pitting and entrapped detrital quartz grains. Authigenic clay minerals are also often encapsulated within concavities and have been overgrown by thin slivers (~10-30 µm) of Ag-depleted gold rims.

Using high-resolution scanning electron microscopy (SEM) imagery, several microscopic features were revealed that are indicative of secondary gold growth (Fig. 2). Original hypogene gold nugget surfaces exhibit stacked and intergrown microcrystalline plates, creating...
Gold from Orogenesis to Alluvial

Surface features (modified after Dunn et al. 2019). (a-c) Striated gold nugget surface with stacked and intergrown microcrystalline plates, covered with abundant supergene spheroidal gold nanoparticles (b-c). (d) Vermiform gold overgrowth on a nugget surface. (e) Spheroidal gold nanoparticles embedded within a mixture of clay minerals and residual organic matter on the surface of a gold nugget.

Polished gold nuggets reveal two distinct zones in cross-section with markedly different Au-Ag ratios. These zones reflect primary hypogene gold and supergene gold overgrowths. The hypogene gold occurs in the core of the nugget and has Ag concentrations between 11-15 wt.%. The supergene gold rims encapsulate the hypogene core and have Ag concentrations of <6 wt.% (Fig. 3).

Figure 3. (a) BSE SEM micrograph of a gold nugget in cross-section (modified after Dunn et al. 2019). Higher Au content of the supergene rim results in a brighter appearance relative to the hypogene core. Red dotted line separates core from rim, with a drastic change in Ag content across this line. (b) Transect of Ag concentration along line X-X’.

4 Physico-chemical conditions of the Amani River sediment column

Six unique lithofacies were identified in the Amani River channel, with the main orebody occurring in the basal conglomeratic horizon. This channel experienced a fluvial incision phase, inferred from the presence of peripheral fluvial terraces and the current river being stratigraphically lower than the upper contact of the most recently deposited lithofacies. This fluvial incision phase was an important geomorphic event regarding secondary gold mineralization, since it lowers the water table (Neal 2009) and exposes stratigraphically lower lithofacies to more oxidizing conditions.

Using dissolved elements present in the pore water of the various lithofacies and bulk soil X-Ray Fluorescence (XRF) geochemical data, redox conditions were established down profile of the sediment column. The sediment column has a moderate acidity (pH levels between 4.5 and 6). This moderate acidity is partially due to the oxidation of sulphide minerals (pyrite and arsenopyrite) associated with gold-bearing clasts derived from mass wasting of the primary ore. Conditions become increasingly reducing with depth, however during the dry season the reducing front is significantly lowered as the
The sediment column becomes less inundated with water and oxidizing conditions prevail at greater depths. This is evident from remnant oximorphic sediment textures (mottles of reddish brown ferrihydrite and yellow brown goethite) preserved throughout the sediment column, indicating a shift from reducing to oxidizing conditions due to fluctuating water table levels (Vepraskas 2001; Hall et al. 2016; Pajohannia et al. 2017).

The average dissolved gold concentration in the auriferous conglomeratic horizon is 0.155 µg/L, roughly 22 times greater than the average background concentration (0.007 µg/L) for the sediment column. In comparison, dissolved sulphur concentrations range between 0.17-5.10 mg/L, which is in range of the geochemical parameters required to describe the speciation of Au-S-H2O as a function of pH and redox state (Fig. 4).

5 Discussion

5.1 Gold cycling in fluctuating chemical environments

Dissolved gold mobility in fluvial systems are attributed to complexation with various ligands (Boyle 1979; Mann 1984; Webster 1986; Vlassopoulos et al. 1990; Hough et al. 2007). Recent work by Craw and Lilly (2016) highlighted the role that thiosulphate ligands play in the short-range mobilisation of gold in supergene environments. Thiosulphate forms a stable Au complex under moderately oxidizing to reducing conditions and mildly acidic to highly alkaline pH (Fig. 4). It is therefore expected to be a dominant Au-complexing ligand in the APGD sediment profile. Destabilization of Au(S2O3)2³⁻ can occur via: (1) reductive biomineralization of gold (Lengke and Southam 2005; Reith et al. 2007; Shuster et al. 2017); (2) exposure to more reducing environments (Shuster et al. 2017) and/or decreases in pH. Eventual destabilization of Au(S2O3)2³⁻ will cause gold to be reduced to its elemental form, resulting in the precipitation of gold nanoparticles on pre-existing gold nugget surfaces, clay minerals and organic matter (Fig. 2b-e).

During the wet season, the redox boundary is expected to shift to higher stratigraphic levels, thereby resulting in the destabilisation of ambient Au(S2O3)2³⁻ complexes. Under these conditions, any gold still solubilized will occur as Au(HS)²⁻, which is stable under reducing conditions and likely the main gold-bearing complex below the water table (Heinrich 2015; Craw and Lilly 2016). Au(HS)²⁻ can be destabilized by minor changes in pH and redox state (Fig. 4) but is likely to remain metastable throughout the wet season. During the dry season, a reverse shift in the redox front will occur and conditions will become more oxidising. This will result in the destabilization of Au(HS)²⁻, leading to additional precipitation of secondary gold. Conditions in the sediment column will now favour the stability of Au(S2O3)2³⁻, and these complexes are expected to persist throughout the dry season. Episodic fluvial incision events will similarly result in shifts in the chemical space experienced by the APGD sediment profile, likely resulting in discrete secondary gold forming events.

5.2 Effects of gold cycling on gold nuggets

Gold nuggets collected from the APGD document the effects of gold cycling under ambient conditions. Active gold cycling is evidenced by the presence of abundant secondary gold nanoparticles (Fig. 2b, c, e), vermiform gold overgrowths (Fig. 2d) and Ag-depleted supergene rims forming on gold nuggets (Fig. 3a). These features confirm that active gold dissolution and re-precipitation occurs within the APGD, enabling the growth of gold under low temperature conditions.

6 Conclusion

Due to the moderately acidic and fluctuating redox nature of the APGD, gold-bearing complexes such as Au(HS)²⁻ and Au(S2O3)2³⁻ will largely be responsible for gold mobility. Fluvial incision events will lower the water table, allowing oxidation fronts to shift to greater depths. This together with seasonal fluctuating redox conditions allows for the solubilization and destabilization of gold-bearing complexes due to slight changes in pH and redox conditions. Destabilization of Au(HS)²⁻ under more
oxidizing conditions and $\text{Au(S}_2\text{O}_3\text{)}_{2}^{3-}$ under more reducing conditions will lead to nanophase gold precipitation on pre-existing gold nuggets, organic and clay particles. This study highlights the influence of geomorphology and seasonality on redox conditions and the importance this has on secondary gold mineralization within a placer environment.

Acknowledgements

This work was supported by the National Research Foundation (NRF Grant number 106006). BvdH acknowledges NRF-DST CIMERA for additional support. The Central Analytical Facilities (CAF) Stellenbosch is thanked for assistance with all the analytical work performed in this study.

References


Boyle RW (1979) The geochemistry of gold and its deposits. Geol Surv Canada Bull 280:583


Mann AW (1984) Mobility of gold and silver in lateritic weathering profiles; some observations from Western Australia. Econ Geol 79:38–49. doi: 10.2113/gsecongeo.79.1.38


Gold from Orogenesis to Alluvial 787
Formation mechanisms of quartz veins in orogenic gold deposits: insights from Grass valley, California, USA

Ryan D Taylor  

Thomas Monecke  
Center for Mineral Resources Science, Department of Geology and Geological Engineering, Colorado School of Mines, U.S.A.

T. James Reynolds  
FLUID INC., Colorado, U.S.A.

Abstract. The orogenic gold veins of Grass Valley, California, USA, compose the historically richest lode gold district in the North American Cordillera. Petrographically, the veins exhibit a range of primary textural relationships allowing the reconstruction of the paragenetic sequence of mineral formation. Two generations of quartz are distinguished by optical cathodoluminescence microscopy and fluid inclusion petrography. Early quartz formed under conditions of variable pressures, ranging from supralithostatic to sublithostatic, whereas late quartz formed entirely at hydrostatic conditions. Subsequent sulfide formation occurred from fluids increasingly buffered by the host rocks. Late growth zones in pyrite are enriched with elements derived from the local host rock and contain abundant gold inclusions. Gold was never observed encapsulated by the quartz, rather it resides along grain boundaries and fractures in the quartz. The results of this study underscore the importance of pressure fluctuations during quartz vein formation but suggest that the bulk of the gold in these orogenic systems was introduced late in the paragenesis when fluid flow occurred at hydrostatic conditions.

1 Introduction

Orogenic gold deposits are formed in metamorphic terranes as a result of the dehydration of crustal rocks undergoing prograde metamorphism. These metamorphic fluids are focused along crustal-scale faults, ultimately forming quartz vein systems in these and related higher order faults. The textures of the orogenic veins record deformation during their formation in the active fault systems, as well as post-mineralization deformation associated with the subsequent evolution of the causative orogen. The minerals that compose the veins are variably susceptible to grain-scale deformation. Characteristic deformational textures of quartz include undulose extinction, deformation lamellae, bulging recrystallization, subgrain rotation recrystallization, and grain boundary migration. Deformation and recrystallization of other abundant vein minerals such as carbonate and sulfides result in the development of distorted cleavages, granoblastic polygonal grain boundaries, and brecciation textures. Recrystallization typically results in a destruction of chemical growth zoning. Interpretation of the paragenetic evolution of these deposits is obscured by these mineral-specific effects of deformation and recrystallization.

This study reports on the occurrence of primary textures in the gold-bearing quartz veins from the Grass Valley district in California (Fig. 1). District-wide gold mineralization occurred in the Middle to Late Jurassic (Snow et al. 2008; Taylor et al. 2015) at mesozonal depths. Based on a combination of optical petrography, optical cathodoluminescence microscopy, fluid inclusion petrography, scanning electron microscopy, and in situ mineral geochemical studies, it could be shown that primary paragenetic relationships can be reconstructed at Grass Valley. The study of these relationships provides new insights into vein formation and the relative timing of gold introduction in orogenic gold deposits.

Figure 1. Geologic map of northern California with the location of Grass Valley (modified from Ernst et al. 2008).
2 Geology

The Grass Valley gold district is located in the Sierra Nevada foothills province of California (Fig. 1). The Sierra Nevada foothills represent a late Paleozoic through Late Jurassic accretionary belt composed of multiple autochthonous and allochthonous terranes that assembled along the North American continental margin and are separated by crustal-scale, terrane-bounding faults (Sharp 1988; Dickinson 2008; Ernst et al. 2008). The Grass Valley district is located within a Jura-Triassic arc belt composed of a late Paleozoic ophiolitic basement overlain by Late Triassic-Early Jurassic arc rocks (Snow and Scherer 2006). Prograde metamorphism of these rocks occurred between approximately 200 and 160 Ma, with peak metamorphism constrained to approximately 170-160 Ma (Bickford and Day 1988; Taylor et al. 2015). The steeply east-dipping Wolf Creek fault zone is located within a few kilometers of the Grass Valley veins and separates the Jura-Triassic arc belt from the Mid-Late Jurassic accretionary arc sequence.

Two distinct vein sets are found in Grass Valley: a N-trending set dominated hosted in the Grass Valley granodiorite (N-S veins) and an E-trending set hosted within the Spring Hill tectonic mélangé of amphibolite facies-grade blocks within a serpentinitized ultramafic matrix of the Jura-Triassic arc belt (E-W veins). The two vein sets have generally similar mineralogy, including quartz, carbonate, micaceous minerals, and pyrite as the dominant sulfide phase. Formation of the N-S vein set occurred at approximately 160 Ma, and the E-W vein set formed at 152 Ma (Snow et al. 2008; Taylor et al. 2015). Over 13 Moz of lode gold were produced from Grass Valley, making it the historically richest lode gold district in the entire North American Cordillera.

3 Materials and methods

Representative vein samples were collected from underground and from drill core. Thin sections of vein material were initially examined with an Olympus BX51 optical microscope. Optical cathodoluminescence (CL) images of quartz were captured using a HC5-LM hot-cathode CL microscope with an attached Peltier-cooled Kappa DX40C CCD camera. Images were automatically captured every 10 seconds to record the short-lived CL. Fluid inclusion microthermometric data were collected using a FLUID INC.-adapted U.S. Geological Survey gas-flow heating and freezing stage. A FEI Quanta FEG 450 scanning electron microscope was used for back-scattered electron (BSE) imaging. A JEOL 8900 electron microprobe with five wavelength dispersive X-ray spectrometers was used in combination with semi-quantitative chemical analyses to characterize mineral chemical differences in zoning observed in BSE images of pyrite.

In situ major and minor geochemical data were collected for pyrite and native gold grains using a JEOL 8900 electron microprobe with five wavelength dispersive X-ray spectrometers. The minor and trace element chemistry of pyrite crystals was collected using a laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS) consisting of a Photon Machines Analyte coupled to a PerkinElmer DRX-e ICP-MS. Analyses were performed using a spot size of 25 μm.

4 Results

The veins at Grass Valley comprise two distinct quartz types, Q1 and Q2 (Fig. 2A). The older Q1 is cloudy in plane polarized light because of the presence of abundant fluid inclusions. The quartz exhibits a short-lived bright blue CL response that degrades to a stable dark red-brown luminescence. The quartz crystals commonly show primary growth zones defined by variable abundances in primary fluid inclusions. The Q1 grains are crosscut by myriads of secondary fluid inclusions formed along healed microfractures that cross cut the primary growth zones. Both primary and secondary fluid inclusions within Q1 display re-equilibration textures (Kontak et al. 2016). Large (5-10 μm), irregularly shaped remnant fluid inclusions appear dark in plane polarized light and planar arrays of secondary neonate inclusions emanate outwards away from the larger relict inclusions forming decrepitated fluid inclusion clusters (Fig. 2B). Domains of Q1 that contain high concentrations of large, re-equilibrated fluid inclusions commonly show a short-lived yellow CL response. Fluid inclusions smaller than ~5 μm in Q1 are preserved and show no evidence of CO2, such as double bubbles or presence of CO2 phases formed during cooling runs.

Quartz Q2 commonly rims Q1 and lacks a visible CL response (Fig. 2C). The Q2 overgrowths appear distinctly clearer in transmitted light due to a lower abundance of primary and secondary fluid inclusions. The Q2 quartz only rarely contains re-equilibrated fluid inclusions, and like Q1 quartz, evidence for any CO2 is lacking, indicating low CO2 contents. Volumetrically, Q2 is less abundant than Q1.

Pyrite is found disseminated throughout the veins and as small stylolite-like stringers. Pyrite is never observed as inclusions within quartz and only occurs along grain boundaries of or within fractures crosscutting the quartz. Pyrite crosses both Q1 and Q2 quartz grains indicating that sulfide formation occurred late in the paragenesis. The grain boundaries between quartz and pyrite are commonly scalloped. Characteristic zoning patterns of pyrite are recognized in high-contrast BSE images and include a dark core (P1), in some cases a core containing brighter domains (P2), which are rimmed by a thin bright growth zone (P3), and an outer euhedral dark rim (P4; Fig. 2D). The patchy P2 zones in the P1 cores appear to result from hydrothermal alteration. The patchy P2 zones originate at the P3 growth zones and irregularly emanate inward into the P1 cores.

The different pyrite zones recognized in BSE images are chemically distinct (Taylor et al. 2018). Invisible Au contents are greatest within P2 zones, with negligible amounts found in P1 cores and P4 rims. Arsenic occurs in elevated concentrations in P3 growth zones, and Ni
and Co are elevated in P3 zones of pyrite contained in the serpentinite-hosted E-W vein set. Inclusions of native gold and galena are found within the P3 growth zones, and within fractures crosscutting both P1 cores and the patchy P2 zones. The P4 rims rarely contain mineral inclusions.

Native gold is paragenetically late and occurs in fractures within quartz, intergrown with chlorite, as fracture fill or inclusions within pyrite, and in contact with galena (Fig. 2E). Native gold is never found encapsulated in the quartz. The gold fineness for each vein set appears to be independent of the textural setting of the gold and host mineral.

5 Discussion

The petrographic evidence displayed by the veins at Grass Valley indicates that they preserve abundant primary textural relationships. Quartz volumetrically dominates the veins. Many of the early Q1 quartz grains exhibit primary growth zoning in CL. In addition, growth zoning is defined by the presence of abundant primary fluid inclusions. Based upon the visible growth zoning defined by fluid inclusions and CL imagery, the quartz crystals are interpreted to have formed during many reoccurring periods of short-lived, high-volume fluid flow related to fault-valve behavior on the controlling fault-fracture system (Sibson 1990). High-amplitude pressure cycling from supralithostatic to sublithostatic conditions during the fault-valve action may explain why the fluid inclusion inventory in the early Q1 quartz has re-equilibrated. Re-equilibration occurs because of the pressure differential between the internal pressure of the fluid inclusions and the confining pressure (Vityk and Bodnar 1995; Kontak et al. 2016). The Al contents of hornblende combined with formation temperatures of the N-S vein-hosting Grass Valley granodiorite (Taylor et al. 2015) suggest formation pressures of 2.2±0.6 kbar and a depth of 8.3±2.3 km under lithostatic pressures for the nearly coeval N-S veins (Mutch et al. 2016); this depth of vein formation is corroborated through the microthermometric investigations. An abrupt change to hydrostatic pressures at this depth will result in a pressure differential of ∼1.4 kbar, which is enough to cause re-equilibration of fluid inclusions larger than 4 μm (Lacazette 1990).

Formation of the late Q2 quartz occurred in a different structural regime. The quartz contains a lower proportion of fluid inclusions and re-equilibrated textures are exceptionally rare. Based upon the lack of visible growth zoning or re-equilibrated fluid inclusions that indicate that significant pressure fluctuations had stopped after Q1 crystallization, this quartz type is interpreted to have formed at hydrostatic conditions that allowed sustained fluid flow through the fault-fracture system. The low CO₂ content of the fluid inclusions contained in the quartz suggests that the fluids were not sourced from substantial depth as fluids released from typical crustal rocks undergoing high-grade metamorphic reactions are characterized by high CO₂ contents (Elmer et al. 2006).

The formation of sulfide minerals and gold largely

Figure 2. Microphotographs of key textures observed in samples from Grass Valley. A) Plane polarized light image of a chalcopyrite grain crosscutting Q1 and Q2 quartz. B) Plane polarized light image of re-equilibrated fluid inclusions within quartz Q1. C) Cathodoluminescence image of quartz Q1 with overprinting yellow CL overgrown by Q2. Bright orange calcite infills the space between adjacent quartz crystals. D) Back-scattered electron image of a pyrite crystal displaying growth zones (P3 and P4) and alteration zoning (P2) around a dark core (P1). E) Reflected light image of gold infilling a fracture in pyrite and its association with galena.
postdate crystallization of both quartz types. These minerals are not encapsulated by quartz and instead are found along grain boundaries and fractures within quartz. Sulfide formation was associated with minor dissolution of quartz as suggested by the cuspatate shape of the pyrite grain boundaries and amoeba-like shapes of base metal sulfides that cut into euhedral Q2 crystal faces.

The compositional zoning of pyrite shows that several distinct growth episodes occurred. The P1 cores contain very low levels of invisible gold. The formation of the P3 growth zones is paragenetically associated with gold and base metal sulfide mineralization. This growth stage resulted in alteration of portions of the P1 cores forming the altered P2 zones having higher levels of invisible gold. The composition of, and inclusions within, the P3 growth zones suggests increased chemical reaction between the hydrothermal fluids with the host rocks. Specifically, the pyrite crystals that are hosted in granodiorite have P3 zones characterized by elevated As, whereas pyrite in veins hosted by serpentinite have elevated As, Ni, and Co; both contain inclusions of galena and gold within the P3 zone. The difference in host rock chemistry also dictated what accessory minerals formed. Telluride minerals, scheelite, and mariposite are found in the serpentinite-hosted veins but not in the granodiorite-hosted veins. Influences of local wall rocks have been well documented to affect geochemical characteristics and mineralogy of orogenic gold deposits (Böhlke 1989).

Chemical equilibrium between the host rock and hydrothermal fluid is also demonstrated during the gold mineralizing event by the correlation between metals derived from the local host rocks (e.g., Pb, Ni, Co) and those elements transported over longer distances by the hydrothermal fluids (e.g., Au, Ag). Equilibration and sulfidation of the wall rocks under hydrostatic conditions may be responsible for the precipitation of the native gold during the late stages of the paragenesis. The textural evidence and mass balance considerations suggest that gold was not remobilized from solid solution gold contained in earlier formed pyrite.

6 Conclusions

The observations of this study suggest that the genetic model of orogenic gold deposits needs to be revised. The previously proposed fault-valve model provides an explanation for the mechanism of fluid flow during the early stage of vein formation and incremental quartz precipitation. Pressure cycling from suprafluid to sublithostatic pressures can account for the observed textural re-equilibration of the fluid inclusion inventory in early vein quartz, which renders the inclusions useless for determining T,P conditions of formation. Gold mineralization at Grass Valley occurred during a subsequent stage of fluid flow that occurred under hydrostatic conditions. Gold precipitation coincided with the equilibration of the hydrothermal fluids with the surrounding wall rock.

Acknowledgments

The Empire Mine State Historic Park granted access to the sampling sites. We are grateful to Bob Pease of the Idaho-Maryland Mining Corporation for providing drill core samples. Erin Marsh is thanked for field assistance. Heather Lowers, Alan Koenig, Erin Marsh, RaeAnn Orkild, and Mike Pribil provided invaluable assistance during the microanalytical work. This study was in part supported by the Mineral Resources Program of the U.S. Geological Survey. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

References


Freixo de Numão Au-W deposit, Northern Portugal: ore features and mineralization controls

Sara Leal, Alexandre Lima
Institute of Earth Sciences, Polo-Porto, University of Porto
Department of Geosciences, Environment and Spatial Planning, University of Porto

Fernando Noronha
Institute of Earth Sciences, Polo-Porto, University of Porto

Abstract. The Freixo de Numão Au-W deposit is located in Vila Nova de Foz Côa region, northern Portugal. Mineralization is hosted in greenschist-facies metasedimentary rocks with lower-Cambrian age. The mineralized structures are subvertical and trend N10° - 40°E, crossing-cut bedding and/or regional foliation, and are post-peak of regional metamorphism. Quartz-sulfide veins and visible hydrothermal alteration characterize this mineralization in the field. The quartz veins record two main stages of mineral deposition (I and II), indicating repeat vein re-opening. Stage-I is characterized by milky quartz and arsenopyrite (Apy-1) and scheelite. Stage-II comprises clear quartz, adularia, chlorite, tourmaline, and metallic minerals, mainly arsenopyrite (Apy-2), chalcopyrite and pyrite, with galena and sphalerite in lesser amounts. The gold (native-Au and electrum) is associated with maldonite, native bismuth, and few Au-Ag phases. A detailed ore study has shown two different gold mode of occurrence: i) native-Au and maldonite, along with Bi-native as droplets in arsenopyrite and chalcopyrite; ii) electrum and Au-Ag phases infill interstitial cavities between arsenopyrite crystals and in its microfractures. These results match with some characteristics of other gold deposits in the European Variscan belt, which revealed a major crustal-scale hydrothermal event responsible by gold mineralization.

1 Introduction

Gold-bearing systems in the European Variscan Belt display a diversity in (a) mineralization style (vein to stockwork, disseminated, or replacement); (b) host rock lithology (volcanic or sedimentary rock, granites); (c) host rocks age (late Proterozoic to Carboniferous), and (d) host rock metamorphic grade (from catazone to epizone or non-metamorphosed rocks) (Bouchout et al. 2005). Due to this diversity, it is very important to understand the distribution of gold in the paragenetic sequence; the identification of typical mineral assemblages; the associations of Te, Bi, and Sb minerals; and evaluation of the factors controlling the ore-forming processes.

The Portuguese gold deposits have atypical characteristics (e.g. mineralogical signatures, structural controls, relationship with magmatic rocks) which are not easily explained by the models (e.g. Orogenic gold vs Intrusion-related gold deposits). The present work made part of a large research project in which the main proposal is the objectives mentioned above.

The known mineralizations in Freixo de Numão area comprises quartz vein structures with sulfide mineralization; tin in pegmatites; and tungsten in calc-silicate metasedimentary rocks (Ramos and Oliveira 1977). Recently, in the area, occurrences of gold are also found in fractures with main NNE-SSW direction, late Variscan in age, that control the emplacement of the Au mineralized quartz-sulfide vein structures. The northwestern part of Iberian Massif is an important Variscan metallogenic province, particularly for gold and base metals.

In this paper is made a first detailed description of the Freixo de Numão gold mineralization, in order to explain the ore minerals and its relationships, which was essential to mineral processing information to the mining companies, in order to helpful the degree of ore liberation. This line of study can be helpful to investigate genetic models for gold deposits, especially in Phanerozoic systems.

2 Geological setting

The Freixo de Numão area (FNA) is part of the Iberian Massif, which constitutes the western-most exposure of the European Variscan Belt, resulting from the collision between Laurussia and the Gondwana, and it is described as staking of large-scale thrust crustal nappes, between 360-320 Ma (Ribeiro et al. 1990). The study area is located in Central Iberian Zone (CIZ) (Julivert et al. 1972), a tectonic-stratigraphic zone characterized by subvertical structures and a large volume of granitic intrusions (Ribeiro et al. 1990).

The tectonic-metamorphic evolution is explained as the result of three main deformation phases (D1, D2, and D3), which are usually considered responsible for the structuration of the NW of the Iberian Massif (Noronha et al. 1979; Ribeiro et al. 1990; Dias and Ribeiro 1995). During and after D3 phase a large volume of granitic rocks intrudes the country metasedimentary rocks. Considering their time of emplacement related with D3 deformational phase can classified as: early-D3 (380-345 Ma); syn-D3 (313-319 Ma), late-D3 (306-311 Ma), late-to post-D3 (ca. 300 Ma) and post-D3 (290-296 Ma) (Dias et al. 1998).

A later brittle deformation phase, post-D3, performing in Iberian Massif, that is characterized by a set of conjugate strike-slip faults (NNW-SSE dextral, NNE-SSW...
sinistral and ENE-WSW), whose geometry is often strongly influenced by pre-existent discontinuities (Ribeiro 1974; Pereira et al. 1993).

In the Iberian Massif, this Late Variscan deformation gave rise to some of the most important observed basement faults, like the NNE-SSW Vilariça and Penacova-Régua-Verín faults in Northern Portugal.

2.1 Regional-deposit scale

The FNA is located in the CIZ, within the western part of a narrow E-W trending metamorphic axis, Marão-Vila Nova de Foz Côa axis (Ribeiro et al. 1990; Dias et al. 2006; Moreira et al. 2010). This belt is bordered by the Variscan Penedono-Mêda-Escalhão massif to the south, and by the Vila Real-Carviçais massif to the north (Ferreira da Silva et al. 1989). In addition to the granites mentioned above, more two small granite plutons intruded in this area: i) Numão granite: biotite>muscovite granite with an emplacement syn to late-D3; ii) Freixo de Numão granite: biotite-rich and it is considered post-tectonic-D3 (Figure 1).

This metamorphic axis belongs to the Pre-Ordovician Schist Greywacke Complex (SGC) (Carrington da Costa 1950; Teixeira 1955) integrated into the so-called Douro Group (Sousa 1982). From stratigraphic and palaeogeographical information, the SGC has been defined as the Super Group Dúrico–Beirão, consisting of the Douro Group, lower-Cambrian in age and Beiras Group Precambrian in age (Oliveira et al. 1992). The Douro Group is composed of several formations Bateiras, Ervedosa do Douro, Rio Pinhão, Pinhão, Desejosa, and S. Domingos from the older to the younger in age (Sousa 1982).

In FNA only outcrops three formations Rio Pinhão, Pinhão and Desejosa. The Rio Pinhão Formation is composed of metagreywackes and metaquartzogreywackes inserted with thin layers of dark phyllites. The Pinhão Formation, consisting in a green colored, thin bedding sequence, characterized by a psammitic (quartz-rich) and pelitic (mica-rich) layering with the particularity of the presence of magnetite crystals and more irregularly pyrite crystals in the psammitic and pelitic layers. The Desejosa Formation is defined by the presence of stripped phyllites that are the result of a thin interchanging of dark with clear layers and metagreywackes (Figure 1). The occurrence of calc-silicate levels in the Desejosa formation is common.

The D1 phase in Foz Côa area induced the formation of wide zones gently folded bounded by coeval narrow bands emphasizing stronger deformation (Moreira et al. 2010). This sequence corresponds to a succession of a large amplitude synclines and narrow anticlines, with an axial trace N100º-N150º (Marques et al. 2002).

In this area, regional metamorphic grade corresponds to greenschist facies conditions, but increases near the granitic plutons, resulting in spotted schists and hornfels. The most significant brittle structures of the region extend in the NNE-SSW direction and correspond to the important sinistral wrench-faults (namely Vilariça Fault) related with the late Variscan phase (D3) of brittle faulting (Figure 1).

3 Sampling and analytical methods

In the fieldwork and sampling, a set of 40 samples were collected from underground workings and 12 samples from drillcores.

The observations of mineral assemblages and chronological successions were carried out by microscopy in transmitted and reflected light, at Institute of Earth Sciences and in Department of Geosciences, Environment and Spatial Planning in the University of Porto.

Complementary studies for characterization of gold minerals were carried out by SEM/EDS performed with a resource to a High-resolution Scanning Electron Microscope with X-Ray Microanalysis: JEOL JSM 6301F/ Oxford INCA Energy 350, in Materials Centre of the University of Porto.

4 The Freixo de Numão deposit

4.1 Vein system

The exposed rocks in underground works are a succession of interlayers of quartzogreywackes, phyllites, quartzites, and calc-silicate rocks, exhibiting a foliation, defined by preferential orientation (S1) of small muscovite and chlorite. The mineralized veins crosscut S1 that is usually parallel to the stratification S0 (N120º).

In the field, it was visible quartzite ridges with a direction N100º-120º; subvertical.

The mineralization occurs in two types: i) disseminated in host rocks (less in the phyllites), and ii) quartz-sulfide veins.

The metasedimentary host rocks are strongly crosscut by a main and systematic vein system (N-S to N40º; 50ºW to sub-vertical) (Figure 2). The vein system consisting of subparallel veins with variable spacing and length.
function of nature of host lithology. Within fine-grained pelitic rocks, the mineralized veins have a small spacing (10-20 cm) and are scarce.

However, in more competent host rocks (quartzite and/or calc-silicate rocks), the veins are locally anastomosed (like a stockwork) and have a larger spacing (> 50 cm). The veins also lack ductile shear markers or lineations. In addition, the veins crosscut all foliations (S0, S1) but lack any displacement.

![Figure 2. Different types of mineralized structures. A – quartz-sulfide veins with chlorite and adularia alteration; B – Vein of early quartz + quartz-sulfide vein crossing-cut quartzitic rocks; C – Disseminated arsenopyrite in calc-silicate rock. Red bar = 2 centimeters.](image)

There is another mineralized vein system, sub-parallel to the calc-silicate and the quartzite rocks, N100°-115°; 70°W – subvertical. Finally, there is a barren vein system N80°; 20°N sometimes is folded.

Petrography of all the different types of mineralized veins indicated that they are extension veins, as reflected by the growth directions of the quartz crystals in some cases it usually found hybrid extension-shear veins with similar textures with quartz grains elongated at an oblique angle near the vein walls (Fig. 2-B).

### 4.2 Relation of gold to other minerals

The quartz veins record two main stages of mineral deposition (I and II), indicating successive periods of vein re-opening.

Stage-I is characterized by milky quartz (mQ), arsenopyrite (Apy-1) and scheelite. Scheelite is the only W-bearing phase at the deposit. It forms coarse-grained euhedral to subhedral grains in the quartz veins cutting calc-silicate rocks, while that hosted in quartzite and calc-silicate rocks is fine-grained and xenomorphic.

Stage-II corresponds to the quartz-sulfide veins formation and comprises clear quartz (cQ), K-feldspar (adularia), chlorite, tourmaline, and metallic minerals, mainly arsenopyrite (Apy-2), chalcopyrite and pyrite, with galena, bismuthinite and sphalerite in lesser amounts.

The gold minerals show two different mode of occurrence: i) native-Au and maldonite (Au2Bi), along with native-Bi as droplets in Apy-2 and chalcopyrite; ii) electrum, and Au-Ag phases infill interstitial cavities between arsenopyrite crystals and in its microfractures (Figure 3). The size of gold particles ranges to 3 microns to 50 microns.

![Figure 3. Different modes of gold occurrence. A – Native-Au + native-Bi in arsenopyrite; B – Maldonite (Mdl) in arsenopyrite; C – Electrum and native-Bi in chalcopyrite; D – Electrum filling fractures in arsenopyrite; E – Maldonite and native-Bi in arsenopyrite; F – Native-Bi in association with Au-Ag phases.](image)

### 4.3 Hydrothermal alteration

At FNA, the hydrothermal alteration is volumetrically restricted to the quartz-sulfide veins system and the mineralized disseminated zones, consisting of i) early silicification characterized by the filling of tensional quartz veinlets (Fig. 2-B); ii) tourmalinization, feldspathization, chloritization associated to the sulfides precipitation.

![Figure 4. Different types of hydrothermal alterations. A – muscovitization; B – Chlorite + adularia associated with quartz-sulfide veins; C – Tourmalinization; D – Muscovite with anomalous birefringence and epidote.](image)

In mineralized disseminated zones related to quartzite rocks, the muscovitization is the main present alteration. It corresponds to subhedral muscovite with symplectic borders, with quartz intergrowth and quartz droplet inclusions (Figure 4 - A). In quartz-sulfide veins, the main hydrothermal alteration is silicification, tourmalinization, K-feldspathization, chloritization, and carbonatization. However, not always present. In most cases, tourmaline
is associated with this silicification (Figure 4 - C). Later, the early quartz undergoes deformation and polygonization. A polygonal quartz results from the second silicification stage, associated with the sulfides (mostly arsenopyrite). In calc-silicate rocks, the silicification, tourmalinization, and sericitization are the most pervasive alterations. In this stage, a muscovite with anomalous birefringence, epidote, chloroziolite and fluorite are frequent (Figure 4 - D). Carbonatization occurs mainly in microcracks crosscutting all lithologies, which along with feldspatization and chloritization represents the last hydrothermal event.

5 Final remarks

The quartz–sulfides bearing veins, which record two main stages of mineral deposition indicating successive periods of vein re-opening.

Gold deposition occurred in two discrete periods: 1) first as minute inclusions (Au-native and maldonite + Bi-native) that are coeval with the formation of Apy-2 and chalcopyrite during the quartz–sulfide stage; 2) later electrum and Au-Ag phases occur filling fractures and interstices between arsenopyrite crystals.

The Freixo de Numão gold mineralization periods imply hydrothermal alteration processes. The association scheelite ± fluorite ± native gold is related to the chlorite ± adularia hydrothermal alteration. The hydrothermal suite suggests a typically low-temperature hydrothermal environment and indicate near-neutral pH conditions, due to the presence of adularia and calcite.

Indirect evidence suggests that the ore-forming fluids can be related to the second and third order structures parallel to the major regional Vilarica fault (late-Variscan strike-slip fault) and/or related to the fracture systems, which controlled the emplacement of the late-to post-tectonic granitoids in the area that provided conduits for subsequent low-temperature mineralizing events (Noronha et al. 2000 and references therein).

Acknowledgments

The first author is financially supported by SFRH/BD/114693/2016 (FCT Portugal). The authors acknowledge the funding by COMPETE 2020 through the Institute of Earth Sciences project (UID / GEO /04683/2013) with POCI-01-0145 reference - FEDER007690. Minaport - Minas de Portugal, Lda are acknowledged for their technical support and assignment of samples.

References

Role of pre-ore barren quartz veins in orogenic-gold mineralization: a case study from Huangjindong deposit, Jiangnan Orogen, China

Liang Zhang, David I. Groves, Li-Qiang Yang, Si-Chen Sun, Jiu-Yi Wang, Rong-Hua Li
State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing

Roberto F. Weinberg
School of Earth, Atmosphere and Environment, Monash University

Sheng-Gang Wu, Lei Gao
Hunan Huangjindong Mining Co. Ltd

Lan-Ling Yuan
402 Geological Prospecting Party, Bureau of Geology and Mineral Exploration and Development of Hunan Province

Abstract. Similar to many orogenic gold deposits globally, two phases of hydrothermal alteration have been defined in the Huangjindong orogenic gold deposit in the Jiangnan Orogen, southern China. The first phase of hydrothermal alteration is pre-ore and largely barren. The geometry of the pre-ore barren quartz veins indicates the formation of these veins was controlled by folds and thrust faults. The cross-cutting relationship between the two phase of hydrothermal alteration and the structures and texture of the ores indicates that the earlier barren veins provide favourable competent hosts for later mineralization. During the mineralization, the overpressured fluids caused hydrofracturing which resulted in the brecciation of the earlier quartz veins. The repeated hydrofracturing resulted in fluid pressure fluctuation which in turn induced the fluid phase separation and subsequent deposition of auriferous quartz-sulfide veins and breccia cements.

1 Introduction

In many orogenic gold deposits, barren pre-ore quartz veins which may be part of a single progressive hydrothermal event or a temporally distinct event relative to the gold mineralization are well developed (Hulin 1929; Kerrich 1986; Dirks and Wilson 1991; Billay et al. 1997; Dugdale and Hagemann 2001; Zhang et al. 2018). The role of such early barren quartz veins has been rarely studied. The Huangjindong gold deposit, Jiangnan Orogen, southern China, with large scale pre-ore barren quartz veins provides an opportunity to study this topic. Thus, in order to constrain this role of the barren quartz veins in the gold ore genesis, structural geometry analysis, petrography, mineralogy, have been carried out on the Huangjindong deposit. The significance of these results in terms of exploration is also examined.

2 Regional and local geology

The Jiangnan Orogen, which hosts ~40 gold deposits with combined gold resources of ~1000 t, is located between the Yangtze and Cathaysia Blocks (Xu et al. 2017). Three major goldfields in the Orogen, including the Huangjindong, are distributed along the first-order crustal-scale Changsha-Pingjiang Fault zone. The Huangjindong goldfield, with estimated gold resources of ~85 t, mainly contains the Quxi gold, Anshan gold-antimony and Huangjindong gold deposits, all along the Changsha-Pingjiang Fault (Fig. 1; Zhang et al. 2018). Located in the footwall of the Changsha-Pingjiang Fault, the Huangjindong gold deposit are hosted by Neoproterozoic metasedimentary rocks. Orebodies in the Huangjindong gold deposit are strictly controlled by E- to WNW- trending thrust faults. Most orebodies dip to the north, whereas several thick orebodies dip to the south (Liu et al. 2017; Sun et al. 2018). The lacking of ore-related mineral and element zonings reveal no local granite-related thermal was inputted, and the formation of the deposit was controlled by regional geothermal gradient. The geochemical and isotopic data show a metamorphic source for the ore fluid and components (Zhang et al. 2018; Groves et al., 2019), together with which, the structural control on the gold mineralization and their spatial distribution demonstrate that the deposit formed during a transpressional phase of orogenesis and can be classified as orogenic gold deposit (Zhang et al. 2018) in the term of the classification of Groves et al. (1998).

3 Alteration and mineralization

Previous study (Zhang et al. 2018) and new field observation in this study show that auriferous arsenopyrite-pyrite-quartz veins, quartz breccias cemented by late arsenopyrite, pyrite, muscovite, and quartz, and disseminated arsenopyrite-pyrite-sericite-quartz altered slate breccias with fine arsenopyrite-pyrite-quartz veinlets account for most of the gold resources. The alteration is dominated by silification, sericite alteration, chloritization and carbonation with significant
arsenopyrite, pyrite, scheelite and minor stibnite, pyrrhotite, chalcopyrite, galena, and sphalerite mineralization. Three mineralization stages including barren quartz-(sericite)-scheelite veins (I), auriferous quartz-sulfides veins (II) and post-gold carbonate-quartz veins (III) were identified. Together with field observation, detail work using optical microscope, scanning electron microscope (SEM) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) trace elements analysis of pyrite and arsenopyrite in this study show that the gold is dominated by native gold associated with hydrothermal quartz and invisible gold in pyrite and arsenopyrite.

Figure 1 Geological map of the Huangjindong goldfield. Modified from Zhang et al. (2018).

4 Formation of early barren quartz veins

South-dipping Orebody 3 at the Huangjindong deposit with major fault-fill barren-quartz shear veins and thin flat extensional veins resembles the geometries of classic thrust-controlled veins in orogenic gold systems (Fig. 2; Groves et al. 2018). The steeper extensional veins on the footwall of the flatter barren major fault-fill vein of north-dipping orebody 1 crosscut the foliation at a high angle and, in combination with drag folds along the hangingwall fault, highlight the classic features of thrust-controlled veins (Fig. 3).

Quartz laminae associated with subparallel elongate slivers of wall rocks in Orebody 3 (Fig. 1) are most likely formed by crack-seal processes. Together with their geometry, these internal structures confirm that they were controlled by fault-valve behavior induced by repeated fluctuations of shear stress and fluid pressure during cyclical seismicity (Sibson et al. 1988, 1989; Cox et al. 1995). Quartz veins in Orebody 1 containing abundant irregular slate breccias (Fig. 3) are commonly interpreted to be a single-stage hydraulic fracture process.

Figure 2 Photograph (a) and sketch (b) showing geometry and alteration and mineralization features of Orebody 3 at the Huangjindong gold deposit.

5 The role of pre-ore barren quartz veins

At the Huangjindong deposit, the syn-ore movement of the ore-controlling WNW-E-trending faults resulted in the fracturing of the pre-ore competent barren quartz veins. Subsequently, these fractures were filled by thin grey quartz veins and breccia matrices containing native gold and gold-bearing arsenopyrite and pyrite (Figs. 2 and 3). It is obviously that the earlier barren quartz veins played no chemical role in ore deposition but were simply the most competent rock units in the more-ductile sericitic
slate for subsequent brittle failure to provide ore-fluid passage to depositional sites (Jaeger 1967).

The intensive brittle failure of the pre-ore barren quartz veins enhanced by supralithostatic fluid pressures resulted in increased permeability (Figs. 2 and 3). This induced a dramatic decrease in pressure which caused significant fluid phase separation resulting in the destabilization of gold-thio-complexes and deposition of the native gold and refractory-gold-bearing arsenopyrite and pyrite in hydrofractures and breccia matrices. Such repeated episodes formed high-grade gold ores.

Figure 3 Photograph (a) and sketch (b) showing geometry and alteration and mineralization features of Orebody 1 at the Huangjindong gold deposit.

6 Implications for exploration

As stated above, the pre-ore competent quartz veins played a critical role in localizing later gold mineralization in the Huangjindong deposit. Thus, earlier geometries of the barren quartz veins may control the structural geometry of subsequently formed orebodies (Figs 2 and 3). This is critical for mine planning.

The full manuscript of this study (Zhang et al. 2019) has been submitted to Mineralium Deposita for peer review.

Acknowledgements

We thank Drs Richard Goldfarb, Franco Pirajno, Stephen Cox and Kun-Feng Qiu for their comments and suggestions for this project. This work was financially supported by National Natural Science Foundation of China (Grant No. 41702070), MOST Special Fund from the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Grant No. MSFGRMR201804) and 111 Project under the Ministry of Education and the State Administration of Foreign Experts Affairs, China (Grant No. B070111).

References


Hulin CD (1929) Structural control on ore deposition. Econ Geol 24:15–29


The Mustajärvi orogenic gold occurrence, Central Lapland Greenstone Belt, Finland

Matthias Mueller
University of Oulu; FireFox Gold Corp.

Petri Peltonen
University of Helsinki; FireFox Gold Corp.

Abstract. The Mustajärvi gold occurrence lies on the southern border of the Central Lapland Greenstone Belt, in proximity to the first-order transcrustal Venejoki thrust system. The occurrence is structurally controlled by the second order Mustajärvi shear zone that is located at the contact between Sodankylä group siliciclastic metasediments and Savukoski group mafic and ultramafic volcanics. The outcropping gold mineralized veins comprise a set of parallel quartz-tourmaline-pyrite veins that show strong pinch and swell features with widths ranging from approx. 0.15 m to 1 m. At a depth of approx. 42 km (Patison et al. 2006; Niiranen et al. 2014), whereas it is uncertain which formation they most likely belong to the Sodankylä group Honkavaara formation with age estimates of 2.3-2.2 Ga (Lehtonen et al. 1998). The metasedimentary rocks are strongly interlayered with individual layers of 0.1 m to 25 m in thickness, where thinner layers typically are tuffs and thicker layers lavas. Furthermore, 0.15 to 3 m thick layers of mafic and ultramafic tuffs are common in the metasedimentary unit (Fig. 1). The graphitic cherts are observed as zones of strong deformation. Gabbro intrusions of unknown formation are present in the SW of the study area. Ground magnetic data and bottom of till (BoT) Cr concentrations indicate that both the siliciclastic metasediments and the volcanics are intruded by them. Not many gold occurrences are known from the Venejoki thrust system, probably due to limited exploration activities and a generally poorer bedrock exposure. With the current study, Mustajärvi is one of the few, if not the first, extensively studied gold occurrence along the Venejoki thrust system.

1 Introduction

The Paleoproterozoic Central Lapland Greenstone Belt (CLGB) has a total reported gold endowment of just over 10 Moz, but with most of this resource defined in solely the giant Suurikuusikko deposit and dozens of other prospective occurrences lacking detailed exploration. One potentially promising target, the Mustajärvi orogenic gold occurrence, lies on the southern border of the CLGB, in proximity to the first order Venejoki thrust zone. Exploration wise, the Venejoki thrust system has mostly been ignored, despite the fact, that, regarding the time and direction of deformation, it is sharing many features with the nearby Sirkka thrust zone which is associated with a majority of known gold occurrences in the Central Lapland Greenstone Belt. The Venejoki thrust zone can be traced to reach the mantle at a depth of approx. 42 km (Patison et al. 2006; Niiranen et al. 2014). Not many gold occurrences are known from the Venejoki thrust system, probably due to limited exploration activities and a generally poorer bedrock exposure. With the current study, Mustajärvi is one of the few, if not the first, extensively studied gold occurrence along the Venejoki thrust system.

Here, we give the first overview of the geological setting, alteration, style of mineralization and structural control of the Mustajärvi occurrence and furthermore emphasize the prospectivity for a more extensive gold mineralized system, especially at greater depths. Few of the presented characteristics of Mustajärvi are atypical for gold occurrences in the CLGB and for orogenic gold systems in general. These features might represent a new type characteristic for gold occurrences along the Venejoki thrust zone.

2 Geological setting

The rock package at Mustajärvi can be divided into two major units, siliciclastic metasediments consisting of banded arkose quartzites, intermediate tuffites and mafic tuffites; and volcanic rocks comprising ultramafic lavas and tuffs, komatiitic basalts, mafic lavas and tuffs, and rare graphitic cherts. The siliciclastic metasediments most likely belong to the Sodankylä group Honkavaara formation with age estimates of 2.3-2.2 Ga (Lehtonen et al. 1998). The metasedimentary rocks are strongly interlayered on a meter to centimetre scale, commonly resulting in a strong layering, typical for tuffites. Observed strong banding, felsic clasts in an intermediate to mafic matrix and an occasional gradual bedding suggest a volcanioclastic sedimentation. The volcanic rock unit is likely part of the 2.2-2.05 Ga Savukoski group (Lehtonen et al. 1998), whereas it is uncertain which formation they represent. The different rock types of the volcanic unit are interlayered with individual layers of 0.1 m to 25 m in thickness, where thinner layers typically are tuffs and thicker layers lavas. Furthermore, 0.15 to 3 m thick layers of mafic and ultramafic tuffs are common in the metasedimentary unit (Fig. 1). The graphitic cherts are tightly interbedded with altered mafic volcanics and occur near the interpreted contact zone between volcanic rocks and siliciclastic metasediments, where they have been observed as zones of strong deformation. Gabbro intrusions of unknown formation are present in the SW of the study area. Ground magnetic data and bottom of till (BoT) Cr concentrations indicate that both the siliciclastic metasediments and the volcanics are intruded by them.

Along the main contact, the Mustajärvi fault zone is interpreted to occur; likely formed due to the competency contrast of the rock types. The fault is indicated by several fault zone-typical geophysical features such as a demagnetization, a low apparent resistivity and a high
chargeability, and by zones of strong deformation. Interpreted from geophysical data, and drill core correlations, the fault zone has a similar orientation to the host rocks, dipping to the SE with ~45 ° (Fig. 1). The siliciclastic metasediments dominantly occur on the NW side of the fault zone and the volcanic rocks dominantly on the SE side. The contact between the rock units is conform and rather gradual, with increasing interlayering between the rock types in proximity to the contact zone (Fig. 1).

The gold mineralization is hosted by a set of parallel quartz-pyrite-tourmaline veins (Fig. 1) that show typical pinch and swell features, with vein widths ranging between 0.15 m to 2 m. The mineralization is not strongly host rock controlled as it has been observed to be hosted by both the siliciclastic metasediments and the volcanics, as well as commonly by the contact of both units. The mineralized veins appear to be generally structurally controlled, with the main mineralization trend being parallel to the Mustajärvi fault zone. A second mineralization trend runs perpendicular to the main trend. Additionally, BoT Au anomalies, outside the area of known gold mineralization, are spatially associated with the interpreted fault zone, further suggesting a strong structural control and expanding the prospective extent of Mustajärvi along strike.

Carbonate veining comprising both calcite and ankerite-dolomite.

Due to an overall relatively strong regional alteration, the mineralization-related alteration is typically ambiguous and mostly difficult to determine. Moreover, there appear to be different mineralization styles at Mustajärvi that each have individual alteration assemblages. The figure 2 tries to give a unified overview of the spatial alteration sequence related to ore-forming fluids that is distinctively different from background alteration and generally applies to most mineralization styles.

Additional to the alteration assemblages given in figure 2, also different types of veins indicate nearby mineralization. Within the intermediate to proximal alteration zone, barren quartz-pyrite ± tourmaline ± carbonate ± albite veins are typical, with pyrite amounting up to 75 % of the vein. Occasionally, gold is clearly anomalous in these veins with concentrations up to 0.4 ppm Au and 4 ppm Te and with similar mineralization related alteration envelopes. Another mineralization indicator is magnetite-pyrite-carbonate veining that occasionally occurs in the proximal alteration zone. These veins can be either barren, anomalous for gold or clearly mineralized. Also, hematite-pyrite-quartz veins with anomalous gold concentrations of up to 0.3 ppm Au were observed in proximity to mineralization.
4 Mineralization

4.1 Petrography of the mineralized veins

The outcropping mineralization at Mustajärvi consists of quartz-pyrite-tourmaline veins with widths ranging between 0.15 m to 1 m. Pyrite, the only sulphide mineral of the mineralized veins, makes up 5 to 25% of the veins with an average of ~10%, whereas the tourmaline amount is strongly varying, ranging from 5% to as much as 35% of the vein. Accessory minerals are white mica and rare monazite. Microprobe analysis shows that gold within the veins is occurring as the Au telluride calaverite and the Au-Bi telluride montbrayite, both as micro inclusions in pyrite. Additionally to Au-(Bi)-tellurides, the veins contain the Ni-telluride melonite, the Bi-telluride tellurobismuthite and the Se-Bi-telluride kawazulite. All telluride minerals occur as micro-inclusions in pyrite, with grain sizes of 1 µm to 10 µm. They are usually emplaced in strings or cracks of goethite (Fig. 3).

In weathered samples, the telluride minerals get remobilized and deposited as free gold, mainly in the matrix of quartz-pyrite-tourmaline veins. Monazite. Microprobe analysis shows that gold within the veins is occurring as the Au telluride calaverite and the Au-Bi telluride montbrayite, both as micro inclusions in pyrite. Additionally to Au-(Bi)-tellurides, the veins contain the Ni-telluride melonite, the Bi-telluride tellurobismuthite and the Se-Bi-telluride kawazulite. All telluride minerals occur as micro-inclusions in pyrite, with grain sizes of 1 µm to 10 µm. They are usually emplaced in strings or clusters in the pyrite grain, whereby melonite occurs more commonly as a single grain disseminated in pyrite and also shows larger grain sizes than the other telluride minerals. No spatial relationship, neither between the tellurides and their location in the host pyrite grain was observed. In weathered samples, the telluride minerals get destroyed during oxidation of pyrite and gold is remobilized and deposited as free gold, mainly in the cracks of goethite (Fig. 3).

During drilling in early 2019, a 2 m wide, high-grade mineralized zone was intersected at approx. 90 m vertical depth, which consisted of massive pyrite (approx. 50%) with only marginal amounts of quartz and comparably little tourmaline. The pyrite zone is mainly oriented along the foliation of the intermediate tuffite host rock. This interval represents the highest grading drill core intersect so far at Mustajärvi with 2 m at 45.1 ppm Au and likely constitutes a different style of mineralization, perhaps typical for greater depths.

4.2 Geochemistry of the mineralized veins

The geochemistry of the mineralized veins shows strong enrichments of elements that are commonly elevated in orogenic gold deposits. At Mustajärvi, these elements include: Au, B, Bi, C (CO₂), Te and Se. Other pathfinder elements that are commonly enriched in orogenic gold deposits, like Ag, As, Sb & W (e.g. McCuaig and Kerrich 1998; Goldfarb et al. 2005) are clearly elevated at Mustajärvi and correlate with gold but are not enriched to the same extent as the former elements (Table 1). The average Au/Ag ratio of 5-10 in orogenic gold deposits (Goldfarb et al., 2005) is notably higher at Mustajärvi with a value of 21.4. Elements that are not commonly recognized to be elevated in orogenic gold deposits but are clearly enriched at Mustajärvi are Co and Ni, and elevated Mo.

Table 1. Element concentrations of unweathered mineralized veins in drill core, exceeding 0.1 ppm Au; and their correlation with selected elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mn</th>
<th>Max.</th>
<th>Avg.</th>
<th>Std. deviation</th>
<th>Correlation of selected elements for unweathered gold mineralization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag ppm</td>
<td>0.50</td>
<td>2.40</td>
<td>0.62</td>
<td>0.44</td>
<td>1.00 0.45 0.40 0.45 0.42 0.38</td>
</tr>
<tr>
<td>Au ppm</td>
<td>0.04</td>
<td>2.50</td>
<td>0.66</td>
<td>0.10</td>
<td>-0.04 0.12 0.09 0.16 0.13</td>
</tr>
<tr>
<td>Se ppm</td>
<td>2.50</td>
<td>19.00</td>
<td>5.29</td>
<td>4.35</td>
<td>0.49 0.54 0.59 0.59 0.61 0.37</td>
</tr>
<tr>
<td>Bi ppm</td>
<td>0.11</td>
<td>73.72</td>
<td>6.46</td>
<td>15.41</td>
<td>0.45 1.00 0.75 0.82 0.74 0.77</td>
</tr>
<tr>
<td>Cu ppm</td>
<td>3.00</td>
<td>581.00</td>
<td>46.06</td>
<td>118.32</td>
<td>0.15 0.00 -0.07 0.08 0.05 -0.16</td>
</tr>
<tr>
<td>Fe ppm</td>
<td>0.03</td>
<td>728.00</td>
<td>42.19</td>
<td>133.68</td>
<td>0.00 0.75 1.00 0.78 0.76 0.59</td>
</tr>
<tr>
<td>K ppm</td>
<td>0.01</td>
<td>12.90</td>
<td>1.91</td>
<td>2.75</td>
<td>-0.24 -0.62 -0.58 -0.66 -0.49 -0.44</td>
</tr>
<tr>
<td>Mg ppm</td>
<td>1.20</td>
<td>2860.00</td>
<td>440.55</td>
<td>759.30</td>
<td>0.45 0.82 0.78 1.00 0.95 0.70</td>
</tr>
<tr>
<td>Mn ppm</td>
<td>7.40</td>
<td>1030.00</td>
<td>110.27</td>
<td>234.42</td>
<td>0.04 0.14 0.01 0.02 -0.06 -0.26</td>
</tr>
<tr>
<td>Mo ppm</td>
<td>1.10</td>
<td>39.10</td>
<td>6.77</td>
<td>8.84</td>
<td>0.42 0.60 0.53 0.68 0.79 0.57</td>
</tr>
<tr>
<td>Ni ppm</td>
<td>0.68</td>
<td>28.40</td>
<td>6.14</td>
<td>7.67</td>
<td>0.48 0.76 0.80 0.83 0.86 0.69</td>
</tr>
<tr>
<td>Pb ppm</td>
<td>0.01</td>
<td>2.31</td>
<td>0.28</td>
<td>0.59</td>
<td>0.10 0.00 0.04 0.09 0.12 0.06</td>
</tr>
<tr>
<td>P ppm</td>
<td>0.01</td>
<td>2.95</td>
<td>0.99</td>
<td>0.90</td>
<td>-0.11 -0.35 -0.14 -0.21 -0.06 -0.26</td>
</tr>
<tr>
<td>Se ppm</td>
<td>35.00</td>
<td>2550.00</td>
<td>548.00</td>
<td>651.34</td>
<td>0.45 -0.59 -0.57 -0.62 -0.46 -0.47</td>
</tr>
<tr>
<td>S ppm</td>
<td>0.50</td>
<td>1040.00</td>
<td>5.28</td>
<td>18.14</td>
<td>0.30 0.54 0.65 0.56 0.59 0.50</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>8.20</td>
<td>689.00</td>
<td>114.81</td>
<td>158.75</td>
<td>0.44 0.72 0.78 0.86 0.86 0.68</td>
</tr>
<tr>
<td>Sb ppm</td>
<td>73.00</td>
<td>2060.00</td>
<td>402.54</td>
<td>537.14</td>
<td>-0.29 -0.35 -0.35 -0.40 -0.31 -0.24</td>
</tr>
<tr>
<td>V ppm</td>
<td>2.50</td>
<td>87.90</td>
<td>6.77</td>
<td>8.13</td>
<td>0.48 0.79 0.72 0.94 0.92 0.70</td>
</tr>
<tr>
<td>Zn ppm</td>
<td>0.02</td>
<td>0.18</td>
<td>0.06</td>
<td>0.05</td>
<td>0.42 0.51 0.66 0.46 0.52 0.27</td>
</tr>
</tbody>
</table>

Te and Co are so highly enriched, that, if the metallurgy permits, they might act as economic by-products in mining. Table 1 emphasizes the described vein mineralogy, with gold strongly correlating with Te and Bi, as it occurs as Au-(Bi)-tellurides. Furthermore gold strongly correlates with S, Se and Co, since the gold tellurides are hosted by pyrite, which is also the host to Se and Co, with Se concentrations of ~0.05%, and Co concentrations of 0.41% in the lattice of pyrite.
Comparisons between unweathered and weathered mineralized rocks show a clear supergene enrichment only in Sb, whereas supergene depletions can be observed in Bi and Se.

5 Structural control

The main mineralization trend is oriented nearly parallel to the main lithological contact and to the orientation of the host rock, with an average strike and dip of ~70°/50° SSE. This is emphasized by BoT Au anomalies and drill core intercepts, which furthermore indicate that the main mineralization trend consists of several parallel aligned veins offset from the main lithological contact. The pattern of the veins could be explained by a set of listric faults originating from the main shear zone or by a system of several smaller shear zones related to the larger Mustajärvi shear. This would explain the strong alteration that repeatedly occurs in the host rock package, without correlating mineralization. A second mineralization trend was observed in a subcropping auriferous vein, which is oriented perpendicular to the main mineralizing trend and strikes near parallel to the main joint direction of the host rocks with an average strike of 150°-160°. This vein trend was proven to continue at depth, where vertical veins, partly auriferous, with a strike of 155° occur. Veins of this second trend appear to have lower grades of Au. This vein trend 2 could represent minor transfer faults within the rock package, partly auriferous due to possible remobilization of mineralization.

The assumed structural setting of Mustajärvi is in accordance with common structural models of orogenic gold deposits (e.g. Goldfarb et al. 2005), describing a first order structure that collects and channelizes auriferous fluids, in this case the regional transcrustal first-order Venejoki thrust fault system that lies approx. 2 km south of Mustajärvi, dipping flatly to the south (Niiranen et al. 2014); and a second order fault that traps the fluids, which is represented by the Mustajärvi fault, including minor third order splays off the second order fault that are potentially represented by the observed auriferous veins.

6 Conclusions

Mustajärvi is a typical orogenic gold occurrence. It has a strong structural control, being hosted by the second-order Mustajärvi shear zone that is interpreted to be a splay off the first-order transcrustal Venejoki thrust complex, situated approx. 2 km south of the occurrence; and is likely to have formed due to the competency contrast between the siliciclastic metasedimentary, and volcanic host rocks. The auriferous veins are interpreted to be related to minor third-order structures associated with the second-order Mustajärvi shear zone.

The geochemistry of the mineralized veins is typical for orogenic gold deposits with strongly enriched elements comprising Au, B, Bi, C (CO₂), Te and Se; and with Ag, As, Sb and W being elevated and positively correlating with gold. Atypical for orogenic gold deposits are the enrichments of Ni and Mo; and a strong enrichment of Co, which however, can also be seen in many gold occurrences along the nearby Sirkka thrust system.

It appears that two different mineralization styles exist at Mustajärvi. The outcropping and surface near mineralized veins are approx. 0.15 m to 1 m wide and consist of mainly quartz, tourmaline and pyrite. The second, higher grade, mineralization style was proven at a vertical depth of 90 m, comprising a 2 m wide zone of massive pyrite mineralization (50 % pyrite) with only little amounts of quartz and relatively low tourmaline contents. This second style of mineralization has yet to be followed up by further drilling and indicates the openness of the gold mineralization in all directions, with great potential for more extensive gold mineralization especially at depth.

Acknowledgements

Acknowledgments go to the FireFox Gold Corp team for a great and fruitful work environment. Furthermore Pasi Eilu and Tero Niiranen from the GTK, and Richard Goldfarb are thanked for their continuous support and expertise that helped to fundamentally improve the quality of this work. Also the University of Oulu, including Eero Hanski, is acknowledged for funding the microprobe work and parts of the thin section studies.

References

Abstract. Using high resolution X-ray Computed Tomography (HRXCT), the distribution of gold in acicular arsenopyrite of pyrite-arsenopyrite association of Suzdal (East Kazakhstan) and Olympiada (Yenisei Ridge, Russia) deposits was investigated. The results of micro X-ray tomographic studies allow drawing conclusions about the distribution patterns of gold in sulphides. It can be used to understand the genesis of productive mineral associations, and to develop optimal technological schemes for gold extraction.

2 Methodology and Instruments

For the purposes of detailed studies, the authors used the Bruker SkySan 2011 and Bruker SkyScan 1172 micro CT-systems, based on the X-ray diffraction methods of the RC and the Geomodel RC (St. Petersburg State University). Analyses of the content of micro-impurities in arsenopyrite were carried out on a JEOL JXA-8100 electron probe micro-analyser, in the Center for Multiple Element and Isotope Studies of the Siberian Branch of the Russian Academy of Sciences. The detection limit for the unilateral 2σ criterion with a confidence level of 97.5% is 30 ppm. The detection limits of other elements in arsenopyrite (wt. %) are: Fe - 0.018, As - 0.06, S - 0.02, Sb - 0.04, Ni - 0.005, Co - 0.004, Zn - 0.043, Cu - 0.02, for Ag (ppm) - 470. The content of noble metals (Au and Ag) was determined by an atomic absorption method using Perkin-Elmer 503 spectrometer with an electrothermal HGA-74 atomizer and a deuterium background corrector, a 3030 system with an HGA-600 atomizer. The detection limit of Au is 5*10^{-8}, Ag is 1*10^{-7} %.

3 Results

Generally, two morphological types of arsenopyrite, acicular-prismatic and coarse-crystalline, are characteristic of the gold-sulphide deposits. At the Suzdal gold deposit (East Kazakhstan) acicular arsenopyrite crystal aggregates have been studied. At the Suzdal gold deposit (East Kazakhstan) acicular arsenopyrite crystal aggregates have been studied. It is found in disseminated ores of the early pyrite-arsenopyrite productive association. It is represented by small crystals and its aggregates ranging in size from few to hundreds micron, forming star-shaped and druse-like accretions of acicular and prismatic crystals (Fig. 2) in metamorphosed carbonaceous siltstones and sandstones. Mineralized carbonaceous terrigenous rocks contain gold up to tens of ppm (Kovalev et al. 2011). The degree of gold content is proportional to the saturation of finely dispersed sulphides, mainly arsenopyrite.
In Fig. 1, a photomicrograph of a polished section (right photo) of typical gold-bearing ore of Suzdal deposit, and HRXCT 3D image (left photo) of microcore (d = 5mm) of the same rock, with disseminated arsenopyrite are illustrated. Arsenopyrite grains have elongated or isometric pseudohexagonal shape. They contain inclusions of sulphides, gold and other minerals.

It is assumed that the deposition of micro-grains and nano-particles of gold in arsenopyrite crystals occurs synchronously with crystal growth. With rapid growth, gold is distributed relatively evenly in the structure of arsenopyrite, with slow growth gold clusters are formed (Fougerouse et al. 2016), and when crystal growth stopped, large visible dendritic crystals or films of gold precipitate along the faces of the arsenopyrite crystals (Voitenko 2014). Arsenopyrite of the Suzdal deposit is characterized by submicroscopic grains of gold, which are extremely unevenly distributed (Fig. 2b).

The chemical composition of arsenopyrite in early productive association is non-stoichiometric. The sulphur content is in the range of 21-24 wt. %, S/As ratios in them are 1.16-1.21. Trace elements (according to microprobe analysis), such as Sb, Ni, and Co, were detected. Silver content in monomineralic samples of arsenopyrite of both morphological differences is low, varying within 0.92-9.1 ppm. Other elements were found in an insignificant number of the samples at concentrations close to the detection limit.

The disseminated gold-arsenopyrite mineralization is the main productive stage at the Olympiada deposit (Yenisei Ridge, Russia). It is associated with carbonate-aluminosilicate and siliceous rocks. It represents the main type of gold-bearing ore. Ore-bearing rocks retain the primary layered and rhythmically layered structure with a wide variation of the chemical composition, both in microlayers and in larger strata. The layers are represented by calcareous, carbonaceous-calcareous-aluminosilicate, siliceous and carbonaceous-siliceous rocks and are composed of carbonates, biotite, sericite, chlorite, zoisite, albite, quartz, with the accessories of tourmaline, rutile and apatite. The abundance of finely interspersed pyrrhotite-arsenopyrite mineralization of these rocks is about 3-5%, however its distribution in layered varieties is extremely uneven. They are commonly characterized by a layer-by-layer distribution with individual layers depleted or enriched in sulphides. Petrographic study of thin sections shows that the acicular arsenopyrite is located in a fine-grained quartz-carbonate-micaceous aggregate, locally interspersed with garnet, biotite and zoisite. The gold content in such samples varies from few to tens of ppm. Arsenopyrite occurs a fine-acicular or fine-prismatic crystals. The size of its crystals varies in length from tens to hundreds of microns (Fig. 3a). There are both intergrowths of single crystals and stellar aggregates of arsenopyrite, which resembled the arsenopyrite of the Suzdal deposit discussed above. Commonly, the crystals have a skeletal structure and contain inclusions of pyrrhotite. Timing relationships of these minerals are not always unequivocally established.

Fine grains of high grade gold were detected in the acicular arsenopyrite. It can also be determined by HRXCT. The monomineralic fractions of acicular arsenopyrite from the OK-108 sample, analyzed by the atomic absorption method, contain 348 ppm Au and 0.92 ppm Ag. The chemical composition of acicular arsenopyrite, according to EMPA, is given in Table 1. The most analyses of arsenopyrite reveal its non-stoichiometric varieties enriched in sulfur and depleted in arsenic. Nickel and Co contents in arsenopyrite is mainly in amounts of up to 0.045 and 0.14 wt. %, respectively.
Figure 2. Aggregates of gold-bearing arsenopyrite crystals (sample Su-27) from the Suzdal deposit (East Kazakhstan). a. A scanning electron microscope image. b. BSE image of arsenopyrite with highlighted points of gold content determined by micro X-ray analysis (wt. %). c and d - HRXCT 3D reconstruction: c – opaque appearance of arsenopyrite; d – arsenopyrite grain is shown in transparent grey contour, the yellow points represent the inclusions of gold.

Table 1. Composition of arsenopyrite in OK-108 sample, Olympiada deposit (in wt. %) (EMPA).

<table>
<thead>
<tr>
<th>S</th>
<th>As</th>
<th>Ni</th>
<th>Fe</th>
<th>Au</th>
<th>Sb</th>
<th>Co</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.02</td>
<td>44.19</td>
<td>0.026</td>
<td>33.60</td>
<td>0</td>
<td>0.23</td>
<td>0.069</td>
<td>99.14</td>
</tr>
<tr>
<td>20.75</td>
<td>44.43</td>
<td>0.045</td>
<td>33.56</td>
<td>0</td>
<td>0.295</td>
<td>0.087</td>
<td>99.17</td>
</tr>
<tr>
<td>20.85</td>
<td>44.82</td>
<td>0.016</td>
<td>33.43</td>
<td>0.057</td>
<td>0.23</td>
<td>0.063</td>
<td>99.47</td>
</tr>
<tr>
<td>21.14</td>
<td>44.10</td>
<td>0.024</td>
<td>33.58</td>
<td>0.047</td>
<td>0.215</td>
<td>0.068</td>
<td>99.19</td>
</tr>
<tr>
<td>20.57</td>
<td>43.90</td>
<td>0.033</td>
<td>33.73</td>
<td>0.005</td>
<td>1.202</td>
<td>0.063</td>
<td>99.52</td>
</tr>
<tr>
<td>19.75</td>
<td>46.76</td>
<td>0</td>
<td>33.40</td>
<td>0</td>
<td>0</td>
<td>0.143</td>
<td>100.06</td>
</tr>
</tbody>
</table>

Analyses were carried out at the IGM SB RAS.

4. Conclusions

Three-dimensional HRXCT reconstruction revealed micro-inclusions of native gold in the central parts of the acicular crystals and aggregates of the arsenopyrite of Suzdal and Olympiada deposits (Figs. 2, 3), although previously, researchers assumed the presence of exclusively “invisible” gold in unspecified form in such acicular crystals. Moreover, gold micro-inclusions were found as well in the acicular arsenopyrite from the Olympiada deposit (Naumov et al. 2015). In addition, according to HRXCT studies of gold distribution in large crystals of arsenopyrite from ores of the Bazovskoye deposit (Yakutia, Russia), it was found that gold shows selective crystallization not only within the aggregate of arsenopyrite crystals in the ore zone, but also among the crystallographic directions of a single arsenopyrite crystal. The question remains unanswered whether these crystallographic directions are planes in the areas of tension during deformation of arsenopyrite aggregates or planes most energetically favorable for gold crystallization (Voitenko, 2014).

In general, methods of high-resolution X-ray microtomography allow one to reliably identify dense phases, such as inclusions of native gold in crystals of a mineral-concentrator (arsenopyrite, pyrite) without destroying the hosted mineral grains. This technique permits:

1. To do some estimation of the amount of gold inclusions in minerals or host rocks and draw reasonable conclusions about the gold content of the ores.

2. To study in detail the distribution patterns of metal inclusions (associated with certain minerals, cracks, crystal growth faces, etc.) and to preliminarily evaluate the morphology of grains and veinlets without destroying the matrix.
3. Applying complex methods (HRXCT combined with quantitative analysis of gold content) to determine the form of the metal; to define which type of gold makes the greatest contribution to the economic productivity of mineralization - the inclusion of native gold or "invisible" gold in the form of nanoparticles or structural impurities.

4. HRXCT studies offer new opportunities for the development of efficient technologies for ore processing in order to maximize the extraction of the gold, silver or PGE minerals.

Acknowledgements

The study was supported by state assignment project 0330-2016-0001 and performed according to Research agreement with St. Petersburg State University No С-103/11 signed 08.09.2017.

References


Constraining the source of the alluvial gold from the Whiteadder river drainage, SE Scotland

Abdulkadir, A.M.¹,², Cunningham J.K.¹, Beard, A.D.¹, Smith, A.S.³
¹ Department of Earth and Planetary Sciences, Birkbeck College, University of London, UK
² Department of Earth Sciences, University College London, UK
³ Helmsdale, Allanton, Duns, UK

Abstract. Alluvial gold grains panned from the Whiteadder River drainage, SE Scotland, are much larger than previously reported. Morphological studies tentatively indicate a maximum dispersal distance of 7.5 km. However, this does not constrain potential sources, since the study area is geologically diverse, supporting a wide range of potential gold mineralisation styles, from orogenic to low T oxidising hydrothermal. A Devonian palaeplacer is also possible, but neither Au grains nor associated heavy minerals were panned from the basal conglomerate matrix. Microchemical characterisation studies reveal heterogeneity both between grains and within individual grains with Ag ranging up to 44% and Cu to 5%; however, grains of pure gold up to 98% Au also occur. Rimmed and non-rimmed grains occur, but chemical heterogeneity is also expressed by sharp boundaries between areas of materially different Ag levels within non-rimmed grains. Mineral inclusion analysis conducted so far has identified only quartz and feldspar (albite), Hg is apparently absent and a possible Pd occurrence is unconfirmed. While low levels of Te exist, the apparent absence of inclusions such as Hg, Pd, Bi tellurides and sulphosalts limit the possibility of constraining the type of source. Current work will expand the data set to confirm microchemical signature/s, and thereafter enable mapping of mineralisation style to potential source.

1 The study area

The study area is located in the Duns area, Southern Scotland, in Berwickshire, near the English and Scottish border. The local geology (Fig. 1) is dominated by turbidites that been regionally metamorphosed to low–grade greenschist facies (Stone et al. 2012). These rocks were intruded by the large granitoid bodies of Priestlaw and Cockburn Law of late Devonian age (Thirwall 1988). Zoning of the Priestlaw pluton involves noritic and basic pyroxene-mica granodiorite compositions. The metasediments around the Cockburn Law pluton have been hornfelsed up to 1 km in width. Alteration of both sediments and the intrusions took place in two phases (Shaw et al. 1995), the first including sulphide veining and the second which oxidised the sulphides and deposited Fe-oxhydroxides and hematite during renewed fracturing. The first phase is compatible with mesothermal orogenic gold mineralisation. However, the oxidised character of the second phase is compatible with the circulation of high E-h and Fe-rich meteoric water following uplift during the early Devonian.

2 The panning campaign

The panning campaign was focused on the area (Fig. 1) near Duns included in the UK government Mineral Resource Program (Shaw et al. 1995), which was conducted by the British Geological Survey (BGS hereafter). Gold panning was carried out within an area of approximately 180 km². The initial process was to sample the sites studied by the BGS to confirm the existence of Au; some sites were reported to exceed 5000 ppb Au. At each site, an attempt was made to ensure comparability by adopting a consistent method. Thus, 10 pans were processed at each location to determine if visible gold could be found in stream/drainage sediments.

Additional pans were taken at locations nearby to those listed by BGS. The total number of pans handled in the year was circa 400. After completion of the BGS sites, sites at Preston Bridge and Stoneshiel Hill were identified as exceptional, with Au grains up to 2.15 mm, much larger than those previously reported by BGS. In 181 panned concentrate samples, BGS recovered gold grains in the size range 0.1-0.3 mm, from sites draining from the Lower Palaeozoic rocks and, notably, none from downstream west of the Devonian conglomerate.

The size of these grains is notable, since visible gold was not detected by BGS from bedrock studies in the project area. In our study, the gold-associated mineral arsenopyrite was detected in the country rock-hosted Hoardweel mine where 1,333 ppb Au had previously been assayed by BGS in minor heavily altered diorite veins. This mine was worked for Cu, rather than gold, and...
visible gold was not reported by BGS from rock samples in the mine or found in our study. The gold grains obtained, together with the heavy minerals consistently associated with them, were prepared for morphogenetic and microchemical analysis following well-established methods (Leake et al. 1992; Knight et al. 1999b; Chapman et al. 2000).

3 Morphogenetic studies

The Au grains collected during this study exhibit a range of size and shape (Fig. 2). There appears to be more than one size population of grains within the project area: coarse grains of >2.15mm, medium grains 1mm to 1.5mm and finer grains of <0.1mm. The shape varies from high angularity, through rounding, to flattening. Significant morphological change in alluvial gold grains is attributed to the distance of travel, or time spent in the fluvial environment (Youngson and Craw, 1999), with two physical weathering processes, hammering and abrasion, causing rounding and flattening (Knight et al. 1999a).

![Figure 2. Four placer Au grains collected during this study that exhibit a range of shapes and sizes; a) Shows angularity with dark minerals; b) Low sphericity and broken edges; c) Rounded edges and flattened surface; d) Distinctive shape and low sphericity with black heavy minerals which are hematite, magnetite and limenite](image)

The parameters which have been used in this study to establish relationships between grain morphology and distance of alluvial transport are: (1) grain outline, (2) surface feature and (3) grain flatness. Results indicate a range of distances. Grains with high angularity/low flatness and surface striations indicate little distance from the source. The presence of extremely flattened grains, permit maximum distances to be estimated at 5 km for Stoneshiel Hill and 7.5 km for Preston Bridge, but caution is required since morphological modification is dependent upon the energy of the fluvial system (Crawford, 2007, Wrighton, 2009).

4 Microchemical analysis

Individual larger gold grains were handpicked using fine-tipped tweezers, mounted in a 25mm diameter epoxy resin blocks and then polished to an (0.25 μm) optical finish using diamond polishing pastes. Samples of the heavy mineral fractions were also mounted as polished blocks. Major element analyses of the gold were obtained using a Jeol JXA8100 Super-probe (WDS) and an Oxford Instruments AZtec system (EDS) at Birkbeck. The analysis was carried out using an accelerating voltage of 15 kV, current of 2.5 × 10⁻⁸ μA, and a beam diameter of 1 μm. The counting times were 40 s on the peak and 20 s each on the high and low backgrounds. Analyses were calibrated against standards of Spec-pure metals with the data corrected using a ZAF program.

![Figure 3. WDS elemental distribution maps for Ag, Au, Cu, of a single gold grain sampled from Stoneshiel Hill showing significant variation in the composition between the Ag and Au contents](image)

Ag, Cu and Te are present in detectable amounts in the gold grains, with trace amounts of the associated elements such as Se, Co, Ni, Zn, Cd and Sb also present in most of the grains. Notably, no Hg, As or Pb was detected. Levels of Ag are dominant but vary widely within grains and between grains. Grains with no rim from Stoneshiel Hill and Preston Bridge are nearly pure Au (99 - 98.5%). Analyses from the cores of rimmed grains range up to 22% Ag at Stoneshiel Hill. Some of the Preston Bridge rimmed gold grains contain cores where Ag exceeds 44 wt.% Cu levels are generally between 0.1 to <5 wt.%, and in some grains below the detection limit. Levels of Cu appear to follow the pattern of variation in Ag content. While leaching of Ag from the rims, thin or wide, can explain the Ag patterns discussed so far, the pattern in one grain (Fig. 3) cannot be explained by leaching; it may be related to the evolution of hydrothermal fluids (Chapman et al. 2009).

This grain has no rim, but within the grain, chemical heterogeneity is expressed as sharp borders between areas of widely varying Ag content. Thus, 20 spot
analyses in one area were <2 wt % Ag, while the adjacent area showed a range of 17-22 wt % Ag.

Another grain which departs from a simple Ag depleted rim pattern (Fig. 4) demonstrates that leaching may be deeply penetrating cracks within this grain. Cumulative percentile plots of the Ag contents of 21 gold grains from the two main sites are given at Fig. 5, potentially indicating the relative enrichment of Ag in the downstream site. However, microchemical analysis is in progress at the date of submission and we urge caution while making this generalisation. Finally, the inclusions found so far in grains from both sites were quartz and feldspar (albite), and no elements/minerals associated with particular microchemical signatures, such as Pd (one unconfirmed identification in one small grain), Hg, bismuth tellurides or sulphosalts (Chapman et al. 2009, 2018) have been found so far.

5 Associated heavy minerals

The alluvial gold in the study area is associated with heavy minerals, which are often used as an Au indicator (e.g. Gleeson and Boyle, 1980). These are hematite, ilmenite and magnetite in typically rounded grains, with some (<25%) stained quartz crystals and alkali feldspar which passed through the sieves. No sulphide minerals (pyrite, arsenopyrite, and chalcopyrite) were identified in hand lens, but the microprobe studies show that pyrite, chalcopyrite and arsenopyrite are present within the heavy minerals. No gold was found within the heavy minerals, but a BSE image analysis showed the presence of monazite, a common accessory mineral in granitic rocks. Panned concentrates taken from the basal Devonian Conglomerate matrix did not contain gold or the heavy minerals associated with the alluvial gold panned during this project at Stoneshiel Hill and Preston Bridge.

Figure 4. WDS elemental element map of grain from Preston Bridge - Au yellow/Ag blue

6 Discussion

The gold grains panned from the Whiteadder River drainage are relatively large, compared to those previously recovered in the area by BGS. The studies carried out to date seek to investigate the origin of this distinctive population of alluvial gold. Morphological characteristics indicate that the grain populations from Stoneshiel Hill, the upstream site, and Preston Bridge, the downstream site, are comparable. They both include grains which are branched and complex in shape, limiting distance from source considerably. However, they also contain flattened/rounded grains suggesting (within the limitations on the methodology noted earlier) a source within a maximum of 5 km for the upstream site and 7.5 km for the downstream site. A small proportion display evolved morphological characteristics which may be inherited from previous cycles of transport and deposition. Mineral inclusion analysis to date shows that most grains contain only inclusions of quartz and albite feldspar. While Te occurs near detection levels in some of the gold grains studied, the apparent absence of the bismuth tellurides and sulphosalts in our work so far may be significant, as is the apparent absence of Hg and the unconfirmed presence of Pd. However, more data is required if alloy chemistry is to be combined with distinctive inclusion chemistry to distinguish between the many microchemical signatures associated with different styles of gold mineralization in Phanerozoic terranes. Mapping these microchemical signatures to mineralisation styles and potential source would be premature. However, the project area gold mineralisation has some similarities with gold deposits at Bohaun, Western Irish Caledonides (Lusty et al. 2011). The veins there have simple mineralogy of quartz-sericite–chlorite with minor sulphides, hematite, rare visible gold with a high silver content (up to 41 wt%), and late barite and dolomite (also present in our study area).
7 Current work

The focus of current work is to confirm the microchemical characterisation, paying particular attention to inclusion mineralogy and chemistry, and also the unusual characteristics of the grains in Fig. 3 and Fig. 4. The objective is to further constrain the possible sources of these relatively large grains of alluvial gold. Acquiring more EMP data to constrain possible microchemical styles is a key priority and this may then require more field work on the Devonian/Silurian contact area if Pd is identified in any grains and the other features of an oxidizing hydrothermal microchemical signature are discovered. The apparent lack of associated heavy minerals in the matrix of the Devonian basal conglomerate noted earlier may need further fieldwork to constrain the possibility of a localised palaeo placer in the study area.

Acknowledgements

This project was partially funded by the School of Science, Department of Earth and Planetary Sciences, Birkbeck College, University of London.

References


Knight JB, Morison SR, and Mortensen JK (1999a) The relationship between placer gold particle shape, rimming, and distance of fluvial transport as exemplified by gold from the Klondike district, Yukon Territory, Canada. Economic Geology. 94:635–648


Youngson JH, and Craw D (1999) Variation in placer style, gold morphology, and gold particle behavior down gravel bedload rivers; an example from the Shotover/Arrow Kawarau Clutha River system, Otago, New Zealand. Economic Geology. 94:615–633
Normalisation of pathfinder element in soil data to aid orogenic gold exploration with an example from southern New Zealand

Adam P. Martin¹, Michael F. Gazley², Rose E. Turnbull¹, Grace Frontin-Rollet³, Delia T. Strong¹
¹GNS Science
²RSC Mining and Mineral Exploration
³NIWA

Abstract. Southern New Zealand is comprised of several distinct basement terranes that have experienced greenschist to zeolite facies metamorphism. The region is actively and historically mined for orogenic gold (± tungsten), but no significant economic deposits have been discovered in the approximately 30 years since world-class gold deposits commenced being developed along the Hyde-Macraes Shear Zone (HMSZ). The Government of New Zealand recently funded an eight-spaced geochemical baseline soil survey over southern New Zealand, in part to aid mineral exploration. In this study, nine orogenic gold pathfinder elements (Ag, As, Au, Bi, Mo, Sb, Sn, Te, W) in subsoil (50 - 70 cm) samples, were z-score normalised using two different matrices to account for lithology and metamorphic grade, both of which vary significantly across the survey area. The resulting interpolated plots show multi-element in soil anomalies associated with known orogenic gold mineralisation, and also, multi-element in soil anomalies in areas were no historical gold mining or exploration has occurred. The latter may warrant further investigation. The importance of normalisation of chemical data in areas of geological complexity is demonstrated and this study shows the value that can be added to multi-element in soil surveys in the exploration for orogenic gold.

1 Introduction

Interrogating the regional patterns of soil chemistry are a well-established exploration tool used in vectoring towards orogenic gold mineralisation (Boyle and Jonasson 1973). Elements typically associated with orogenic gold include silver (Ag), arsenic (As), gold (Au), bismuth (Bi), molybdenum (Mo), antimony (Sb), tin (Sn), tellurium (Te) and tungsten (W), amongst other elements, which can disperse to form a halo many times larger than the orebody itself (Kelley et al. 2006). Measuring these pathfinder elements in soil can potentially vector towards gold mineralisation, but this is made more difficult when the basement geology underlying the soil sites is complicated by faulting, differing lithologies and/or varying metamorphic grade. One way to overcome these difficulties is to normalise pathfinder element in soil data to account for the dominant geological variables. In this study, nine elements in subsoil (50 - 70 cm-depth) sampled on an eight-spaced grid from a geologically complex sample locations

Figure 1. A location and geology map of southern New Zealand. Sample locations are shown as triangle s (1st survey) or circle s (2-survey). The geological map is shown only to highlight the complexity of underlying geology. The reader is referred to online resources for a full discussion of the geology of southern New Zealand (data.gns.cri.nz/geology/).

The southern New Zealand survey area covers approximately 40 000 km² (Fig. 1). The region has had significant, historical alluvial and hard-rock gold mining (Christie 2016) and gold is actively mined along a c. 30 km length of the regionally significant, Hyde-Macraes Shear Zone (Allibone et al. 2018; Doyle et al. 2016). The region is underlain by a varied basement geology, overprinted by zeolite to upper greenschist facies metamorphism. The data were z-score normalised (auto scaled) using two different matrices to remove the bias from stratigraphy and metamorphic grade in the chemical data, which are the two strongest controls on soil chemistry in this region (Martin et al. 2016). Interpolated plots of the data were mapped, and the chemical patterns discussed.

Gold from Orogenesis to Alluvial 811
Figure 2 Arsenic data used in this study. A. Raw data. B. Data after z-score transformation to account for stratigraphy and metamorphic grade. The tight overlap in distribution curves in the normalized data suggests that most of the variance has been accounted for by stratigraphy and metamorphic grade; this is in agreement with other studies.

2 Results

Following Singer and Kouda (2001) the data for the nine pathfinder elements (Ag, As, Au, Bi, Mo, Sb, Sn, Te, W) were transformed and standardised by implementation of a z-score normalisation whereby the element mean in a population is subtracted, and then divided by the standard deviation of that element in that population. This was done sequentially, first accounting for lithology and then for metamorphic grade. Distribution plots of the treated data are tight relative to the untreated data (Fig. 2) suggesting that lithology and metamorphic grade account for most of the variation. Examples of the interpolated plots of these results (Fig. 3) show regional variation unrelated to lithology or metamorphic grade.

2.1 Arsenic

In the normalised data many high arsenic anomalies occur at the mapped boundary of the Caples and Rakaia terranes (Fig. 3). High As anomalies in Rakaia Terrane rocks are associated with the Hyde-Macraes Shear Zone, and several other orogenic gold mine sites (Fig. 3). Other orogenic gold deposits are associated with As lows (Fig. 3). In the west of the survey area, orogenic gold deposits are associated with high As anomalies. Known orogenic gold deposits in the Caples Terrane are associated with As lows. Arsenic mobility in schist rock has been inferred to increase with increasing metamorphic grade, up to and including, biotite facies (Pitcairn et al. 2010).

3 Discussion

3.1 Select pathfinder element associations

Prior to this study, As had been considered the most useful pathfinder element in soil for orogenic gold mineralisation along the Hyde-Macraes Shear Zone. The regionally significant, multi-element in soil anomaly in the data from this study, associated with the mined section of the Hyde-Macraes Shear Zone, suggests additional pathfinder elements may be useful. Differences between the northwest and southeast ends of the mined portion of the Hyde-Macraes Shear Zone are evident in the soil chemistry data, with the southwest-end high in W and Sb, relative to the northeast-end that is high in Ag, Au, Mo, Sn and Te. Chemical variation along the Hyde-Macraes Shear Zone has been suggested previously, for example in Hg content of gold grains (MacKenzie and Craw 2005) or the presence or absence of siderite veins (Jones et al. 2007).

Different pathfinder elements in soil are associated with Mesozoic-aged orogenic gold relative to Miocene-aged orogenic gold in southern New Zealand. Mesozoic gold mineralisation is typically associated with high As, Au and Sb and low Bi, Sn and Te in soil. Miocene gold mineralisation here is associated with low Ag, Bi, Mo, Sn and W, and moderate Au, Sb and Te anomalies in soil. Variability in the mineral chemistry and bulk chemistry of orogenic deposits in East Otago has been well documented (e.g. Craw et al. 2007; MacKenzie and Craw 2005; Patterson 1986). Of relevance is the breakdown of pyrite to pyrrhotite in the Otago Schist releasing Au, As, Ag, Hg and Sb (Cave et al. 2017; Pitcairn et al. 2010), and the breakdown of rutile to titanite releasing W and As (Cave et al. 2017; Cave et al. 2015).
3.2 Implications for orogenic gold exploration in southern New Zealand

It is generally thought that the geochemical footprint of the Hyde-Macraes Shear Zone is subtle and on the scale of metres to hundreds of metres (e.g. Jones et al. 2007), with enrichment of As and Au and the breakdown of metamorphic titanite to rutile (Craw et al. 2007; Pitcairn et al. 2006). This study suggests a Hyde-Macraes Shear Zone size deposit has the potential to be detected by multiple pathfinder elements in subsoil (50 – 70 cm-depth) samples collected on an eight-spaced grid. The timing and pressure-temperature conditions under which mineralisation occurred affects which minerals form and breakdown, and element mobility (Cave et al. 2017; Pitcairn et al. 2010), leading to variation of pathfinder element and concentration associated with each deposit. Consideration of the element associations and concentrations in soil survey samples should suggest the mineralisation style present in southern New Zealand.

4 Summary and conclusions

Nine pathfinder elements (Ag, As, Au, Bi, Mo, Sn, Te, W) in soil, useful in exploration for orogenic gold, were z-score normalised using two different matrices to account for lithology and metamorphic grade, which vary significantly across the survey area. The close spatial correlation between historic orogenic gold deposits and high pathfinder element anomalies supports the suitability of this treatment of the data. Different pathfinder element associations are found between deposits of a similar style, and between deposit styles. This relates to the timing of mineralisation, the pressure-temperature conditions during formation, the breakdown of rutile to titanite releasing W, and the breakdown of pyrite to pyrrhotite releasing, amongst other elements, Ag, As, Au, Sb and Te, during regional metamorphism. The actively mined portions of the Hyde-Macraes Shear Zone stand out as a regionally significant, multi-element anomaly in the soil chemistry. This deposit has a chemical footprint in soil that is shown to be detectable at an eight - sample spacing, considerably greater than the chemical footprint previously inferred from hard-rock samples. Soil chemistry along strike of the Hyde-Macraes Shear Zone varies, hinting at a complexity in the alteration chemistry associated with mineralisation along this feature. Several parts of the survey area, which have not been previously mined and have been explored only at a reconnaissance level (if at all), have multiple soil element anomalies similar to those in soil collected above orogenic gold deposits in the region. These areas may reward additional exploration effort. This study demonstrates the usefulness of analysing for multiple pathfinder elements in soil samples when searching for orogenic gold deposits, in southern New Zealand and elsewhere. It also highlights the utility of regional geochemical soil baseline surveys and the benefit of careful data treatment to avoid false positives.

Acknowledgements

The collection of soil samples that this work is developed from was funded by the Government of New Zealand through a GNS Science strategic development fund, Ministry of Business, Innovation and Employment and New Zealand Petroleum and Minerals.

References


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


The giant Muruntau deposit (Uzbekistan) – Au-Bi-Te-W type of orogenic gold deposits hosted by black shales

Rustam Koneev  
National University of Uzbekistan, Tashkent, Uzbekistan

Reimar Seltmann, Alla Dolgopolova  
Natural History Museum, Department of Earth Sciences, CERCAMS, London, UK

Mamat Karabaev  
Institute of Geology and Geophysics, Tashkent, Uzbekistan

Abstract. Mineralization of the Muruntau ore field was studied using electron microscopes and microanalyzers. In result, a standard series of mineral-geochemical ore types has been established: /Au-W/Au-Bi-Te/Au-As/Au-Ag-Te/Au-Ag-Se/Au-Sb/Au-Hg/. The industrial resource of gold is determined by /Au-Bi-Te/ and /Au-As/ types combined with /Au-W/. Native gold and maldonite nano-inclusions were identified in arsenopyrite and pyrite. The Muruntau deposit is proposed to be classified as Au-Bi-Te-W type of orogenic gold deposits hosted by black shale strata and associated with intrusions.

1 Introduction

The Muruntau gold deposit is one of the largest gold deposits in the world, one of the top-10 members in terms of reserves and annual production. From the moment of discovery, the deposit was classified as “quartz-pyrite-arsenopyrite-gold ore formation” (I.Kh. Khamrabayev), then “gold-quartz geological-industrial type” with the gold-scheelite-quartz association (I.M. Golovanov). In recent years, Muruntau has been referred to orogenic deposits (Groves et al. 1998) or “black shale” deposits in “carbonaceous-terrigenous strata” (M.S. Rafailovich, S.G. Kryazhev). Vasilevsky et al. (2004) assigned the Muruntau deposit for the first time to the “gold-tellurium-bismuth-rare-metal” type, formed by the standard series of geochemical types /Au-W/Au-As/Au-Te/Au-Ag/Au-Sb/Au-Hg/.

2 Methodology

From the study of refractory gold ores hosted by primary sulfides, we can conclude that contained gold is a typical nano-mineral, ranging in size from 100 to 0.001 μm, represented by the native metal or compounds with Bi, Sb, As, Te, Se, Hg, which is distinguished in arsenopyrite, pyrite, quartz, antimonite, less often in other minerals. The study of such ores was made possible thanks to the methods and approaches developed in nanotechnology (Koneev et al. 2010). The main focus of the research was on sulphides of gravity concentrates from which gold is extracted; non-metallic minerals and carbonaceous matter are wastes from the ore enrichment.

Studies were conducted on Cameca SX-50 electron probe microanalyzer at NHM London; Superprobe 8800R in the IGG of the State Committee on Geology of the Republic of Uzbekistan, Carl Zeiss (SEM-EDX) at the Center for Advanced Technologies, Tashkent.

3 Geology of ore field

Descriptions of the geological structure of the Muruntau ore field and of the Kyzykum region are numerous (Kempe et al. 2015, 2016; Dolgopolova et al. 2017; and references therein).

The deposits of the Muruntau ore field are confined to the South Tienshan orogenic belt or the Turkestan Accretionary Complex of the Kyzykum-Nurata segment (Fig. 1). The deposits are located in the rocks of the Besapan Formation (Fig. 2), at the intersection point of the sub-latitudinal fault of the Muruntau-Kosmanachi direction and the South-Western Muruntau-Daugyztau fault. The ages of granitoid intrusions of the Kyzykum region and of arsenopyrite (Muruntau pit “central vein”) and molybdenite (Myutenbay pit) from gold ores are consistently at ~285-295 Ma (Morelli et al. 2007; Seltmann et al. 2008). At the Muruntau ore field, the intrusion of the Murun granite was opened by the SG-10 deep drill hole at a depth of 4005 m. Recent studies link it with the massive thermal aureole contributing to the uniqueness of the gold deposit (Wall et al. 2004).

4 Research results

Previously carried out geochemical studies of the ores of Muruntau and Myutenbay (Koneev et al. 2010; Vasilevsky et al. 2004) showed that, compared to the average contents of gold and associated elements in the Earth’s crust (Clarke values), the abundances of Au, As,
Figure 1. a) Tectonic setting of the Altaids collage; b) Location of key mineral deposits in the Tien Shan with relations to major terranes (after Seltmann et al. 2014).

Figure 2. Geological sketch of the Muruntau region: ts1, ts2 - Lower and Upper Taskazgan; bs1-4 - Grey, black, variegated, green Besapan; Mz-Kz – Meso-to Cenozoic platform cover. Super-deep borehole SG-10 and deep satellite boreholes MS-1 to 4 are also indicated (after Kremenetsky in Kempe et al. 2015).

Table 1. Chemical composition of bismuth minerals from the Muruntau ore field deposits (mass.%)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Au</th>
<th>Ag</th>
<th>Bi</th>
<th>Sb</th>
<th>As</th>
<th>Te</th>
<th>Se</th>
<th>S</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maldonite Au₂Bi</td>
<td>62.08</td>
<td>0.63</td>
<td>34.29</td>
<td>-</td>
<td>-</td>
<td>0.34</td>
<td>2.09</td>
<td>-</td>
<td>99.43</td>
</tr>
<tr>
<td></td>
<td>64.68</td>
<td>-</td>
<td>34.80</td>
<td>0.72</td>
<td>-</td>
<td>-</td>
<td>0.18</td>
<td>-</td>
<td>100.38</td>
</tr>
<tr>
<td></td>
<td>64.25</td>
<td>-</td>
<td>35.32</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.76</td>
<td>-</td>
<td>100.33</td>
</tr>
<tr>
<td>Hedleyite Bi₃Te₃</td>
<td>-</td>
<td>-</td>
<td>77.00</td>
<td>-</td>
<td>-</td>
<td>22.98</td>
<td>0.27</td>
<td>-</td>
<td>100.25</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
<td>0.22</td>
<td>76.96</td>
<td>0.38</td>
<td>-</td>
<td>20.23</td>
<td>1.45</td>
<td>-</td>
<td>99.02</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>74.23</td>
<td>-</td>
<td>-</td>
<td>23.37</td>
<td>2.43</td>
<td>-</td>
<td>100.03</td>
</tr>
<tr>
<td>Se- hedleyite Bi₁(Te,Se)</td>
<td>-</td>
<td>0.21</td>
<td>0.87</td>
<td>78.32</td>
<td>-</td>
<td>-</td>
<td>11.62</td>
<td>7.98</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>0.81</td>
<td>76.48</td>
<td>-</td>
<td>-</td>
<td>12.51</td>
<td>8.67</td>
<td>1.08</td>
<td>98.74</td>
</tr>
<tr>
<td>Pilsenite Bi₄Te₂</td>
<td>-</td>
<td>-</td>
<td>65.15</td>
<td>0.70</td>
<td>-</td>
<td>32.79</td>
<td>1.70</td>
<td>0.26</td>
<td>100.6</td>
</tr>
<tr>
<td></td>
<td>0.61</td>
<td>0.25</td>
<td>65.50</td>
<td>0.63</td>
<td>-</td>
<td>33.37</td>
<td>1.21</td>
<td>0.23</td>
<td>100.94</td>
</tr>
<tr>
<td>Tsumoite Bi₄Te</td>
<td>-</td>
<td>-</td>
<td>61.85</td>
<td>-</td>
<td>-</td>
<td>38.31</td>
<td>-</td>
<td>0.66</td>
<td>100.82</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>61.87</td>
<td>-</td>
<td>-</td>
<td>35.03</td>
<td>3.62</td>
<td>-</td>
<td>100.52</td>
</tr>
<tr>
<td>Tellurobismuthite Bi₂Te₃</td>
<td>-</td>
<td>-</td>
<td>55.14</td>
<td>-</td>
<td>-</td>
<td>43.75</td>
<td>-</td>
<td>0.26</td>
<td>99.15</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td>0.87</td>
<td>78.32</td>
<td>-</td>
<td>-</td>
<td>11.62</td>
<td>7.98</td>
<td>0.94</td>
<td>98.86</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
<td>0.81</td>
<td>76.48</td>
<td>-</td>
<td>-</td>
<td>12.51</td>
<td>8.67</td>
<td>1.08</td>
<td>98.74</td>
</tr>
<tr>
<td>Joséite A Bi₄TeS₂</td>
<td>-</td>
<td>-</td>
<td>81.60</td>
<td>-</td>
<td>-</td>
<td>9.78</td>
<td>1.46</td>
<td>7.16</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>81.81</td>
<td>-</td>
<td>-</td>
<td>9.56</td>
<td>2.54</td>
<td>6.09</td>
<td>100.00</td>
</tr>
<tr>
<td>Joséite B Bi₄Te₂S</td>
<td>-</td>
<td>-</td>
<td>74.15</td>
<td>1.42</td>
<td>20.58</td>
<td>-</td>
<td>2.64</td>
<td>-</td>
<td>98.80</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>74.69</td>
<td>-</td>
<td>-</td>
<td>21.83</td>
<td>0.24</td>
<td>2.93</td>
<td>99.69</td>
</tr>
<tr>
<td>Ingodite Bi₄TeS</td>
<td>-</td>
<td>-</td>
<td>72.70</td>
<td>2.40</td>
<td>22.10</td>
<td>0.20</td>
<td>4.11</td>
<td>-</td>
<td>101.51</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>72.06</td>
<td>-</td>
<td>-</td>
<td>22.13</td>
<td>-</td>
<td>5.03</td>
<td>99.22</td>
</tr>
<tr>
<td>Sulphotsumoite Bi₃Te₃S</td>
<td>-</td>
<td>-</td>
<td>68.19</td>
<td>-</td>
<td>-</td>
<td>26.83</td>
<td>1.63</td>
<td>3.59</td>
<td>100.24</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>68.45</td>
<td>-</td>
<td>-</td>
<td>26.52</td>
<td>1.39</td>
<td>3.84</td>
<td>100.20</td>
</tr>
<tr>
<td>Tetradymite Bi₂Te₂S</td>
<td>-</td>
<td>-</td>
<td>58.06</td>
<td>0.62</td>
<td>36.03</td>
<td>1.63</td>
<td>4.31</td>
<td>-</td>
<td>100.65</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td>58.03</td>
<td>0.57</td>
<td>35.29</td>
<td>1.14</td>
<td>4.55</td>
<td>-</td>
<td>99.58</td>
</tr>
</tbody>
</table>
Table 2. Stages of the hydrothermal process and the sequence of mineralization of the Muruntau ore field

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Stages of mineral formation (ore types)</th>
<th>The introduction of syenito-clarites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheelite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molybdinite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi sulfotellurides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi tellurides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfarsenomuthides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb, Sb, Ag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maldonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gold (950-950 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-arsenopyrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-pyrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penetlandite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobaltite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanogold</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hessite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stützite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Altaite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acartite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naumannite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aguilarte</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Claustralite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrum (750-400 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antimonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfarsenomuthides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe, Cu, Ag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gold (800-850 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cinnabar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kongsbergite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg-gold</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Te, Bi are enriched in the ores by factor 100-1000; Ag, Se, Sb, W and Mo still by factor 10 and more. The concentration ratios of the remaining ore elements do not exceed single units.

In addition to gold, maldonite (Au2Bi), tellurides, and Bi sulphotellurides (Table 1) are often found in primary ores, which form close intergrowths and micro-nano-ensembles in the matrix of arsenopyrite and pyrite (Fig. 3, line I). In gold-bearing arsenopyrite, zones enriched with gold are distinguished; micro-nanoparticles of native gold and arsenopyrite are observed in arsenic pyrite; gold also forms larger particles and plates (films) in arsenopyrite (Fig. 3, line II). In arsenopyrite, nanoparticles have spherical, oval and film forms of gold, maldonite and headleyite with sizes of 308-670 nm (Fig. 3, line III).

Ore bodies of the Muruntau deposit represent a combination of different types of gold ores: /Au-W/Au-Bi-Te/Au-Ag-Se/Au-Sb/Au-Hg/ (Tab. 2). However, the industrial resource of gold is determined only by two types: /Au-Bi-Te/ and /Au-As/, which, together with the low-gold Au-W type, contain 85% of the Au reserves at Muruntau.

5 Discussion

Why is the definition of the Muruntau deposit as an Au-Bi-Te-W type important for understanding the genesis, sources of gold, gold distribution, ore processing and ore recovery issues? In recent years, Au-Bi-Te-W type is considered as a type of gold deposits related to or associated with intrusions (Baker et al. 2005). Such deposits include Kidston, Fort Knox, Timbarra, Pogo, as well as Jilau (Tajikistan). The latter is an Au-W deposit with arsenopyrite-pyrite, chalcopyrite-pyrrhotite and gold-bismuth-telluride associations in skarns and granitoids. Also at Muruntau, skarnification was observed locally in drill core in the form of characteristic skarn minerals (diopside, hedenbergite, garnets). Geochemically, the presence of Hg, Te, Ni, and Co is considered as indicators of deep sources. In chondrites, their average content is ten times higher than in the rocks of the Earth's crust (g/t): Au – 0.17-0.0043; Te – 0.5-0.001; Hg – 3-0.083; Ni – 1%-58. According to the results obtained, Muruntau represents the Au-Bi-Te-W type of orogenic gold deposits associated with granitoid intrusions but the size and uniqueness of this complex mineral system can only be explained by the involvement of deep crust or mantle processes.

Acknowledgements

The research was conducted with the support of the OT-F8-01 grant of the Ministry of Innovation Development of the Republic of Uzbekistan.

References


http://dx.doi.org/10.1016/j.gsf.2015.09.005


Impurities in pyrite from the gold deposits of Central Aldan ore area (Sakha-Yakutia, Russia): study using LA ICP-MS

Elena V Belogub, Konstantin A Novoselov, Dmitriy A Artem’ev
Institute of Mineralogy RAS, Miass, Russia

Olga N Filimonova
Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry RAS, Moscow, Russia

Abstract. Composition of pyrite from Samolazovskoe, Lunnoe and Ryabinove gold deposits (Central Aldan ore region, Russia) was studied using optical, SEM and LA-ICP-MS methods. It was found that fine-grained aggregates of pyrite from the fluorite-bearing ores of Lunnoye and Samolazovskoe deposits are highly enriched with Au, Ag, Tl, As, Sb and Hg, compared to euhedral pyrite from the same ores as well as subhedral and euhedral pyrite from ores of Ryabinove deposit. Typical for gold-bearing pyrites Au-As correlation is less pronounced in the studied fine-grained iron disulfide aggregates than that of Au-Sb and Au-Tl. X-ray absorption spectra show a statistical distribution of isomorphic Au and As in the pyrite structure. It is possible that such behavior of Au is characteristic for fluorite-containing metasomatic association which had high activity of Tl, Sb, As and Hg during its formation. Also, high growth rate of pyrite promotes the capture of impurities.

1 Introduction

Pyrite is one of the major gold companions in sulfide ores of deposits of various genetic types. Pyrite impurities reflect ore formation conditions (Large et al., 2007, 2009 et al.) Often, pyrite concentrates gold, which leads to considerable difficulties in the processing of ores. Gold in pyrite is either chemically bound or forms micro-inclusions of Au own minerals. Various forms of gold and sets of impurities in ores require specific approaches to ore processing. In situ use of highly sensitive inductively-coupled plasma mass spectrometry (ICP-MS) with laser ablation (LA) allows not only to analyse the impurities, but also to determine their distribution in minerals and evaluate the compositions of minerals they form.

Pyrites from sulfide ores of four now exploiting deposits of Central Aldan ore area were studied. These deposits represent different genetic types and technological species of ores. Our aim is to compare the patterns of distribution of gold and associated impurities in pyrite from these deposits.

2 Methods

Before LA-ICP-MS analysis petrography of ores was studied using optical (Axioscope A.1) and scanning electron microscopy (Vega3 Tescan with EDA). The analyzes of pyrite composition were carried on an Agilent 7700x mass spectrometer with laser console New Wave Research UP-213 and software package MassHunter. Pressed sulfide USGS MASS-1 and glass NIST SRM-612 standards were used for calibration and calculation [Wilson et al., 2002, Danyushevsky et al., 2011]. The calculation was performed on the lolite software using 57Fe as an internal standard.

One sample of fine-grained Au-bearing arsenian pyrite from Samolazovskoe deposit was studied by means of X-ray absorption spectroscopy. The Au L3-edge and As K-edge X-ray absorption spectra were recorded at BM16 FAME-UHD beamline of ESRF (Grenoble, France). The High Energy Resolution Fluorescence Detection mode (HERFD) was used to record Au spectrum. Simultaneously the Total Fluorescence Yield (TFY) As spectrum was acquired.

3 Geological outline

The Central Aldan ore region (CA) is located on the Aldan shield - a protrusion of the crystalline basement of the Siberian platform. The geological structure of the area is two-tiered. The lower tier is crystalline basement composed of Early Proterozoic gneisses and crystalline schists cut by Proterozoic intrusions of normal and moderately alkaline granitoids. The upper tier is a platform cover formed by Vendian - Lower Cambrian carbonate and Jurassic terrigenous rocks. Gold deposits are genetically associated with Mesozoic alkaline and subcalcine intrusives and hydrothermal alteration of Pre Mesozoic rocks in tectonic zones [Borisenko et al., 2011]. CA includes about 96 % of ore gold reserves and 66 % of alluvial gold of South Sakha [Volkov, Kochetkov, 2009]. Many of these deposits are currently exploited.

In addition to oxidized ore there are several technological types of primary gold ores of CA: 1) zones with Au-U mineralization associated with pyrite-sericite-carbonate-KFs±fluorite alteration of Proterozoic gneisses and granitoids (Lunnoe deposit); 2) Veinlet-disseminated ores associated with roscoelite-carbonate-fluorite-quartz alteration of syenite (Samolazovskoe deposit); 3) veinlet-disseminated Au-Cu-porphyry (Ryabinove deposit, Muscovite limb) or Au-porphry (Ryabinove deposit, Noviy limb) ores in Mesozoic alkaline intrusives. We do not consider skarn type ores and Au-quartz veins which are also present in the CA. Average gold content in ores usually varies from 1 to 10 ppm, rarely reaching 30 ppm.
4 Mineralogy of ores

The *Lunnoe deposit* is represented by several zones of alteration confined to the sublatitudinal long-lived faults. The main ore minerals are iron disulfides. Extremely fine-grained massive pyrite-marcasite aggregates and larger euhedral pyrite crystals form uneven impregnations in metasomatites and sometimes are present in quartz-fluorite veins. Native gold, chalcopyrite, sphalerite, pyrrhotite, acanthite, magnetite, hematite, titanium oxides (leucoxene), brannerite, uranium micas [unpublished data Grechishnikov et al., 2013], Te-canfieldite, hessite, and Ag-Tl sulfosalts (our data) were found as rare minerals.

At the *Samolazovskoe deposit* ores are located in altered syenites and skarned carbonates at the contact with syenite massif. Only syenite-located ores were the subject of our study. The richest ore is pyrite-quartz-fluorite veins. Pyrite forms rich fine-grained dissemination, micronodules with marcasite, subhedral and euhedral crystals in gangue matrix (Fig. 1). Sometimes euhedral pyrite crystals replace fine-grained iron disulfide aggregates (Fig.1a). There are clearly zoned and optically homogeneous pyrite crystals (Fig. 1b). The temporal sequence of their formation is unclear. Galena, sphalerite and chalcopyrite are minor minerals while native gold and silver, silver and mercury sulfides, hessite, coloradoite, tiemannite, tetrahedrite and its V-bearing and Bi-bearing varieties, luzonite, burnonite, molybdenite, carrolite, bornite are rare [Borisenko et al., 2015, our data].

The ores of the *Muscovite limb of the Ryabinovoye deposit* are localized in sericitized and silicified porphyritic syenite. Euhedral and subhedral pyrite as well as chalcopyrite, bornite, chalcocite and galena are major ore minerals while pyrrhotite and hematite are less spread. Precious metals were found in the native form (gold), sulfides (utenbogardite), tellurides (hessite, petzite, Pt-Pd telluride) (Kovalenker et al., 1996).

Ores of the *Noviy limb of the Ryabinovoye deposit* are concentrated in the stock of altered porphyry pseudoleucite syenite. Higher gold content on the periphery of the stock is associated with sericitization and kaolinitization of feldspar as well as with development of disseminated pyrite. Chalcopyrite, sphalerite and pyrrhotite are minor minerals. Fahlore, galena, gold, petzite, and hessite are rare. Pyrite here is divided into subhedral porous and later euhedral dense varieties.

![Figure 1.](image1.png)

**Figure 1.** Fine-grained mass and subhedral pyrite (a) and zonal brecciated (b) pyrite from ores of Samolazovskoe deposit.

![Figure 2.](image2.png)

**Figure 2.** Euhedral dense pyrite from ore of Muscovite limb (a) and subhedral porous pyrite of Noviy limb (b) of Ryabinovoe deposit.
5 Chemical composition of pyrite

Maximum content of Au, Ag, As, Sb, Hg, Tl, and Pb impurities were found in fine-grained iron disulfide aggregates from Lunnoe and Samolazovskoe deposits. There is a positive correlation among the contents of all these elements. The most pronounced positive correlations are in pairs Au-Ag, Au-Tl, Au-Sb. The pair Au-As has lower correlation (Fig. 3).

Gold content in fine-grained aggregates of iron disulfides is (average/maximal) 304/656 ppm (Samolazovskoe) and 72/556 ppm (Lunnoe), which exceeds the gold content in the coarser-grained euhedral pyrite by two orders of magnitude and higher: average Au content is 28 ppm in euhedral homogeneous pyrite and 3.4 ppm in zonal pyrite of Samolazovskoe deposit, and 0.4 ppm in euhedral pyrite of Lunnoe deposit. Ablation dynamics show a relatively uniform distribution of impurities in pyrite from these deposits.

According to XANES spectroscopy of fine-grained Au enriched pyrite from Samolazovskoe deposit, the oxidation state of Au is +1, whereas most As in these pyrites exhibit formal oxidation state -1. The sample also contains a small admixture of As-bearing oxidized phase. The best fit of the experimental Au L3-edge EXAFS spectrum is achieved when assumed that Au substitutes Fe in the structure of pyrite (NS ~ 6, RAu-S ~ 2.40 ± 0.01 Å). RAu-S and RAu-Fe of distant coordination shells correspond to the pure pyrite structure. Therefore, the admixture of As has no effect on the local atomic environment of Au in pyrite. As substitutes S in a pyrite structure. The first coordination shell consists of S (NS ~ 1, RAs-S = 2.25 ± 0.04 Å) and Fe (NFe ~ 3, RAs-Fe = 2.32 ± 0.02 Å). The fitting of the distant coordination shells confirmed that As replaces S1- in pyrite structure. Due to the small additional fraction of As-O compounds (e.g., As3+2O3), O atoms were also detected in the first coordination shell of As (NO ~ 0.4, RAs-O = 1.74 ± 0.05 Å). We did not observe a contribution of any heavy atom to As K-edge EXAFS spectrum up to the distant coordination shells which confirms random (statistical) distribution of Au and As in the pyrite structure.

The content of impurities in pyrite of both limbs of the Ryabinovoe deposit varies widely. Single enormous high values are typical for Cu, Pb, Te, Au. This, as well as the dynamics of ablation, indicates the presence of submicron or nano-scale inclusions of own minerals of these elements. Excluding anomalously high values related to inclusions, the average gold content in pyrite of the Muscovite limb of the Ryabinovoye deposit is only 0.14 ppm, that of Noviy limb is about 1 ppm in porous pyrite and less than 0.01 ppm in dense one. Concordant behavior of Au, Ag and Te during ablation suggests that precious metals in pyrite from both limbs of Ryabinovoe deposit are present as micro inclusions of native Au with Ag admixture and tellurides of Au and Ag. Highest Au content in the porous pyrite of the Novy limb positively correlates with Ag (Fig. 2). No significant correlation links were revealed for Muskovitoviy limb.
6 Discussion

As a result of the research, we found that the fine-grained aggregates of iron disulfides, which are specific for veinlet disseminated fluorite-bearing ores of the Samolazovskoe and Lunnoye deposits, are significantly enriched with Au, Ag, Tl, Sb, As, and Hg compared to the euhedral pyrite of all deposits studied in the work. This may occur due to a higher growth rate of fine-grained aggregates and their larger specific surface area, which contributes to the capture of impurities both as chemically bonding and nanoinclusions of minerals, since the association of impurities in fine-grained pyrite aggregates corresponds to the association of rare mineral species found in ores of these deposits.

Despite the high As content in Au enriched pyrite, the typical for gold-bearing pyrites Au-As correlation (Reich et al., 2005; Large et al., 2009) is less pronounced in the studied samples from Samolazovskoe and Lunnoye deposits than Au-Sb, Au-Tl and Au-Hg.

Chemical bond between Au and As in the above-described fine-grained pyrite was not identified by X-ray spectroscopy. Thus, As is not the cause of incorporation of gold into the pyrite structure. However, it is proved that at least part of the gold in the pyrite forms chemical bond with sulfur. It is possible that such Au behavior is characteristic of fluorite-containing metasomatic associations which have high activity of Tl, Sb, As, Hg, and other impurities during their formation.

The impurities content is significantly lower in larger euhedral pyrite from ores of all studied deposits. This may occur due to their lower growth rate, which does not contribute to the capture of incoherent (non-structural) impurities. Rarely observed higher Au content in this morphological type of pyrite is caused by inclusions of native gold or gold-bearing tellurides. It should be noted that both native gold and Au-Ag tellurides were found in the ores of both limbs of the Ryabinovoye deposit.

7 Conclusion

As a result of optical, SEM and LA-ICP-MS studies it was found that fine-grained aggregates of iron disulfides from the fluorite-bearing ores of Lunnoye and Samolazovskoe deposits are much enriched with Au, Ag, Tl, Sb, As and Hg, compared with euhedral pyrite from the same deposits as well as subhedral and euhedral pyrite from ores of Ryabinovo deposit.

The Au-Sb, Au-Tl and Au-Hg correlations in the studied fine-grained pyrite aggregates are higher, then Au-As. X-ray absorption spectra correspond to the random distribution of isomorphic Au and As in the pyrite structure. Au and As are not chemically bound in this morphological type of iron disulfides.

It is suggested that this behavior of Au is characteristic for fluorite-containing metasomatic associations which were formed with high activity of Hg, Tl, Sb, As and a high growth rate of iron disulfides.

High concentrations of gold and related toxic elements at the Samolazovskoe and Lunnoye deposits require a special approach both for enrichment and for storage of waste.

Acknowledgements

We are grateful to Seligdar corporation for assistance in the field work. The work was supported by the Institute of Mineralogy.

References


Mineralogical and geochemical characteristics of the Sekisovka gold deposit (East Kazakhstan)

Marina Mizernaya, Anastassiya Miroshnikova, Arkady Mizerny
East Kazakhstan State Technical University, Ust-Kamenogorsk, Kazakhstan

Evgeniy Naumov
Central Research Institute of Geological Prospecting for Base and Precious Metals, Russia
Russian State University for Geological Prospecting, Moscow, Russia

Alla Dolgopolova, Reimar Seltmann
CERCAMS, Department of Earth Sciences, Natural History Museum, London, UK

Abstract. The Sekisovka deposit is located in eastern Kazakhstan, within the Aleysk subzone of Rudny Altai, part of the fragments of an ancient paleo-continent. The deposit is situated within the Sekisovska multi-phased plagiogranite massif of the Late Carboniferous to Permian collision-related Zmeinogorsk complex. The deposit is characterized by gold-sulphide bearing mineralised zones and stockworks with geochemical, metasomatic and mineralogical zoning formed in the magmatic rocks of the Zmeinogorsk complex. NW striking ore-controlling faults, occurrence of fluid-explosive breccias, propylitic and beresite (quartz-sericite-albite-calcite-pyrite) alteration zones are typical. Gold is irregularly distributed and embedded in the cementing mass of the explosive hydrothermal breccias and tends to concentrate at the boundaries between breccias and igneous rocks.

1 Introduction

Sekisovka-type gold mineralization is widespread in the Shemonaikha district of the Rudny Altai and is controlled by the NW-trending Shemonaikha-Sekisovka Fault Zone. The Sekisovka deposit is most representative and is hosted in the collision-related gabbr odiiorite-diorite-granodiorite-granite pluton belonging to the Middle-Late Carboniferous Zmeinogorsk Complex (Fig. 1). The plutonic rocks are intruded by quartz albitophyre, felsite, and plagiogranite porphyry dikes and pegmatite veins and intersected by explosion breccia pipes with fragments of weathered intrusive rocks replaced with kaolinite and hydromica are cemented by compact or porous, roughly banded and patchy quartz-goethite-hydrogoethite aggregate with abundant pseudomorphs after pyrite. Oxidized and fresh pyrite crystals (octahedrons, pentagonal dodecahedrons, combined forms) occur in the lower part of oxidation zone (Rafailovich 2009).

The primary hydrothermal explosion breccias develop along the NW-trending main fault, mainly at intersections with pinnate fracture zones. The zone of brecciated rocks extends for >1.5 km and is 50-200 m wide; vertical range of brecciated bodies – 500-600m.

Two breccia types are distinguished; by time of formation and by composition of fragments: (i) early breccia of gabbro-diorite to diorite and (ii) late polymictic heteroclastic breccia combining unsorted fragments of rocks pertaining to all intrusive phases from gabbroic rocks to plagiogranite porphyry and felsite dikes (Freiman and Selifonov 1982).

The ore field is comprised of intrusive rocks of the Sekisovka massif, where all four formation stages of the Zmeinogorsk Complex can be found. Granodiorites and diorites of the second intrusion phase and plagiogranites of the third phase dominate over other stages and collectively account for >90%.

Magmatic rocks of the Sekisovka massif can be combined into two main series: gabbro-diorite (gabbro, gabbro-diorite, diorite), and plagiogranite (granodiorite, plagiogranite, granite). Most typical igneous textures are shown in Figure 2. Post-granite dikes of mafic and felsic compositions are widely distributed within the ore field; they tend to confine to areas of fault intersections. Mineralized zones are also located here.
Characteristic feature of the deposit is a spatial overlapping of dike branches with breccia bodies. Common roots of dikes and associated breccia bodies indicate a single magma chamber. Both gabbro-diorite and plagiogranites series show similar patterns and are enriched in K, Zn, Pb but strongly depleted in Nb, P and Ti (Fig. 3). Gabbro-diorite series show flat REE patterns with almost unnoticeable Eu anomaly and slight enrichment in light REEs relative to heavy REEs (Fig. 4). Granite porphyry dikes show very different REE behavior with strong enrichment in light REEs compared to heavy REE and slight negative to even positive Eu anomaly (Fig. 4). Dike samples represent most evolved granitoid melts and indicate alteration due to fluid channeling into dike structures.
The Rb vs. (Y+Nb) plot shows a distinct feature of all granitoids related to volcanic arc (granites of I-type with dominant fractionation of hornblende) (Dolgopolova et al. 2017) (Fig. 5).

Figure 5. Tectonic discrimination diagram (Pearce et al. 1984) for samples of the Sekisovka deposit with symbols as in Fig. 3.

3 Mineralization

Gold mineralization is spatially and genetically associated with sulfides in the stockworks. However, a direct correlation between the volume of sulfides and gold is not established. The highest gold concentrations occur at the contacts between various types of breccias, as well as along the contacts of breccias with diorites and dikes of felsic composition (Naumov et al. 2013).

The breccias are subdivided into fine- and coarse-clastic varieties. The former occur at intersections of variously oriented faults. Fragments of 1-20 cm in size are severely beresitized. The coarse-clastic breccias with fragments of 0.2-20 m in size are located at a distance of faults in the outer parts of explosive bodies. Only 3-5 cm wide margins of large fragments are subject to beresitization (Rafailovich 2009).

Two mineral assemblages develop in the primary ore (Rafailovich 2002). The assemblage comprising gold, quartz, magnetite, pyrrhotite, marcasite, pyrite, scheelite, bismuthinite, molybdenite, and chalcopyrite is related to the early breccia and occurs at the middle and lower levels. The gold–base-metal mineralization (gold II, native silver, quartz, chalcopyrite, aikinite, galena, sphalerite, greenockite, tellurides, tennantite) was formed at the late stage, being confined to the mixed breccia localized at the upper levels of breccia bodies and controlled by dikes of quartz albitophyre, granite porphyry, and felsite. The quartz–sulfide and quartz–carbonate–sulfide pockets and veinlets are predominant. Gold occurs in free form, as tellurides, and as finely dispersed admixture in sulfides (Fig. 6).

The chronological sequence of the studied mineral assemblages is as follows:
- magnetite–pyrrhotite–pyrite–quartz,
- chalcopyrite–pyrite–pyrrhotite–quartz,
- gold–tennantite–sphalerite–greenockite–quartz, and

Au, Bi, and Ag are indicative of the mineralization; Mo, W, Cu, Pb, Zn, Te, Co are accompanying components. Gold is characterized by bimodal distribution in both oxidation zone and primary ore (Fig. 7). In the oxidation zone, grades of 10–60 g/t Au are predominant (42.5%), while contents of 1–6 g/t Au are of subordinate abundance (32.1%). The maximum Au concentration in the oxidized ore is 200–250 g/t; the average grade is 23 g/t Au. In the primary ore, concentrations of 2–6 g/t Au dominate (44.5%), while concentrations of 20–60 g/t are subordinate. In some samples, the Au content reaches 500–600 g/t (ore shoots).

The geochemical field of Au-bearing breccias is inhomogeneous with variable ratios of elements in orebodies, primary halos, and zones of dispersed mineralization.

Gold is the main component in ore and mineralized rocks; Ag and Bi are the main companion elements of Au; Mo, W, Cu, Pb, and Zn are less abundant. The geochemical halos and dispersed mineralization are characterized by elevated contrast of Mo and W. The halos surrounding orebodies are distinguished from zones of the dispersed mineralization by much higher concentrations of noble metals, Mo, and W.

The orebodies hosted in breccia reveal distinct vertical geochemical zoning (from bottom upward): Mo–Bi–Au–Ag–Cu–Pb, Zn. The Cu/Mo ratio varies from 7 at the lower levels to 160 at the middle and upper levels. The formation sequence of primary halos is expressed in
the series W, Mo → Bi, Au → Cu, Pb, Zn. The Pb/W ratio changes from 4 in subore halos to 27 in supraore halos. The geochemical zoning of orebodies and primary halos is a reflection of mineralogical zoning: magnetite, marcasite, pyrrhotite, scheelite, molybdenite → native gold, bismuthinite, aikinite → chalcopyrite, fahlore → sphalerite, galena.

Figure 7. Distribution of Au, Ag, and Au/Ag ratio in primary (solid line) and oxidized (dashed line) ores in the Sekisovka deposit. After the data of the Vostkaznedra Geological Survey. N is number of samples (after Rafailovich, 2009).

4 Conclusions

The hydrothermally altered explosion breccia controlling localization of the stockwork, vein–stockwork, and linear–banded stringer–disseminated gold–silver mineralization are the most important feature of the Sekisovka-type gold deposits. The intramineral dikes of quartz albitophyre, plagiogranite porphyry, and felsite divide the formation of Au–Fe–Cu–Mo–W and Au– base-metal associations in time.

Gold and silver concentrate in both primary and oxidized ores of the Sekisovka deposit. The supergene ore is enriched in noble metals by 3–5 times relative to the primary ore. The Au/Ag curves are identical for the primary and oxidized ores, indicating the close geochemical affinity of both metals under hypogene and supergene conditions. The orebodies, primary geochemical halos, and pyrite as the major sulfide in breccia are characterized by similar geochemical spectra. This criterion is recommended for using in forecasting and prospecting of new ore-bearing breccia bodies.

For estimating the depth of erosion and the vertical range of mineralization, it is important to account for the mineralogical and geochemical zoning of orebodies, primary geochemical halos, and typomorphic features of Au-bearing pyrites, including their habit, unit-cell parameters, geochemistry, and ratios of trace elements are additional criteria.

There is a decrease of gold concentration in all types of breccia with depth. There is an increase in gold concentration in proximity to contacts between breccias of different types, breccias with igneous rocks, including post-granite dikes.

The most productive horizon at the deposit is from +320 m up to -40 m. From east to west there is increasing intensity of mineralization with depth. Superimposed projection of ore branches of ore bodies indicates a plunge of ore shoots. This implies as practical application the potential for discovery of possible new ore pillars deeply embedded at the western flank of the deposit. The eastern flank of the deposit is evidently of low fertility.

Acknowledgements

This is a contribution to grant of MES of RK AP 05131489 and to the IGCP-662 project co-sponsored by IUGS-UNESCO.

References


Rafailovich MS 2002 Models of Vertical Geochemical Zoning of Gold Deposits and Their Implications for Prospecting Ust-Kamenogorsk, 166 pp (In Russian).

Gold as a powerful proxy to trace gold and unravelling gold systems, an insight into French Guiana (France)

Anthony Pochon, Anne-Marie Desaulty, Laurent Bailly, Philippe Lach, Jérémie Melletton, Isabelle Duhamel-Achin
BRGM, F-45060, Orléans, France

Abstract. Despite of the gold exploration since 150 years, there is a limited understanding of gold deposits in the French Guiana. To improve our knowledge, alluvial, eluvial and primary gold grains from the Sophie-Repentir and Saint-Elie goldfields (French Guiana) have been characterised by EPMA and LA-ICP-MS analyses. Preliminary results show a good discrimination between the two orogenic gold districts. Whereas the gold grains population of the Saint-Elie is characterised by a low content of silver (i.e. mainly less than 6 wt%), a suite of Bi mineral inclusions and a Sb-Bi-Cd fingerprint, gold from the Sophie-Repentir is enriched in silver (up to ~ 20 wt%), Cu-poor and associated with a wider range of tellurides. These features also allow matching an alluvial gold population to its corresponding lode source with confidence and raise questions about the processes controlling the trace elements behaviour.

1 Introduction

The French Guiana represents the first French gold province and belongs to the Guiana shield in South America. It has produced at least 213 tons of gold since 1855 (Cassard et al. 2008 and references therein). Furthermore, because French Guiana has a deeply weathered landscape (i.e. lateritisation), primary gold deposits are rarely outcropping. In such conditions, the use of indicator mineral studies is necessary for exploration of undercover gold deposits. The best indicator mineral of gold deposits is gold itself (McClenaghan and Cabri 2011) because it is a dense mineral, chemically stable and easily found in the erosional products of gold systems (i.e. placers).

Gold displays a range of intrinsic mineralogical characteristics such as its shape, size or chemical composition (i.e. minor and trace elements). These features can be used to provide information for relationships between placer and lode deposits in exploration but also informing about ore-forming processes. Considering this, a powerful technique was largely developed by the British Geological Survey (e.g. Leake et al. 1997, Chapman et al. 2000) for gold exploration, named “microchemical analysis” of gold. It is based on two types of mineralogical information linked to the environment of formation (Chapman et al. 2000): (i) the determination of the minor alloying elements content (Ag, Cu and Hg) and (ii) the identification of mineral inclusions in gold grains. In addition, the improvement of analytical tools allows analyses of trace elements (e.g. Sb, Pd, Pt, Bi) of gold by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), mainly for tracing archeological gold objects (Watling et al. 1999), for traceability of ore gold (Dixon 2014, Augé et al. 2016) but also for tracing lode sources (Banks et al. 2018).

This project focus on the chemical characterisation of gold from French Guiana for which few data are known in comparison with others areas from the Guiana Shield or from the West-African craton. For this reason, LA-ICP-MS analysis of gold, coupled with the “classical” microchemical analysis, is applied to two gold grain populations from French Guiana in order to better understand the gold-forming processes and better constrain gold exploration.

2 Gold in French Guiana

The known gold deposits are located in the mid-north part of the French Guiana (Fig. 1). They are mainly hosted by the Paleoproterozoic Paramaca Greenstone Belt (PGB), interpreted as the remnant of a volcanic arc sequence formed during the Transamazonian orogeny (2.18 to 2.13 Ga). It forms two regional-scale synformal structures located to the north and south of the Mesorhyacian Central TTG (Tonalite Trondhjemite Granodiorite) complex (Delor et al. 2003, Enjolvy 2008). Three types of primary gold deposits have been identified in the PGB (Milesi et al. 2003): (i) stratabound gold deposits hosted by the volcano-sedimentary rocks of the Paramaca Formation, where gold is associated with disseminated sulphides; (ii) gold-bearing conglomerates with disseminated gold within the Upper Detrital Unit of the North Guiana Trough; and (iii) “classical” orogenic gold deposits which consist of quartz-carbonate-sulphide veins and stockworks, essentially hosted by the Paramaca Formation and granitoids. The Sophie-Repentir (SR) and the Saint Elie (SE) gold districts discussed in this study belong to the orogenic type. To date, most of the gold production of the French Guiana is coming from placers of Pliocene to Quaternary age.

The SR gold district is located along the SR shear zone, which is a major metalloclock for gold deposits in this area (Machairas 1963). This N130°E trending structure of 19 km long, hosts numerous gold-bearing quartz vein-type zones and derived placers. The northern part of the structure, the Sophie-Dagogbert area, hosts several lodes distributed around the Sophie, Salomon, and Absinthe creeks (e.g. the Tabou, the Gros Chantier, and Dagobert lodes). The southern part of the structure, the Saint Léon-Repentir area, is characterised by numerous lodes distributed around the Saint Léon creek (e.g. Repentin and Félix lodes). The historical production of the SR district is estimated at 25 t of alluvial gold and 3.3 t of primary gold. The SR shear zone is located at the contact...
between the Paramaca formation and the Central TTG complex. Primary mineralisation consists of sulphides-bearing quartz veins with associated alteration halos (i.e. silification). Pyrite is the most dominant sulphide and can be found (i) as isolated crystals inside quartz, (ii) as impregnations in the crushed zone at the wall rock of mylonites or (iii) in veinlets within mylonites. Gold appears frequently as free grains (up to 1 mm in size) within quartz veins or in cracks, as inclusions and/or in the crystal lattice of pyrite. Pyrite and gold are commonly associated with subordinated galena, chalcopyrite, covellite, sphalerite, bismuthinite, Bi- and Au-Ag tellurides. The paragenetic evolution could be resumed by an early ductile stage with gold-rich sulphides formation within mylonitic zones followed by a brittle deformation stage forming a dense network of quartz veins with free gold.

Gold commonly occurs along contacts between pyrite and pyrrhotite, within cracks in pyrite and as inclusions in galena and tellurides.

3 Sampling and methods

Some 450 gold grains from the studied areas were collected during a BRGM in-house project funded by WWF (World Wildlife Fund), aiming to assess the traceability of gold of French Guiana (Augé et al. 2016). When possible, a representative population of each grains type (alluvial, eluvial, and primary) were mounted in polished sections, in order to determine the microchemical signatures of gold.

Optical microscope (reflected light) and scanning electron (SEM) microscope were used to identify the nature of mineral inclusions within gold alloy. The minor alloy composition (Table 1) have been determined using a Cameca SXFive electron microprobe (operating at 20 KeV and 40 nA with a counting time of 20 s for each element) at the ISTO facilities (Orléans, France). The content of Ag within a population of gold grains is displayed in cumulative percentile plots (Fig. 2), which allows a direct and best comparison of populations with different numbers of grains (Chapman et al. 2000). Trace elements of gold were determined by in situ LA-ICP-MS at the BRGM laboratory (Orléans, France) using an excimer laser (193 nm) CETAC Excite coupled to ThermoScientific X serie II quadrupole ICP-MS. Ablation spot of 85 µm with a laser fluence of 12 J/cm² and a repetition rate of 8 Hz were used. Quantification of gold is carried out using Ag as internal standard. A large spot size has been used in order to increase the signal because most elements are close to the detection limits (LOD). Moreover, the value of LOD is assigned to each values below the latter.

4 “Microchemical signature” of gold

Sophie-Repentir district. Primary gold grains from the Dagobert lode, observed in this study and recovered from shaking table, range in size from 50 to 500 µm. They are associated with base-metal sulphides (pyrite, galena and chalcopyrite) and tellurides (hesstite, calaverite, petzite altaite, Table 1). The Ag content of gold grains is ranging between 4.20 and 11.36 wt%. Copper is frequently below LOD but detected up to 0.19 wt%, whereas Hg is always below LOD. Alluvial gold grains, from the Marc creek, are classically coarser than primary gold grains and range in size from 100 to 3000 µm. Galena, Bi- and Pb tellurides represent the main mineral inclusions contained in these gold grains. In contrast to primary gold grains from the Dagobert lodes, alluvial grains from the Marc creek are characterised by highly variable Ag content (from 1.96 to 22.60 wt%) and rather similar Cu and Hg content (up to 0.18 wt% and below LOD, respectively). Figure 2 illustrates the statistical distribution of the Ag content of primary and alluvial gold. There are strong similarities of the Ag content between all the samples. Primary gold grains from the two Dagobert lodes are extremely similar and only 20 % of the population show a different composition. The statistical distribution of the Ag content of primary and alluvial gold grains also shows strong
similarities. About 70% of alluvial population fit well with the primary population indicating that almost gold from Marc creek could come from the Dagobert lodes.

Table 1. Characteristics of studied gold grains from French Guiana

<table>
<thead>
<tr>
<th>Sample</th>
<th>No.</th>
<th>Ag</th>
<th>Cu</th>
<th>Hg</th>
<th>Ore mineral association*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sophie-Repentir district</td>
<td>LOD</td>
<td>0.3%</td>
<td>0.05%</td>
<td>0.2%</td>
<td>Py, Gn, Bi, Cpy, BiTe, AgTe, PbTe</td>
</tr>
<tr>
<td>Dagobert lode 1</td>
<td>120</td>
<td>2.40-11.36</td>
<td>0.67</td>
<td>0.08</td>
<td>bdl, BiTe, Apy</td>
</tr>
<tr>
<td>Dagobert lode 2</td>
<td>52</td>
<td>4.61-8.36</td>
<td>0.59</td>
<td>0.06</td>
<td>bdl, BiTe, PbTe</td>
</tr>
<tr>
<td>Marc creek (Upstream)</td>
<td>42</td>
<td>1.96-22.80</td>
<td>3.74</td>
<td>0.07</td>
<td>bdl, BiTe</td>
</tr>
<tr>
<td>Marc creek</td>
<td>48</td>
<td>2.57-19.93</td>
<td>6.46</td>
<td>0.08</td>
<td>bdl</td>
</tr>
<tr>
<td>Saint-Elie district</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unk. lode (SE concession)</td>
<td>41</td>
<td>1.79-7.87</td>
<td>3.92</td>
<td>0.11</td>
<td>bdl, BiTe, BiS, BiTe, Apy</td>
</tr>
<tr>
<td>Unk. lode (St-Auguste area)</td>
<td>56</td>
<td>1.80-4.88</td>
<td>2.58</td>
<td>0.12</td>
<td>bdl, BiTe, BiS, BiTe, Apy</td>
</tr>
<tr>
<td>St-Auguste creek</td>
<td>105</td>
<td>1.57-4.85</td>
<td>3.00</td>
<td>0.13</td>
<td>bdl, BiTe, Apy</td>
</tr>
</tbody>
</table>

* = observed in this study, AgTe = Ag tellurides, Apy = arsenopyrite, AuTe = calaverite, bdl = below detection limit, BiTeS = tetradymite group, BiTe = Bi tellurides, Cpy = chalcopyrite, Gn = galena, No. = Number of gold grains, PbTe = albatite, Py = pyrite, Unk = unknown, LOD = limit of detection.

Saint-Elie district. Primary gold grains are coming from two different lodes of the SE district, an unknown lode from the SE concession, and a lode from the St-Auguste area. Grain size ranges between 600 and 1200 µm. About 35% of gold grains contain inclusions, mainly represented by Bi-tellurides (e.g. hedleyite), tetradymite, Bi alloy (probably maldonite) and native Bi. Gold grains from the two lodes are characterised by different Ag content from 1.97 to 7.87 wt% for grains coming from the SE concession and from 1.80 to 4.88 wt% for those coming from the St-Auguste area (Table 1).

Figure 2. Cumulative plots of Ag content of gold particles from the the SR district and the SE district.

5 LA-ICP-MS signatures

Preliminary results of the trace elements analysis (Fig. 3) show that Cu is well detected in LA-ICP-MS whereas this is not always the case with EPMA. However, the Cu content measured by LA-ICP-MS is consistent with the Cu content obtained by EPMA.

The Cu content ranges from 10 to 1620 ppm in the SR district (mean value of 690 ppm) and from 270 to 3205 ppm in the SE district with a 1085 ppm mean value (Fig. 3a, b). The content of PGE (Fig. 3b, c, d), mainly controlled by the Pd content, is close between gold from the two district with mean values of 0.75 ppm (SR district) and 1.15 ppm (SE district), respectively. This similarity is likely because gold mineralisation is hosted by the PGB, mainly composed of ultramafic-mafic rocks. On the other hand, bivariate plots show a distinct behavior of Sb between the two gold districts (Fig. 3a, c, e), with a median value of Sb (1.01 ppm) at least 20 times greater in gold grains of the SE district compared to the SR gold (0.052 ppm). Same observation can be made about the cadmium content (Fig. 3f), with a mean value of 2 ppm for the SE gold grains, 40 times greater than the mean value of SR gold. This is supported by the observation of greenockite in the paragenesis from the SE district (Lafrance et al. 1999). The Bi content graphically appears as similar between the SR and SE gold grains with a close mean value (0.11 ppm for SR gold and 0.17 ppm for SE gold); however, 52% of Bi values are below LOD (0.009 ppm) for SR gold, compared with 95% of values above LOD for the SE gold grains. This indicates that the gold coming from the SE district is relatively more enriched in Bi, which is consistent with the abundance of Bi mineral inclusions observed in gold grains.

In the same way that cumulative Ag percentile (Fig. 2), trace elements can assist to distinguish a gold population from another. Displayed diamonds on the Figure 3, representing alluvial SR gold and eluvial SE gold, confidently fall in the field of their supposed source (Fig. 3).
Concluding remarks
Preliminary results of the chemical characterisation of alluvial-eluvial gold and the gold from their supposed lode source have shown several distinction between two orogenic goldfields hosted in the same greenstone belt. The signature of gold from the SE district is defined by the strong presence of bismuth in both gold alloy and inclusions of Bi-tellurides or tetradymite. Cadmium is also a specific feature of the SE gold as evidenced by the relative high Cd content and the greenockite in the paragenesis. Trace elements analysis by LA-ICP-MS therefore has a powerful potential for elements, such as Sb, Cd, Bi or PGE, rarely detected by the EPMA method. Additional data from others goldfields in French Guiana are needed to go further in the understanding of orogenic processes related to gold systems.

Acknowledgements
This project is funded by the BRGM Carnot Institute. The authors gratefully thanks Prof. Georges Beaudoin (U. Laval) for providing us gold matrix-matched reference materials for calibration.

References
Characterization of gold grains from Bigorne deposit: search indicators to hypogene mineralization. Preliminary studies.

Sara Leal, Alexandre Lima1,2, Fernando Noronha1
1Institute of Earth Sciences, Polo-Porto, University of Porto, Portugal
2Department of Geosciences, Environment and Spatial Planning, University of Porto, Portugal

Abstract. The Bigorne gold deposit (northern Portugal) located in the European Variscan belt is a system of gold-bearing quartz veins, which crosscut late-to post-D3 biotite granites. The mineralized structures correspond to sheet-veins system parallel to the late-Variscan strike-slip fault Penacova-Régua-Verín (NNE-SSW).

In Bigorne veins, it was possible to define two types of gold occurrence: I - Native gold, as free particles; II - Au-Bi minerals in association with native-Bi and Bi-Te minerals.

The gold minerals from mineralized veins and the gold grains sampled in superficial environments reveal similar chemical composition where the Au occurs in association with Ag, Cu, and Cd. This fact provides evidence of very limited transport and therefore a restricted and single local source for gold primary particles from the mineralized veins.

It is very important to improve the geological and mineralogical knowledge about gold occurrences in Portugal to improve the knowledge of the Phanerozoic gold systems.

1 Introduction

The Central Iberian Zone (CIZ) presents an exceptional geological interest for its great exploration potential for a number of critical elements (Te, Bi, and Sb) and gold.

In Northern Portugal, gold deposits are hosted in Variscan granites (e.g. Penedono, Grovelas, Jales, and Limarinho) and in Palaeozoic metasediments (e.g. Valongo, França, Gralheira, and Tresminas) (Noronha et al. 2000 and references therein; Fuertes-Fuente et al., 2016). These gold mineralizations show a strong correlation to shear zones (syn-D3) (Mateus and Noronha 2010 and references therein), however, there are other significant alignments, such as those which are subparallel to major NNE-SSW regional faults (Noronha et al. 2000; Mateus and Noronha 2010). The primary gold particles in Northern Portugal occur more frequently as inclusions within sulfur-rich minerals, such as pyrite and arsenopyrite or in the limits of the grains of these sulfides. Gold occurs as a native metal, commonly in alloy with silver, and in some cases mercury, copper, and other elements. Gold grains liberated from the veins into superficial sediments during weathering are chemically stable and may be characterized according to morphology, alloy composition and suite of mineral inclusions. The morphology and chemistry of alluvial gold grains and their inclusions are potential indicators of characterizing the primary gold mineralization, mineralization style, and the potential host rock (e.g., Townley et al., 2003; Chapman et al. 2011).

In this paper, a detailed description of hypogene gold assemblage and of gold grains from superficial environments was made in Bigorne deposit. The main objective is a comparative study, in order to test this approach (describe for authors cited above) in Portuguese deposits. In this case, the comparison between the gold particles from mineralized veins (hypogene gold) and the gold grains from detritical deposits (alluvial and eluvial deposits).

2 Geological setting

Bigorne region is located in the CIZ (Figure 1), which corresponds to the autochthonous of the Variscan basement of the Iberian Massif (Julivert et al. 1972). The region is mainly composed of Variscan granitoids emplaced into Neoproterozoic–Early Palaeozoic sedimentary sequences, which were variably affected by regional metamorphism and deformation during the Variscan orogeny (Sousa 1982; Ribeiro 1990). The CIZ tectonic-metamorphic evolution is described as the result of two main deformation phases (D1 and D2), during which the crust reached its maximum thickness, followed by a late, post-thickening, ductile-brittle tectonic event (D3) (Noronha et al. 1979; Ribeiro et al. 1990).

2.1 Lithostratigraphy

The lithostratigraphy is variably metamorphosed and comprises metapelites and metagreywackes belonging to Schist-Greywacke Complex (SGC) with lower-Cambrian age (Carrington da Costa, 1950); an Ordovician clastic succession of stable marine platform sediments; and Silurian black schist (Teixeira, 1955; Teixeira et al., 1968). The pelitic rocks, sandstones, and greywackes were transformed into slate, quartzite, phyllite, spotted schist and hornfels as a result of variable metamorphic conditions attained during Variscan times.

The emplacement of voluminous amounts of granitic magmas during and slightly after D3 (316 to 300 Ma: Costa et al. 2014) generated low-P–high-T contact aureoles in this zone.
2.2 Granitic rocks

Variscan intrusions cover about 90% of the total exposure area. The intrusive sequence consists of (1) syn-D3 (U-Pb ages: 317Ma) biotite granites, and a volumetrically dominant (2) late and late- to post-tectonic association formed by granodiorite–monzogranite and biotite–muscovite granites (ca. 304) (Ferreira et al. 1987; Costa 2011; Costa et al. 2014). They form a large, composite batholith consisting of volumetrically dominant plutons of biotite monzogranites and two-mica granites and minor spots bodies of granodiorites. Small masses of leucogranites are also observed.

2.3 Tectonic setting

The main structures significant to gold mineralization of the region can be described to the effects of D3 phase from the Variscan Orogeny. Later ductile-brittle structures as NNE-SSW Penacova-Régua-Verín fault (PRVF) must be mentioned. The PRVF is one of the late Variscan deep crustal structure, which belongs to the NNE–SSW trending brittle system that crosscuts the whole of Northern Portugal (Pereira et al., 1993; Marques et al., 2002). The PRVF was nucleated on D3 phase and reactivated latter as a sinistral strike-slip fault with transtensional component (Pereira et al. 1993). There is an important alluvial deposit (Figure 1) associated with the Balsemão River that corresponds to a NNE-SSW strike-slip fault, parallel to the main PRVF (Teixeira et al., 1968).

3 Samples and analytical techniques

Representative rock samples were collected at Bigorne outcrop. The petrographic studies were carried out using a Leica optical microscope at DGAOT-FCUP and observations were made in reflected light. Gold grains samples were collected from two detritical deposits on Balsemão River (alluvial samples) and in Lagoa S. João area (eluvial samples). In this study, gold grains were isolated by routine techniques of sluice box and panning to concentrate heavy minerals. Gold grains were hand-picked from the heavies under the binocular microscope. The grains were photographed to record their morphological characteristics prior to mounting according to size, setting in epoxy resin and polishing as described in Chapman et al. (2000). The samples were studied SEM-EDS and EPM (Cameca SX100 incorporating Secondary Electrons, Backscattered Electrons, Absorbed Detectors, and Energy Dispersive Spectrometry) at Oviedo University (Spain).

4 Bigorne gold deposit

4.1 Deposit-scale structure

The gold mineralization occurs disseminated or along a network of microfractures and quartz veins of variable length (wide from centimetric up to metric dimensions) in granitic rocks, commonly in sheeted vein array (Figure 2). The veins fill (2-10cm) extensional fractures developed during the late stages of ductile-brittle deformation.

The main vein trending observed in the outcrops is N10°-20°E; 70°W and N20°-40°E; 60°-75°-80°W. On a regional scale, gold deposits tend to occur near large transcrustal “first-order” regional faults and shear zones that functioned as major conduits for mineralizing fluids (e.g. Mateus and Noronha 2010). In this case, at deposit-scale, however, the ore shoots are frequently localizing within “second- and third-order” structures, subparallel to the main structure (PRVF).
4.1 Mineral assemblage from mineralized veins

Arsenopyrite is the commonest sulfide in the mineralized veins. The grains are commonly allotriomorphic to subidiomorphic, in the latter case showing well-developed faces at the border of aggregates. The arsenopyrite is optically homogeneous and in most cases, the content of Au, Ag, Te, Bi, Sb were below their respective detection limits. Most of the fractures are filled by late-developed scorodite. Other sulfides present, but in lesser quantity is pyrite and chalcopyrite.

Pyrite shows tiny inclusions of chalcopyrite, sphalerite and galena. Weathering processes have oxidized the primary sulfides and leading to the growth of supergene minerals, mainly scorodite (FeAsO₄·2H₂O), goethite (FeO(OH)) and covellite (CuS).

Gold occurs as native-Au (Figure 3-A) in a lesser amount as maldonite (Au₂Bi) (Figure 3-B) associated with native-Bi (Figure 3-D); hedleyite (Bi₇Te₃) also occurs associated with native gold. Maldonite and hedleyite appear as small irregular inclusions or cavity infillings in arsenopyrite crystals (5µm up to 30 µm). They often form composite grains or aggregates (Figure 3-C). Gold particles are irregular and appear included in arsenopyrite, pyrite and scorodite, as well as along grain boundaries. The size of gold particles varies between 5µm up to 100µm. The Ag content of native-Au is commonly low (mean 9.20 wt.%); in scorodite particles contain Ag up to 7.77 wt.%. Bismuthinite and native bismuth were observed included in arsenopyrite. However, native bismuth is also present in aggregates associated with gold, maldonite, and hedleyite.

Figure 3. A – Photomicrograph of coarse native gold in pyrite and arsenopyrite. Backscattered electron images: B-C-D: B – Maldonite (Mld) in arsenopyrite; C – Maldonite in association with Bi-Te minerals (hedleyite); D - Maldonite with native bismuth.

5 Gold particles

5.1 Grain morphology and chemical composition

The gold grains were grouped according to grain morphology, chemical composition and were calculated the fineness for each group (100×Au/(Au+Ag); Fisher 1945). Most of the grains exhibit rounded shapes with smooth outlines. However, it is possible to distinguish two groups: (I) rounded and well-rounded particles of high fineness and homogeneous structure (Figure 4-A and 5-A); and (II) rounded to sub-rounded high fineness particles with heterogeneous inner structure (Figure 4-B and 5-B). The main gold grains from Group I are flaky and have a small size (Figure 4-A). The outline is relatively regular and surface topography tends to be smooth. The grains from Group II present a bigger size (> 250 µm) and have a more angular shape (Figure 4-B).

Figure 4. Examples of gold grains from detrital deposits. A – Group I. B – Group II.

Figure 5. Back-scattered Electron (BSE) images of some gold grains. A – Example of gold grains from Group I; B - Example of gold grains from Group II. In these grains, the presence of Au- enriched rims is common.

Overall, the gold alloy composition is predominantly a binary Au-Ag alloy with a minor contribution from Cu and Cd (Table 1). In both cases, the mineral inclusions were not found in these studied grains.
Table 1. Electron microprobe analysis of gold from Bigorne area (mean values in wt.%; (n) number of gold grains studied).

<table>
<thead>
<tr>
<th>Type of gold</th>
<th>Au</th>
<th>Ag</th>
<th>Cu</th>
<th>Cd</th>
<th>Fineness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineralized veins (n=10)</td>
<td>89.69</td>
<td>9.04</td>
<td>0.037</td>
<td>0.069</td>
<td>770-963</td>
</tr>
<tr>
<td>Group I (n=10)</td>
<td>93.47</td>
<td>6.29</td>
<td>0.10</td>
<td>0.05</td>
<td>929-942</td>
</tr>
<tr>
<td>Group II (n=12)</td>
<td>93.62</td>
<td>6.10</td>
<td>0.02</td>
<td>0.05</td>
<td>876-994</td>
</tr>
</tbody>
</table>

6 Conclusions

Regardless of the association of native-Au with maldonite and hedleyite in some aggregates minerals present in mineralized veins, this association is not founded in gold grains from superficial environments (but it is necessary to take into account that sampling is small yet). The gold particles have similar chemical composition (Au-Ag alloy). The rounded and homogeneous gold grains from Group I correspond to the alluvial sample. Sub-rounded, gold grains become enlarged and the presence of Au-robust interpretations and the application in other grains). For future works, gold grain studies such as this as silver leaching (from the eluvial to the alluvial gold superficial environments) and supergene process such of supergene regrowth (from mineralized veins to enriched rims in individual grains, suggest the existence of gold grains from superficial environments in relation to transport. These characteristics match with other deposits, as placers. The fact of the grains has similar characteristics from eluvial and alluvial samples provides evidence of very limited transport and therefore a restricted local source (Townley et al., 2003; Chapman et al. 2011). The same chemical compositions of the all types of gold (hypogene, alluvial and eluvial) suggest a single episode of gold deposition.

However, we must emphasize an increase of the size of gold grains from superficial environments in relation to the particles from mineralized veins. Considering that, gold grains become enlarged and the presence of Au-enriched rings in individual grains, suggest the existence of supergene regrowth (from mineralized veins to superficial environments) and supergene process such as silver leaching (from the eluvial to the alluvial gold grains). For future works, gold grain studies such as this require sufficiently large populations of grains to develop robust interpretations and the application in other Portuguese gold deposits with different characteristics.

Acknowledgments

The first author is financially supported by SFRH/BD/114693/2016 (FCT Portugal). The authors acknowledge the funding by COMPETE 2020 through the Institute of Earth Sciences project (UID / GEO /04683/2013) with POCI-01-0145 reference - FEDER007690.

References


Pb-Zn-Sb-Ni-Au mineralization from the Kizhnica area, central Kosovo: new data on the listwaenite type mineralization

Sławomir Mederski, Jaroslav Pršek, Katarzyna Hincyngier
AGH University of Science and Technology, Kraków

Abstract. Polymetallic and listwaenite-type mineralization from the areas adjacent to the abandoned Kizhnica mine in Kosovo has been investigated. Presence of sphalerite, galena, chalcopyrite, pyrite, stibnite, Pb-Sb sulfosalts (boulangerite, semseyite, chevanite and jamesonite), berthierite, Fe-Mn carbonates and quartz were identified in massive - vein - banded ore. Galena, sphalerite, boulangerite, pyrite, gersdorffite, ullmannite, arsenopyrite, tetrahedrite, pyrrhotite and native Au were confirmed in listwaenite-type of mineralization. The chemical composition of major ore minerals is presented in this paper.

1 Introduction

Kosovo is characterized by presence of numerous Pb-Zn deposits, which belong to the Trepça Mineral Belt (TMB). These deposits are located in the Vardar Zone, belt extending from Bosnia through Kosovo, Macedonia and Greece to Turkey (Hyseni et al. 2010). Vardar Zone in Kosovo is characterized by Paleozoic (Veles Series) and Mesozoic rocks, Jurassic ophiolites (serpentinites, peridotite), Cretaceous and younger igneous rocks, Oligocene-Miocene volcanic rocks (e.g. andesites, trachytes and dacites) and pyroclastic volcanic rocks (tuffs) (Hyseni et al. 2010). The Oligocene-Miocene ore mineralization in Kosovo is related to the post-collisional magmatic activity. Three regional NNW-trending mineralization zones within the Belt are present: (1) Batiava – Artana Zone; (2) Belo Brdo – Stan Terg – Hajvalia Zone; (3) – Crnac Zone. Base metal mineralization in Kosovo occurs as skarn, carbonate replacement and vein deposits. Among the main Pb-Zn orebodies occur listwaenites, which are host rocks for the dispersed Ni mineralization. In Kosovo, listwaenite mineralization was recognized in the Crnac deposit in Rogozna Mountains (Radosavljevic et al. 2015) and in the Stan Terg area (Bal et al. unpublished). In Crnac deposit millerite, bravoite, niccolite and members of the gersdorffite-ullmannite series occur in paragenesis with base metal minerals. Cu mineralization occurrence in serpentinites from the Kizhnica area was noted by Werner (2017), but typical listwaenite-type mineralization rich in nickel and gold hasn’t been described yet.

2 Geology

In the Hajvali-Kizhnica-Badovc region 3 structural zones (Fig. 1), which control Pb-Zn mineralization, are present: Hajvali-Badovc; Kizhnica; Okosnica (Durmishaj et al. 2015).

The area consists of Paleozoic and Mesozoic magmatic, metamorphic (serpentinites, gneisses) and sedimentary rocks (flysch), Neogene volcanic rocks (andesites) and Pliocene sediments (Fig. 1). The polymetallic mineralization in Kizhnica Pb-Zn-Ag deposit occurs as lenses, irregular veins, and stockwork-impregnations at the contact between the Jurassic serpentinites and the Cretaceous flysch series, usually close to the andesite intrusions (1.6 x 0.3 km wide zone) (Kołodzieczyk et al. 2016b).

Besides the main ore bodies exploited during the 20th century as an open pit, there are numerous polymetallic occurrences in the Kizhnica area. Preliminary studies indicate that the large scale mineral zonation in the whole massif can be inferred. Moreover, alteration typical for porphyry-epithermal systems has been observed in the hills.

3 Samples and investigation methods

3.1 Investigated material

Representative samples of various ore types (massive - vein - banded ore and listwaenite-type ore) were collected from the old dumps, approximately 1 km to the south from the Kizhnica open pit (Fig. 1). The location is related to the Hajvali-Badovc structural zone. Banded ore is composed of zones of sulfides, sulfosalts and Fe-Mn carbonates. Greenish listwaenite-type ore is partially brecciated and enriched in galena, sphalerite and Ni sulfarsenides.

3.2 Analytical techniques

Preliminary investigation of polymetallic mineralization from the Kizhnica area was conducted in reflected-light microscopy. Chemical analyses of representative ore samples were determined by a JEOL JXA-8230 Super Probe electron microprobe (EPMA) at the Critical Elements Laboratory AGH-KGHM in Kraków. Operating conditions were an accelerating voltage of 20 kV, a beam current 20 nA, peak time of 20 sec, and a background time of 10 sec. Following standards: natural: (pyrite, stibnite, chalcopyrite, galena, arsenopyrite, greenockite, cinnabar, herzenbergite) or synthetic (native Ag, native Bi, Sb$_2$Se$_3$, In$_2$S$_3$, GeS, GaAs, pure Co and Ni) and spectral lines: Ag(L$_\alpha$), Pb(M$_\alpha$), S(K$_\alpha$), Sb(L$_\alpha$), Fe(K$_\alpha$), Bi(M$_\alpha$), As(L$_\alpha$) for sulfosalts, stibnite and berthierite, Sb(L$_\alpha$), S(K$_\alpha$), Fe(K$_\alpha$), Co(K$_\alpha$), Ni(K$_\alpha$), Cu(K$_\alpha$), Bi(M$_\alpha$), As(L$_\alpha$) for Ni minerals, pyrite and arsenopyrite, S(K$_\alpha$), Zn(K$_\alpha$), Fe(K$_\alpha$), In(L$_\alpha$), Sn(L$_\alpha$), Cd(L$_\alpha$), Cu(L$_\alpha$), Hg(M$_\alpha$), Mn(K$_\alpha$), Ga(L$_\alpha$), Ge(L$_\alpha$) for sphalerite.

4 Pb-Zn-Sb-Ni-Au mineralization

The Zn-Pb-Sb-Au-Ni mineralization can be divided into two types: massive ore and listwaenite-type ore. Three mineralization stages were distinguished in dominant - massive type. First stage is represented by main sulfides (sphalerite, galena, chalcopyrite, pyrite and stibnite), Pb-Sb sulfosalts (boulangerite, semseyite, chovanite and jamesonite), berthierite, Fe-Mn carbonates and quartz. Second stage is represented by idiomorphic prismatic marcasite crystals and Fe-Mn carbonates. Third – breccia – stage is represented by carbonates, quartz, pyrite and older angular sulfide and sulfosalts fragments. The listwaenite-type ore is enriched in galena veinlets, separate sphalerite and boulangierite aggregates and disseminated pyrite - arsenopyrite - gersdorffite mineralization. Intense brecciation of listwaenites is observed. Galena is rich in mineral inclusions such as pyrite, tetrahedrite and pyrrhotite. Gersdorffite occurs as idiomorphic zoned crystals, commonly around dissolved pyrite aggregates. Ullmannite was also identified as a zones in gersdorffite crystals. Additionally, native gold grains occur in the quartz-sphalerite listwaenite-breccia.

![Figure 2](image-url)  
Figure 2. Reflected light (a; b; c) and BSE (d; e; f) photomicrographs demonstrating ore paragenesis in massive ore and listwaenite-type ore.  
a. Idiomorphic crystals of semseyite (sy), sphalerite (sph) and Fe-Mn carbonates (Fe-Mn cb) from ore. b. Polysynthetic twinning of stibnite (stbn). c. Separate native Au crystals (Au) at the edge of sphalerite aggregate. d. Oscillatory zoned sphalerite aggregates consisting of Fe-poor and Fe-rich zones; semseyite. e. Aggregate composed of gersdorffite (grf) in the core, ullmannite (ulm) in the center and transition Sb-bearing gersdorffite at the contact between ullmannite and external gersdorffite; galena (gn) and pyrite (py). f. Zonal gersdorffite with dissolved zones and replaced by galena; sphalerite.

4.1 Sphalerite
Sphalerite is a dominant mineral of massive ore and typically is intergrown with galena and sulfosalts (Fig. 2 a; d). Isolated sphalerite aggregates are also observed, mostly within the listwaenite-type ore. The sphalerite of both types shows zonality in the BSE images (Fig. d) which is due to differences in Fe content (0.8-22.7 wt.%). Sphalerite crystals from the listwaenites-type ore is much more enriched in trace elements than typical sphalerite from the massive ore e.g. in indium (0.07-0.75 wt.%). Gallium and cadmium are abundant with relatively elevated contents (Ga: ~0.07 wt.%; Cd: ~0.14 wt.%) from both mineralization styles. Sphalerite contains as admixtures up to 2.16 wt.% Cu, up to 0.51 wt.% Mn, up to 0.33 wt.% Sn.

4.2 Pb-Sb sulfosalts, stibnite and berthierite

Several generations of sulfosalts are observed. Boulangerite, semseyite, chovanite, jamesonite were recognized in the massive ore. Semseyite is the most widespread sulfosalt in the samples and occurs as zones up to 1 cm composed of idiomorphic crystals (Fig. 2 a). There are also big autonomous aggregates overgrown by sphalerite and galena (Fig. 2 d). Additionally, semseyite and boulangerite are observed as separate aggregates in the listwaenite ore. Chovanite was recognized as small inclusions up to several μm enclosed in semseyite crystals. Transition into chemical composition of boulangerite – semseyite – chovanite series are observed. Boulangerite contains 55.4-55.7 wt.% Pb and 24.9-27 wt.% Sb, semseyite has 50.7-53.9 wt.% Pb and 26.5-30.2 wt.% Sb, but chovanite has 49.2-50 wt.% Pb and 27.1-28.6 wt.% Sb. The Bi content in these sulfosalts ranges 0.17 to 0.34 wt.%, Fe content is up to 0.28 wt.%. As content is approximately 0.22 wt.%. Another sulfosalt present in the samples is jamesonite, which fills microfractures in quartz. Jamesonite is characterized by homogenous chemical composition and has approximate formula (Pb<sub>1.12</sub>Fe<sub>0.88</sub>Bi<sub>0.03</sub>Cu<sub>0.01</sub>Sb<sub>5.75</sub>As<sub>0.19</sub>). It is depleted in antimony and iron, however is enriched in lead and arsenic.

Stibnite is present in the form of prismatic crystals up to several cm intergrown with pyrite and berthierite in massive Sb ore (Fig. 2 b). Stibnite with approximate formula Sb<sub>1.8</sub>As<sub>0.08</sub>Bi<sub>0.03</sub>Cu<sub>0.01</sub>Sb<sub>5.75</sub>As<sub>0.19</sub> is characterized by homogenous chemical composition. Berthierite occurs as rounded aggregates up to 50 μm spreaded in stibnite only. It contains As (~0.7 wt.%) and Bi (0.08-0.15 wt.%).

4.3 Gersdorffite-ullmannite, arsenopyrite and native Au related to the listwaenite mineralization

Gersdorffite was found only in the listwaenites-type ore and forms separate idiomorphic crystals up to 150 μm. These crystals often occur as numerous accumulation at the edges of galena and sphalerite aggregates. Gersdorffite are characterized by zonality, some of the zones were dissolved and replaced by galena and quartz (Fig. 2 f). Dissolved, rounded pyrite crystals are common in the gersdorffite aggregate’s core (Fig. 2 e). These pyrites are enriched in cobalt (up to 4 wt.%) and nickel (~2.4 wt.%). The Kizhnica gersdorffite is characterized by variable Ni and Fe content, Ni ranges from 0.66 to 0.99 apfu, Fe ranges from 0.01 to 0.32 apfu. Zonation of crystals related to the iron content is irregular. Low-Fe gersdorffite dominate in the samples. Low content of Co in gersdorffite is observed (up to 0.1 apfu). Most of the gersdorffite have relatively constant content of arsenic (0.92-1.04 apfu). One of the gersdorffite aggregate is characterized by presence of ullmannite zone and transition zone between them (gersdorffite-ullmannite solid solution - GUS) (Fig. 2 e).

Arsenopyrite is observed in listwaenite-type ore and forms separate crystals up to 200 μm. Deficiency of As content (~0.9 apfu) in comparison to S content (~1.08 apfu) is observed.

Native Au is rare and forms small grains (up to 25 μm) at the edge of sphalerite aggregates (Fig. 2 c). Native gold contains Ag (12-13 wt.%) and Hg (~0.5 wt.%)

5 Discussion and conclusions

Obtained chemical composition of main ore minerals from massive ore and listwaenite-type ore were compared to the sulfides, sulfosalts and sulfarsenides from the polymetallic occurrences within the Vardar Zone as well as listwaenite-hosted mineral occurrences.

High Fe admixture in sphalerites is common for many Pb-Zn deposits in Kosovo (Kolodziejczyk et al. 2016b). Therefore, elevated Fe content in sphalerites polymetallic occurrences and deposits within the Vardar Zone this study (~10 wt.%) is typical for Trepça Mineral Belt. Elevated Fe content was confirmed in Artana and Stan Terg. ~8.42 wt.% and ~9.25 wt.%, respectively. Iron admixture in sphalerite from Kizhnica open pit is ~11.88 wt.%. Sphalerite from listwaenite-type ore is characterized by enrichment trace elements content e.g. indium, gallium and cadmium. Particular attention should be given to increased indium content in sphalerites from listwaenite-type ore (0.07-0.75 wt.%). In many cases extreme In content is strictly related to the Sn mineralization e.g. Potosi deposit (Bolivia), where indium content in sphalerite was detected up to 9.6 wt.%, however Sn reaches ~5 wt.% (Murakami & Ishihara 2013). Much more similarities in indium admixtures from Kizhnica sphalerites are observed compared to the ZnS from Bolivar deposit, Bolivia (In: up to 0.69 wt.%; Sn: up to 0.3 wt.%) and Ashio deposit, Japan (In: up to 0.77 wt.; Sn: ~ 0.4 wt.%). In this study tin content in sphalerites reaches up to 0.33 wt.%. Sphalerites from Kizhnica mine is characterized by increased Sn content up to 663 ppm (Kolodziejczyk et al. 2016b).

Presence of Pb-Sb sulfosalts is common in many polymetallic occurrences and deposits within the Vardar Zone. Boulangerite was confirmed in Stan Terg and Drazhnje deposit. Semseyite is widespread e.g. in Rogozna ore field (Radosavljević et al. 2015) and...
Kamariza area in Greece (Voudouris et al. 2018). Similar Pb-Sb sulfosalts (boulangerite – semseyite – chovanite) are observed in Vllahi area, Kosovo (Węgrzynowicz et al. unpublished).

The chemical composition of gersdorffite-ullmannite solid solution (GUS) from Kizhnica, shows a lot of similarities with GUS from Clemence mine (Kamariza area, Greece), where Fe content varying from ~1.5 to 9.0 wt.% and Ni content is from ~24 to 32 wt.% (Voudouris et al. 2018). Perfect linear correlation between Fe–Ni related to the substitution in the gersdorffite structure is observed (Fig. 3). In Kosovo gersdorffite was described by Radosavljević et al. (2015) in Rogozna ore field, where presence of GUS was verified. In Rogozna gersdorffite, Sb-bearing gersdorffite, and As-bearing ullmannite occur, thus the Sb-part of solid solution is much more widespread than in the Kizhnica area. Additionally, unpublished data from Stan Terg area – Melenica and Mazhiq (Wojtalone et al. unpublished) show several similarities with chemical composition of Fe-poor gersdorffite from the listwaenites, where similar trend in Ni–Fe substitution is observed. Ni mineralization from the Stan Terg area are related to this same tectonic zone as Kizhnica mineralization.

Au occurrences in listwaenites are known from numerous localities e.g. Svetluka in Bulgaria (Kunov et al. 2007). Voudouris et al. (2018) reported native Au related to the vein-type Pb-Ni-Bi-Au-Ag mineralization in Kamariza area, Greece, containing 11.50-18.56 wt.% Ag. In Kosovo, Kołodziejczyk et al. (2016a) described native gold in skarn related associations (~90 wt.% Au) and electrum from Ag-minerals associations dispersed in galena from the Stan Terg deposit. Native gold from this study has increased content of Hg (~0.5 wt.%), similar to the gold from Stan Terg (up to 0.72 wt.%). Presence of native gold in listwaenites from Kosovo was confirmed in Rogozna ore field (Radosavljević et al. 2015). In the Kizhnica area, presence of gold was reported 4 km to the east from this locality (Slivovo project), but in different host rocks – calcareous sedimentary units. However, source of the fluids responsible for the mineralization is the same – hydrothermal solutions related to the younger generation of andesites.

In summary, there are many similarities between Pb-Zn-Sb-Ni-Au mineralization from the Kizhnica area and same mineralization type from other part of Vardar Zone e.g. Crmac deposit (Kosovo) and Clemence mine (Kamariza area, Greece). Especially interesting from the mineralogical point of view seems listwaenite-type mineralization, where increased contents of Ni, Au and In can suggest future surveys.

Acknowledgements

Research was founded by AGH grant No. 11.11.140.320. We are grateful to Adam Włodek from the Laboratory of Critical Elements at AGH-UST, Faculty of Geology, Geophysics and Environmental Protection for help during EMPA data collection.

References


The gold Zun-Kholbinskoe deposit (Russia, Republic of Buryatia): ore mineralogy, geochemistry, geochronology

Anikina E., Aristov V., Chugaev A., Borisovsky S.
IGEM RAS, Moscow, Russian Federation

Travin A
IGM SB RAS, Novosibirsk, Russian Federation

Abstract. Zun-Kholbinskoe intrusion related gold deposit is located in the southeastern part of the Altai-Sayan folded area. Short veins and mineralized zones are occurred in shear zone between Neoproterozoic dolomitized and marbled limestones and granodiorites. The main type of metasomatism is sericitic alteration for aluminosilicate and carbonate-aluminosilicate rocks. Main ore mineral have been recorded: pyrite, pyrrhotite, sphalerite, chalcopyrite, galena, tetrahedrite, electrum. The deposit was formed in 2 stages. The development of ore-forming processes occurred in the time interval of 380-360 Ma. We assume that the ores associated with the polymetallic mineralization in the upper and peripheral areas of the deposit should be expected.

1 Introduction

Altai-Sayan gold province is one of the largest in Russia. A significant share of its resources is connected with deposits located in the territory of the Eastern Sayan. Despite the long history of studying the region, there are still many controversial issues related to the formation models, conditions of localization of gold deposits. We have studied the mineralogical and geochemical features and carried out geochronological studies of the Zun-Kholbinskoye gold deposit. Determination the prospects of mineralization in the upper and peripheral parts in the deposit was a main target of researches. The sequence of geological events and regularities of distribution of valuable components and their minerals in deposit were studied for this purpose.

The Zun-Kholbinskoe deposit is located in the southeastern part of the Altai-Sayan folded area. The area of the region is composed of Archean-Proterozoic crystalline schists and gneisses, terrigenous-carbonate rocks, granitoids and rocks of the ophiolitic association (Fig. 1). The tectonic position of the deposit is defined as the accretion-collision zone on the oceanic crust in the zone of collisional interaction of the Siberian platform with the continental crust. The main role in the control of mineralization belongs to large shear faults. Geologically and structurally, the deposit is coinciding with the suture zone, which divides the Late Archean (~2.7 billion years) rocks and the Neoproterozoic (~0.8 billion years) granitoids. Dikes of different composition form a radial series in the southeast and southern parts of the area.

Gold ore mineralization is controlled by tectonic zones of folding, schistosity and cataclase (shear zone). The host rocks are granodiorites, dolomitized and marbled limestones as well as rocks of tectonic mélanges. Within the ore field are limestones deposited in wide synclines with flat-dipping bedding in the joints and steep on the slopes. The main type of metasomatism is sericitic alteration for aluminosilicate and carbonate-aluminosilicate rocks.

2 Methods

The chemical composition of minerals was performed on the JXA-8200 (JEOL Ltd., Japan) electron microprobe with five wavelength-dispersive spectrometers at the IGEM RAS. The operating conditions involved a voltage of 20 kV and a probe current of 20 nA and a beam diameter of 1 μm.

Figure 1. The geological scheme of the region (according to the data of PJSC “Buryatzoloto” is simplified). 1 – Neogene basalts; 2 – Upper Paleozoic granitoids and alkaline rocks; 3 – Upper Devonian conglomerates; 4 – Paleozoic plagiogranites; 5 - ophiolites; 6-8 – stratified Cambrian-Devonian deposits: 6 – terrigenous-volcanogenic; 7 – terrigenous; 8 – terrigenous and carbonate; 9 – Archean gneisses of the Gargan block; 10 – Zun-Kholbinskoe gold deposit.

The age of metasomatites was determined using ⁴⁰Ar/³⁹Ar and Rb-Sr methods. ⁴⁰Ar/³⁹Ar studies of sericite were executed in the laboratory of isotope-analytical methods of the IGM SB RAS according to the methodology (Travin et al. 2009). The study of the Rb-Sr isotopic system of rocks and rock-forming minerals was carried out at the IGEM RAS according to the methodology (Chugaev et al. 2017). In total, 9 samples of metasomatites were analyzed.

Concentrations of rock-forming elements were performed by x-ray fluorescence analysis (XRF) on a vacuum spectrometer of sequential action in IGEM RAS. The spectrometer is equipped with a 4 kW x – ray tube with Rh anode.
The atomic emission determination of elements was performed using an iCAP-6500 Duo spectrometer (Thermo Scientific, United States). Quadrupole mass spectrometer X-7 (Thermo Scientific, USA) was used for mass spectral determination of elements.

3 Results

3.1 Ore mineralogy

Ore bodies are represented by steeply dipping mineralized zones and veins. 2 events of formation of ore mineralization were revealed. The first led to the formation of the bulk of coarse pyrite, which forms the basis of the ore bodies. Later mineralization is represented by polysulphide associations (Fig 2). The main ore minerals have been identified: pyrite, pyrrhotite, sphalerite, chalcopyrite, galena, tetrahedrite, electrum.

Figure 2. Polysulphide vein in early pyrite. Sulphides are represented by galena (Gn), chalcopyrite (Cp), tetrahedrite (Fhl) and sphalerite with emulsion impregnation of chalcopyrite (S1 + Cp). The transparent polished section. Reflected-light image.

Early pyrite forms clusters of aggregates that form subvertical curved bands. These bands have a sinsedimentational appearance, i.e. after their formation, they were deformed together with the host rocks. This pyrite makes up 80% of the total amount of ore minerals. Pyrite has inclusions and veinlets along the cracks of all other minerals (Fig. 2b). In chemical composition, it is uniform and devoid of impurities.

Pyrrhotite is found in various quantities at all levels of the deposit. As a rule, it forms relics, largely dissolved by later ore-forming fluids. The composition of pyrrhotite corresponds to the formula Fe0.90-0.95S1.01-1.08. Component variations: Fe – 59.1-61.4 wt.%, S – 38.0-39.7 wt.%, Ni – 0.1-0.3 wt.%, Co – 0.1-0.6 wt.%

Chalcopyrite was observed in two basic forms: emulsion impregnation into the sphalerite and intergrowths with other sulphides in the intergranular space of pyrite and barren matrix. Its presence determines the copper content in the ore. In terms of its chemical composition, chalcopyrite is represented by a stoichiometric pure species.

Sphalerite is a widespread ore mineral. Most often sphalerite is part of polysulphide aggregates alongside with galena, chalcopyrite and pyrrhotite. The chemical composition of sphalerite: Zn 53.1-66 wt.%, Fe 1.1-9.3 wt.%, Cd 0.3-2.9 wt.%, S 30.7-37.5 wt.%

Galena forms inclusions in early pyrite and is a part of polysulphide aggregates (figure 2b) in close accretion with sphalerite and chalcopyrite. Variations in the content of chemical elements in galena are: Pb – from 77.8 to 87.9 wt.%, S – from 12.7 to 16.6 wt.%, Ag – from 0 to 1.9 wt.%, Bi – from 0 to 7.8 wt.%, Cu – from 0 to 2.8 wt.%. It should be noted that in the upper levels of the deposit there is a clear correlation between bismuth and silver (field A in Fig. 3). On the lower horizons, bismuth is part of the galena independently (field B in Fig. 3).

Fahlores were noted in single samples. Two types of fahlores were identified: tetrahedrite (Ag<9 wt.%) in association with galena, sphalerite and chalcopyrite and freibergite (Ag>23 wt.%) in intergrowth with galena. Compositional variations in the pair Ag–Cu and Fe–Zn are noted. The chemical composition of the fahlores of the tetrahedrite-freibergite series varies: Ag – from 3.65 to 26.0 wt.%, Cu – from 19.0 to 35.8 wt.%, Fe – from 4.2 to 6.9 wt.%, Zn – from 0.2 to 2.5 wt.%, Sb – from 25.9 to 28.2 wt.%, S – from 22.3 to 25.4 wt.%. Some grains of fahlores have a zonal structure (Fig. 4).

Figure 3. The ratio of bismuth and silver in galena. Explanations in the text

Figure 4. Zonal structure of the fahlore (Fhl) in intergrowth with galena (Gn). BSE image

Intermetallic compounds of gold and silver are
observed everywhere. Their sizes vary from first up to 40 µm. By the ratio of Au/Ag, all compounds fall into the composition field of the electrum. It should be noted that the mass fraction of gold in the compounds has a large variations in the lower horizons of the deposit. The gold purity decreases in the upper and peripheral sites of the deposit. Electrum is found in pyrite, pyrrhotite, and barren matrix as inclusions. In addition, electrum is formed in an intergrowth with various sulphides, demonstrating its later formation time.

The close connection between electrum and galena attracts attention (Fig. 5). It is predominantly localized in the intergrains and microcracks. The ratio of elements in the compound varies from 1:0.26 (Au/Ag = 3.88) to 1:6.88 (Au/Ag = 0.15).

3.2 Geochemistry

To identify the geochemical features of rocks and ores of the deposit, several indicators were chosen: \( \Sigma \text{LREE}/\Sigma \text{HREE}, \text{Hf/Sm, Nb/La, Th/La, Eu/Eu*}, \text{Ce/Ce*}, \text{Zr/Hf, U/Th, Co/Ni, Au/Ag}. \)

Zr/Hf ratio in ores varies from 5 to 1752 (average 93), with Y/Ho - from 25 to 52 (average 36). Most of the values are outside the field 26<Zr/Hf<46 and 24<Y/Ho<34. It may indicate a significant fractionation (active interaction) between the rocks and the fluid.

The average \( \Sigma \text{LREE}/\Sigma \text{HREE} \) ratio in granitoids is 8-12, in limestone – 5.5, in ores – 8.8. The dispersion of REE contents may indicate a REE differentiation in ore-bearing fluids. In all ores the Hf/Sm, Nb/La and Th/La ratios are less than 1, which does not contradict the assumption of the presence of the Cl- or SO\(_4\) in the composition of the ore-forming fluid.

The average Ce/Ce* value in ores is 0.9 with variations from 0.7 to 1.2. The average values of Eu/Eu* fluctuate around 1 with variations from 0.4 to 3.6. These data can reflect the variation in oxygen fugacity at almost constant temperature of an ore-forming fluid (Bau, 1991).

U/Th and Co/Ni ratios were used as an indicator of the redox characteristics of the fluid (Kun et al. 2014). U/Th values for ores in altered granodiorites vary from 0.2 to 1.2, for ores in tectonic mélanges and limestones - from 0.17 to 16. The value of Co/Ni in ores almost exceeds 0.2 (in altered granodiorites 0.9, in tectonic mélanges 1.4). The obtained data are consistent with the assumption of the fluid’s and environment redox variation during ore deposition.

The polymodal distribution of the gold-silver ratio in ores has been established (Fig. 6). The redistribution of gold and silver during the metamorphism of ores is a possible reason for the increase in Au/Ag contrast ratio.

Based on correlation and common factor analysis for ore elements, two geochemical association are recognized: Te-Bi-Ag-Au-(±As±Mo) and Cd-Zn-Pb-Sb-Cu-Ag. First one is close to historical ore shoots with high grades ores. Elements of the second association is typical for poor ores, upper parts and flanks of ore bodies, but complex and high grades correspond to swells in ore bodies. Hence, multiplicative indicators for express evaluation of mineralization intensivity can be proposing. The high values of the first indicator (Te*Au*As) can correspond with high-grade ore shoots and the second (Sb*Ag*Pb) - to the swelling of the ore bodies.

3.3 Geochronology

The geochronological study was carried out for the ore bearing metasomatites – quartz-sericite and quartz-carbonate-sericite rocks. According to geological and mineralogical data, metasomatites are paragenetic with Au-bearing mineralization: they were formed during common hydrothermal event. Metasomatites are formed by Neoproterozoic granitoids of different composition.

For the majority of \(^{40}\text{Ar}-^{39}\text{Ar} \) sericites studied, age spectra have the form of a "ladder upwards". Only for two samples spectra with good age plateaus were obtained. The \(^{40}\text{Ar}-^{39}\text{Ar} \) dates calculated for them are 370±6 (2σ), 367±7 Ma (Fig. 7). Rb-Sr data were also obtained for 9 samples of metasomatites. Data analysis using the method of isochronous construction showed that only two samples obtained isochrones with the following parameters: T = 363±6 Ma, MCWD = 6, \(^{87}\text{Sr}/^{86}\text{Sr} \) 0 = 0.7133±9 (2σ); T = 377±4 Ma, MCWD = 5, \(^{87}\text{Sr}/^{86}\text{Sr} \) 0 = 0.7126±3 (Fig. 8). It can be seen that the Rb-Sr isochronal ages are close to each other and coincide with the above \(^{40}\text{Ar}-^{39}\text{Ar} \) ages.
The results of the study of K-Ar and Rb-Sr isotopic systems indicate that near ore metasomatites were subjected to superimposed hydrothermal processes, which resulted in a partial loss (less than 5%) of radiogenic $^{40}$Ar, as well as the redistribution of Sr in the volume of individual samples.

Figure 7. $^{40}$Ar/$^{39}$Ar age spectrum of sericite from near vein metasomatites of ore zone.

Figure 8. Rb–Sr isotopic diagram for sericite, bulk metasomatite probe, light fraction, heavy fraction and acid extract.

4 Conclusion

The gold-sulphide Zun-Kholbinskoe deposit was formed in 2 stages. In the first stage, coarse crystalline ores, mainly consisting of pyrite, were formed. Most likely, early mineralization was deposited near simultaneously with the introduction of granodiorite. Ore-forming occurred quickly, under nonequilibrium conditions. It led to significant differences in the gold purity and the indistinctly manifested processes of differentiation of the substance. This is most pronounced on the lower horizons.

The consistency of datings obtained by different geochronological methods gives reason to conclude about the Late Devonian age of formation of the first stage of mineralization. The development of ore-forming processes occurred in the time interval of 380-360 Ma. This interval partially overlaps with the period of development in the region of Paleozoic collisional magmatism, one of the peaks of which occurred at the time 400-370 million years ago (Vorontsov, Sandimirov 2010). Geochronological studies also showed that the K-Ar and Rb-Sr isotope systems were broken in most of the studied samples as a result of the impact on the rocks of later hydrothermal processes. This conclusion does not contradict the existing ideas about the polychronic formation of mineralization on the deposit (Gorokhovsky et al. 2016).

The proportion of polymetallic mineralization in ores significantly increases at the second stage of formation. They mainly occupy peripheral and upper parts. The sequence of mineral associations indicates a decrease in the time of the role of iron in the mineral-forming solution and a reduction of sulfur fugacity. According to Liu et al. (2013) hydrothermal fluids containing Cl effectively concentrate LREE, but are poor in HREE. In all ores of Zun-Holbinskoe deposit, the average Hf/Sm, Nb/La and Th/La values are less than 1, which indicates the presence of Cl ion in the composition of the ore-forming fluid. We assume that the ores associated with the polymetallic mineralization in the upper and peripheral areas of the deposit should be expected. While the amount of gold increases, and its purity is reduced.

Acknowledgements

The study was supported by the PJSC "Buryatgoldoloto" (contract No. L/BZ-15-0000191) and Program of Fundamental Research.

References


The source of Au and S of the orogenic gold deposits in the Llamas de Cabrera district (Iberian Variscan Massif)

Fernando Gómez-Fernández¹, John K. Cunningham², Pablo Caldevilla¹, Antonio Herrero-Hernández³ and Andrew D. Beard ²

¹Área de Prospección e Investigación Minera, Universidad de León, Spain
²Department of Earth and Planetary Sciences, Birkbeck College, University of London, UK
³Grupo de Investigación INGEOMAT, E.S.T.I. de Minas, Universidad de León, León, Spain

Abstract. Using optical scanning electron microscopy, electron microprobe and sulphur isotopic analysis, pyrite and graphite in black slates and volcanic rocks from Luarca Formation were studied. Four types of pyrite are present in the black slates. In ascending order according to their evolutionary degree: framboidal, framboidal evolved, subhedral macroscopic, and euhedral macroscopic pyrite. The content in Au, As and other metals are significantly higher in the framboidal than in the other pyrite types. The gold included in the pyrite and probably also in the organic matter would have been released during diagenesis and Variscan metamorphism, in order to form the orogenic gold deposits in the district. δ³⁴S distribution in Luarca Formation pyrites is similar to that of sulphides from the gold deposits in the district, with mean values of 13.8‰ and 12.4‰ respectively, although in the pyrites from the black slates the variability range is wider. The data gathered are in agreement with the existence of two sulphur sources, marine sulphate and magmatic sulphur, the former being the main source of the sulphur involved in these processes.

1 Geological setting

The Llamas de Cabrera Gold mining district, mined during the Roman Empire and rediscovered by Matías and Gómez-Fernández (2003), is located in the northern limb of the Truchas Synform (Central Iberian Zone, Iberian Variscan Massif; Figure 1). This synform is a complex structure formed by the coaxial interference of Variscan phase1 and phase 3 events and several North verging phase 2 thrust structures (Marcos 1973; Pérez-Estaún 1975). The rock main schistosity (S₁) was developed during phase 1. The Palaeozoic sedimentary record spans all of the Ordovician system, represented by a large succession of siliciclastic formations, mainly slates, phyllites and quartzites. Due to their metallocenic interest, two formations stand out: the Lower to Middle Ordovician Armorican Quartzite (Matte 1968), dominated by massive white quartzite, and the Middle Ordovician Luarca Formation (Barrois 1882), made up of a monotonous succession of black slates, with local intercalations of volcanic rocks with a bimodal composition (basalts and rhyolites; González Menéndez et al. in press). Gold deposits are hosted in the upper layers of the Armorican Quartzite and occasionally in slates from Luarca Formation.

2 Initial hypothesis

The aim of this work is to determinate the origin of gold and sulphur of the orogenic gold deposits in the Llamas de Cabrera district. For Herail (1984), the origin of gold of these deposits would be in gold palaeoplacers presents in the Armorican Quartzite. However, for Gómez-Fernández et al. (2012b) the gold present in the quartzite has a hydrothermal origin, like the rest of the primary gold deposits in the sector.

Regardless of the background mentioned in the previous paragraph, according to the starting hypothesis of the present work, the gold would have been carried, into the sedimentary basin contemporaneously with the deposition of the Luarca Formation. The provenance of this gold and the description of its transport into the sedimentary basin go beyond the object of this work. Such gold would have been concentrated in the framboidal biogenic pyrites and the organic matter, within anoxic to euxinic sedimentary environments. During the advanced diagenesis and the early metamorphism, pyrite recrystallizes to form coarser sub to euhedral pyrites. At
the same time, organic matter evolves to graphite. These processes release gold, arsenic, sulphur and other metals to the metamorphic/hydrothermal fluids (Large et al. 2011). Such gold would have deposited later in extensional areas.

Previous work on the Truchas Synform (Ward and Gómez-Fernández 2003; Gómez-Fernández et al. 2009a, b; Cárdenes et al. 2016), revealed the coexistence of several sulphides (pyrite and pyrrhotite among them) in black slates (Luarca Formation and others). Likewise, these authors cite the presence of frambooidal, subhedral and euhedral pyrites, which represent several evolutionary stages, as stated in the model from Large et al. (2011).

3 Methodology

The slates and the volcanic rocks from the Luarca Formation were sampled near and far to the ore deposits. Polished thin sections and mounts from these samples were studied in the University of León (Spain) using an Olympus BS51 petrographic microscope and a JEOL JSM-6480 scanning electron microscope, equipped with an Oxford D6679 EDS detector. Compositional analyses on pyrites and graphite were carried out using an electron microprobe (CAMEBAX SX-100) employing wavelength dispersive spectrometry at the Severo Ochoa Centre (Universidad de Oviedo, Spain). The diameter of the electron beam was 2 μm and all determinations were performed at a potential of 20 kV and a beam current of 20 nA. ZnS (Zn), Auº (Au), Niº (Ni), Pyr_mac (S, Fe), MoS2 (Mo), Ag, Ag2Te_mac (Ag, Te), Stib (Sb), Coº (Co), Cuº (Cu), Aspy_mac (As), HgS (S) and PbS (Pb) were used as standards for determination of the respective elements in brackets. The limits of detection vary in each of the 2514 analyses made. At the bottom of Table 1, their minimum values are shown.

Furthermore, 13 sulphur stable isotope analyses were made following standard procedures (Robinson and Kusakabe 1975), in pyrites coarse enough so that these techniques could be applied. Cubic pyrites more than 7 mm wide were analyzed in both nucleus and rims. Analyses were performed at the Servicio General de Isótopos Estables of Salamanca University (Spain) in which SO2 gas was liberated by combusting with excess Cu2O at 1075 °C, in vacuum conditions. Liberated gases were analyzed on a VG Isotech SIRA II mass spectrometer, and standard corrections were applied to raw δ34S values to produce true δ34S values. The standards employed were the international standards NBS-123 or NBS-127. These gave δ34S values of +17.1‰, −31.5‰, and −4.6‰ respectively, with 1σ reproducibility better than ±0.2‰. Data were reported in δ34S notation as permil (%) variations from the Vienna Canyon Diablo Troilite (V-CDT) standard.

It is expected that the frambooidal pyrites, described in the following section (Types I and II), not valid for the techniques above mentioned due to their small size, will be analyzed in future work using NanoSIMS. For the same reason, many of the Type III pyrites will be analyzed by LA-ICP-MS.

4 Results

4.1 Pyrites and graphite: morphology and types

Pyrite and graphite are two of the accessory minerals in the slates of the Luarca Formation (Gómez-Fernández et al. 2009a, b). Graphite appears as elongated crystals parallel to S1, with thickness reaching 8 µm. It shows a laminar inner structure, parallel to the crystal edges. Regarding the pyrite, according to its morphology and its relation to the main schistosity of the slate, 4 types are distinguished (Figure 2):

- Type I: Framboidal pyrite, formed by spherical raspberry-like aggregates up to 50 µm in diameter, composed of numerous spherical grains whose diameter is approximately 2 µm (Fig. 2A). They were formed in sedimentary environments under anoxic to euxinic conditions, and they are of biogenic origin (Folk 2005; Cavalazzi et al. 2014).

- Type II: Framboidal pyrite evolved, generated by overgrowth of crystals upon frambooids (Wei et al. 2012). The frambooidal structure is still evident, with coalescence between crystals and development of subhedral shapes.

- Type III. Subhedral macroscopic pyrite. It appears along with carbonates, quartz and other sulphides. They form porphyritic aggregates, elongated parallel to S1 and outlined by it (Fig. 2A), which reflects their pre-kinematic to syn-kinematic character. Their dimensions are varied and may reach 1 x 10 mm.

- Type IV. Euhedral macroscopic pyrites, usually cube...
shaped (Fig. 2B) and occasionally forming euhedral to subhedral aggregates. On the one hand, they crosscut the S1 and on the other hand they usually present pressure shadows, which indicates they formed after phase 1 and before the last episode of Variscan deformation.

The volcanic rocks from the Luarca Formation show scarce euhedral pyrites, often cubical, up to 5 mm wide. Even though their morphology is similar to Type IV in slates, their temporal relation to the Variscan deformation has not been established.

### 4.2 Electron microprobe

The average metal content in the different types of pyrite and graphite, obtained by EMPA, is summarized in Table 1.

**Table 1. Mean metal content in pyrite types in the studied slates and volcanic rocks (EMPA data)**

<table>
<thead>
<tr>
<th>Host rock</th>
<th>Pyrite Type</th>
<th>Graphe</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>Volc. rocks</th>
<th>Slate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slate</td>
<td>Slate</td>
<td>Slate</td>
<td>Slate</td>
<td>Slate</td>
<td>Slate</td>
<td>Volc. rocks</td>
<td>Slate</td>
<td></td>
</tr>
<tr>
<td>N =</td>
<td>54</td>
<td>15</td>
<td>31</td>
<td>48</td>
<td>45</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As ppm</td>
<td>1999</td>
<td>1185</td>
<td>581</td>
<td>707</td>
<td>598</td>
<td>27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni ppm</td>
<td>1112</td>
<td>798</td>
<td>2345</td>
<td>272</td>
<td>117</td>
<td>N.D.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu ppm</td>
<td>236</td>
<td>523</td>
<td>241</td>
<td>105</td>
<td>46</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn ppm</td>
<td>650</td>
<td>22</td>
<td>17</td>
<td>12</td>
<td>55</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo ppm</td>
<td>144</td>
<td>21</td>
<td>31</td>
<td>27</td>
<td>45</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag ppm</td>
<td>170</td>
<td>189</td>
<td>166</td>
<td>163</td>
<td>136</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb ppm</td>
<td>53</td>
<td>5</td>
<td>21</td>
<td>28</td>
<td>34</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te ppm</td>
<td>50</td>
<td>22</td>
<td>22</td>
<td>21</td>
<td>18</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au ppm</td>
<td>217</td>
<td>54</td>
<td>40</td>
<td>44</td>
<td>52</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg ppm</td>
<td>208</td>
<td>66</td>
<td>94</td>
<td>80</td>
<td>181</td>
<td>78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S (%)</td>
<td>53.45</td>
<td>53.46</td>
<td>53.77</td>
<td>53.39</td>
<td>53.33</td>
<td>0.0067</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe (%)</td>
<td>45.39</td>
<td>45.68</td>
<td>45.63</td>
<td>46.19</td>
<td>45.93</td>
<td>0.2800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (%)</td>
<td>99.55</td>
<td>99.43</td>
<td>99.75</td>
<td>99.73</td>
<td>99.38</td>
<td>0.3185</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N = Number of analyses. N.D. = not determined. Lower detection limits(ppm): As (218); Ni(125); Cu(92); Zn(171); Mo (291); Ag(108); Sb(104); Te(99); Au(275); Hg(449); S(69); Fe(70).

As for the slates, the Au, As, Te, Hg, Sb, Mo and Zn contents are significantly higher in framboidal pyrites than in the other types. On the other hand, Ni, Cu and Ag contents do not follow a clear pattern.

The metal contents in framboidal pyrites have the same order of magnitude than those reported by Zhao et al. (2008) in framboidal pyrite from Southwestern Guizhou (China).

4.3 Stable isotopes

Collectively, the analyzed pyrites show a high variability in positive δ34S values (Table 2). The pyrites hosted in volcanic rocks show values of 7.6 and 7.8 ‰. Among the pyrites hosted in slates, the Type III ones show δ34S between 13.6 and 20.8 ‰, whereas the Type IV vary greatly, between 2.1 and 28.4 ‰. The sulphur distribution does not show big differences between the nucleus and the rims of the cubes.

**Table 2. δ34S_CDT in pyrites from types III and IV**

<table>
<thead>
<tr>
<th>Rock</th>
<th>Sample</th>
<th>Shape</th>
<th>Pyrite Type</th>
<th>δ34S_CDT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slate</td>
<td>11</td>
<td>Subhedral</td>
<td>III</td>
<td>13.6</td>
</tr>
<tr>
<td>Slate</td>
<td>29S</td>
<td>Subhedral</td>
<td>III</td>
<td>20.8</td>
</tr>
<tr>
<td>Slate</td>
<td>29S</td>
<td>Cube</td>
<td>IV</td>
<td>10.7</td>
</tr>
<tr>
<td>Slate</td>
<td>9</td>
<td>Aggregate</td>
<td>IV</td>
<td>20.5</td>
</tr>
<tr>
<td>Slate</td>
<td>7G03</td>
<td>Cube</td>
<td>IV</td>
<td>10.1</td>
</tr>
<tr>
<td>Slate</td>
<td>7G36</td>
<td>Cube</td>
<td>IV</td>
<td>16.6</td>
</tr>
<tr>
<td>Slate</td>
<td>43</td>
<td>Cube core</td>
<td>IV</td>
<td>28.4</td>
</tr>
<tr>
<td>Slate</td>
<td>43</td>
<td>Cube rim</td>
<td>IV</td>
<td>28.1</td>
</tr>
<tr>
<td>Slate</td>
<td>44</td>
<td>Cube</td>
<td>IV</td>
<td>8.3</td>
</tr>
<tr>
<td>Slate</td>
<td>M23</td>
<td>Cube core</td>
<td>IV</td>
<td>2.1</td>
</tr>
<tr>
<td>Slate</td>
<td>M23</td>
<td>Cube rim</td>
<td>IV</td>
<td>4.7</td>
</tr>
<tr>
<td>Volcanics</td>
<td>CF2-1</td>
<td>Cube</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>Volcanics</td>
<td>CF2-2</td>
<td>Cube</td>
<td>7.6</td>
<td></td>
</tr>
</tbody>
</table>

5 Discussion and conclusions

The distribution of metals in the different pyrite types from the Luarca slates is in line with the hypothesis of Large et al. (2011). Au and As contents are higher in framboidal pyrites and lower in other pyrite types, which can be interpreted as the result of the evolution to euhedral (Sawlowicz 1993; Merinero and Cárdenes 2008). Gold contents in graphite are also high enough to have been a meaningful gold source during the hydrothermal processes.

Table 3 shows a comparative summary regarding δ34S distribution in the sulphides from Llamas de Cabrera Gold District deposits and the pyrites from Luarca Formation. Both compositions are similar, with a wider variability range in pyrites than in slates. This feature may reflect that the sulphides from Luarca slates have provided sulphur to the hydrothermal fluid system. The hydrothermal transport would tend to homogenize the δ34S, so that ores would display more constant values than the sources.

The interpretation of δ34S results must be unavoidably incomplete, due to lack of δ34S data from the precursor framboidal pyrites (Types I and II). Nevertheless, the isotopic distribution of the most evolved pyrites (Types III and IV) is in agreement with the coexistence of two sources of sulphur: a) marine SO4, with heavy sulphur
Table 3. Comparison between δ34SCDT from sulphides in the ore deposits and the regional country rocks

<table>
<thead>
<tr>
<th>Ore deposits (*)</th>
<th>Luarca Fm. (**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ34SCDT (Apy,Py,Sph)</td>
<td>δ34SCDT (Py)</td>
</tr>
<tr>
<td>Number of analyses</td>
<td>17</td>
</tr>
<tr>
<td>Minimum</td>
<td>8.0</td>
</tr>
<tr>
<td>Maximum</td>
<td>23.1</td>
</tr>
<tr>
<td>Mean</td>
<td>12.4</td>
</tr>
</tbody>
</table>

(*) Gómez-Fernández et al. (2012a). (**) Data from Table 2

Abbreviations: Apy = arsenopyrite, Py = pyrite, Sph = sphalerite

(Huston 1999), which would have been reduced to H2S in anoxic to euxinic conditions and b) magmatic sulphur, much lighter, related to the deposition of volcanic rocks. Taking into account what has been observed in other orogenic gold deposits, it is probable that the marine sulphate has been highly dominant over the magmatic sulphur (Goldfarb et al. 2005; Large et al. 2011). Nevertheless, obtaining isotopic data from types I and II pyrites will allow refining of this model.

The data presented in this paper supports the initial hypothesis, according to whether the immediate origin of gold in the district deposits would be in the sulphides and the organic matter from Luarca Formation black slates. This gold would have been released to the environment as a consequence from the evolution of pyrite and organic matter during the diagenesis and the Variscan metamorphism to give rise to the deposits. Marine sulphate would have been the main source of the sulphur involved in these processes.

Acknowledgements

This project was funded by Project 0284_ESMIMET_3_E (INTERREG V-A Spain-Portugal Cooperation Programme, 2014-20) and by Project LE167G18 (Junta de Castilla y León, Spain).

References

Gómez-Fernández F, Ward C, Bauluz B (2009b) XRD, electron microscopy (EMPA, SEM, TEM) and XRF characterization of roofing slates from NW Spain. Cad Lab Xeel Laxe 34, 127–142

Acknowledgements

This project was funded by Project 0284_ESMIMET_3_E (INTERREG V-A Spain-Portugal Cooperation Programme, 2014-20) and by Project LE167G18 (Junta de Castilla y León, Spain).

References

Gómez-Fernández F, Ward C, Bauluz B (2009b) XRD, electron microscopy (EMPA, SEM, TEM) and XRF characterization of roofing slates from NW Spain. Cad Lab Xeel Laxe 34, 127–142
Understanding of the genesis of an orogenic gold deposit in the Central Cordillera of Colombia: constraints on gold grade variation

Daniel G. Sandoval M., Juan C. Molano M.
Universidad Nacional de Colombia. Bogotá

Diego Peñaloza
Sector Resources Ltda Colombia

Abstract. Microthermometrical and microchemical studies are useful tools to constrain fluid evolution. Understanding the distribution of temperature and the chemical controls in a mine could offer us insight into the pathway of the fluid and several other formational processes. In Santa Isabel, Colombia, a fluid of the CO₂-H₂O-CH₄±N₂ system, with a probable metamorphic origin, formed the deposit of Las Animas mine. Additionally, the decreasing temperature eastward from 324°C to 295°C, correlating with the increasing gold concentration, suggested the fluid flowed in that direction and underwent boiling, which in turn, triggered a phase separation process and mineral precipitation, witnessed by coexisting vapor-rich and liquid-rich fluid inclusions with similar Tₘ. Despite these results, boiling only could not be accountable for the gold enrichment but findings of sulfotellurides and gold-enriched As-free pyrite with a local distribution along minor fractures suggest a gold remobilization event by Bi-Te melts that could have occurred and continued favoring gold enrichment in the eastern side of the mine.

1 Introduction

Orogenic gold deposits formed from characteristic low-salinity CO₂-CH₄-rich fluids in compressional to tranpressional environments (Goldfarb et al. 2005). Despite this, there are also great differences in mineral assemblage, temperature and pressure of formation and gold grade (Groves et al. 1998). While phase separation is accountable for gold enrichment in most of orogenic gold deposits (Wilkinson and Johnston 1996; Wilkinson 2001), it could be an inefficient mechanism to explain contrasting gold grade in a mine. Recently, Bi-Te melts have been under study for their role in gold remobilization in metamorphic conditions (Cook and Ciobanu 2008; Ciobanu et al. 2010).

Along the South American Cordillera, numerous gold deposits occurred (Sillitoe 2008), one of them is Las Animas mine, located in the Central Cordillera of Colombia, that has recently gained recognition for being reevaluated as one of the first orogenic gold deposit discovered in Colombia based on microthermometrical and structural analyses (Acevedo 2010). Historically, the higher gold grades have been found in the eastern side of the mine, but this enrichment is poorly constrained.

Fluid inclusion and paragenetic data have been obtained in previous studies, along with structural and textural description of the main vein of the mine (Acevedo 2010; Correa 2012; Acevedo et al. 2014). Nonetheless, the paragenetic stages have never been linked to the mineral chemistry and the microthermometrical data to identify the possible range of each stage and the main ore-forming mechanisms that favored gold grade in the eastern side of the mine. Here, a detailed study of paragenesis, gold and accessory minerals chemistry, and fluid inclusions provides insight into the mechanisms that control gold grade in the mine.

2 Geological setting

The area of the Las Animas mine, Colombia, comprises Neoproterozoic Cajamarca Complex amphibolites and graphitic-quartz-sericite schists, that underwent greenschists-grade metamorphism during the final stage of the amalgamation of Pangea in the Permo-Triassic boundary (Vinasco et al. 2006; Villagómez 2010; Cochrane et al. 2014). Later, this metamorphic sequence was intruded by the Paleocene Santa Isabel granodiorite stock, ~53 Ma (Villagómez and Spikings 2013; Gómez et al. 2015). The eastern segment of the sequence is truncated by north-trending Otú-Pericos fault, a major dextral fault that separates two continental terrains (Feininger 1970) (geological map in Rodriguez and Nuñez (1986). Locally, the Las Animas deposit is hosted by Cajamarca Complex amphibolites and comprises a gently-dipping lode structure hosted by third-order Las Animas and Berlin faults associated with a splay off the Otú-Pericos fault (Acevedo 2010; Correa 2012).

3 Mineral chemistry and vein stages

This study proposes a composite paragenetic sequence (Fig. 1), according to textural and cross-cutting relationships. It was possible to identify that the lode structure is predominantly formed from massive white quartz and it was reopened by multiple events following Stage 1 and re-filled by gold-sulphides-sulphotellurides assemblages. The detailed paragenesis is as it follows:

Stage 1 – first barren event
Approximately 50-75 vol.% of the multigenerational quartz was formed early in the lode history and it is classified as Stage 1. Although it is strongly deformed
and recrystallized by the subsequent stages, these crystals reach up to 5000 µm.

Stage 2 – early Au-sulphides mineralization
It is marked by a widespread quartz-gold-pyrite 2-sphalerite 1-galena assemblage. On the one side, gold from this stage has the lowest fineness observed (Fig. 2) and it is classified as electrum (Allan and Wood 2001). On the other side, sphalerite is Cd-poor (0.367-1.929 wt%) and pyrite is enriched in Ni (up to 352 ppm) and As (up to 675 ppm).

Stage 3 – late Au-sulphides-sulphotellurides mineralization
Although this stage is limited to the east of the mine, it is accountable for the highest gold degree recorded in the mine. It comprises an early gold 2-sericite-sphalerite 2, pyrite 2-galena that gradually evolves to gold 2-lillianite-sulphotellurides: joseite β-tetradymite.

In contrast to the previous stage, gold 2 is classified as native gold (Allan and Wood 2001) due to its higher fineness (Fig. 2), sphalerite 2 is Cd-rich (up to 4.792 wt.%) and pyrite is depleted in Ni and As with 18 and 41 ppm, respectively. Moreover, some As-free pyrite have Au contents of up to 350 ppm.

Stage 4 – second barren event
Widespread. The last stage dominated by quartz comprises veinlets of roughly 10 to 30 µm that cross-cut the previous stages. It is of little economic importance.

Stage 5 – late barren event
Widespread. Filled and healed fractures and spaces left by the previous event. It is also considered of little economic importance.

Figure 1. Composite paragenetic sequence of the Las Animas mine. All events have a great extent corroborated by microprobe analyses, except the event 3, confined to the eastern side of the mine.

4 Microthermometry and Raman spectroscopy of fluid inclusions
Microthermometrical measurements and 65 Raman spectroscopy analyses from 107 fluid inclusions (FI) in quartz from three sectors of the mine were obtained.

The sectors were defined as follows: eastern side, central side and western side. It is worth mentioning that the study was focused on primary inclusion assemblages to understand temperature variations from stage 2 in the mine. No data could be recovered from stage 3 due to reequilibration of FI.

4.1 Microthermometrical results
All fluid inclusions measured make part of the H2O-CO2-CH4 system. Besides, it was found that the homogenization temperature decreases from 317-324°C on the west to 295-315°C on the east, which coincides with an apparently rise in salinity from 1-3% NaCl equiv. to 1.2-3.8% NaCl equiv.

Additionally, the distribution of the FIs in a homogenization temperature (°C) vs salinity (%NaCl equiv.) suggests that the main precipitation mechanism was boiling (Fig. 3), which, in turn, produced phase separation and gold-sulphides precipitation (Wilkinson 2001).
equiv.) of the measured CO2-rich fluid inclusion. The orange dots represent the fluid inclusions in quartz, in paragenesis with gold, of the western side of the mine and the blue ones illustrate the fluid inclusions, in the same paragenesis, on the west. The distribution of the data suggests boiling (Wilkinson 2001; Camprubí 2010).

4.2 Raman analyses

CO2, CH4 and N2 were the most common gases in fluid inclusions measured in the entire mine. Additionally, some detections of C2H6 and H2S were achieved in the eastern side of the mine.

Finally, densities of CO2 of each FI were calculated (Wang et al. 2011) to determine pressure of formation (Steele-MacInnis 2018). It was found that the early Au-sulphides mineralization event formed at around 1784.2-1800.7 bars in the western side of the mine and at roughly 1661.8-1740.8 bars in the eastern.

Figure 4. Raman spectrum of one fluid inclusion in the eastern side of the mine. The spectrum allows to distinguish between the diverse volatile species in the gaseous phase of the fluid inclusion. The most common volatiles are CO2, N2 and CH4, distinguished by the peak position in the spectrum (Burke 2001; Frezzotti et al. 2012). Some detections of C2H6 and H2S were also observed. CO2 peaks: at ~1285 and ~1388; CH4 peak: ~2917; N2 peak: ~2330; H2S peak: ~2611.

5 Discussion

5.1 Implications of the microthermometrical and Raman spectra results

On the one side, the presence of low salinity CO2-rich fluid inclusions could support the formation of the hydrothermal fluid as a result of a devolatilization process within the greenschists to amphibolite facies transition (Phillips 1993). Moreover, the presence of CH4 and C2H6 could suggest interaction of the hydrothermal fluid with graphite- or organic matter-rich lithologies (Hrstka 2012), such as the Cajamarca Complex graphitic schists. Finally, the detection of H2S confirms its role as one of the ligands that carries gold in ionic complex in reduced environments (Goldfarb et al. 2005) such as this one.

On the other side, it was observed that multiple microthermometrical variables change eastward, for instance, a decline in temperature and pressure from 324°C to 295°C and 1800.7 bars to 1661.8 bars, respectively, which coincides with an apparent rise in salinity (in some FI). The previous data could suggest that the hydrothermal fluid flowed up eastward and underwent boiling, which led to phase separation, destabilization of Au (HS)2-complexes and the subsequent gold-sulphide precipitation (Phillips 1993; Goldfarb 2010).

5.2 Implications of the microchemical results

Based on the microchemical results, it was possible to constrain the distribution of the stages in the mine. The stages 1,2,4 and 5 are widely distribute while the stage 3 is concentrated in the eastern side of the mine.

The presence of sulfotellurides, their textural relationships with gold, the higher fineness of Au 2, Aurich As-free pyrite and strong structural control of this mineral assemblages suggest that gold remobilization by Bi-Te melts could have played an additional important role in local enrichments of gold (>100g/Tn Au), especially in dilatational spaces during deformation events (Ciobanu et al. 2006).

6 Conclusion

The hydrothermal fluid was probably formed as a result of metamorphic devolatilization. It also interacted with Cajamarca Complex graphitic schists and migrated eastward to the Cajamarca Complex amphibolites.

The process of boiling is the mechanism responsible for gold mineralization during stage 2 and it is witnessed by the decrease in temperature and pressure and the rise in salinity eastward. This process produced a decline in gold solubility and triggered gold precipitation, which favored gold enrichment in the eastern side of the mine. Nonetheless, findings of sulfotellurides suggests that gold remobilization by Bi-Te melts could have played an important role in local enrichments of Au 2 (>100g/Tn Au) in the eastern side of the mine.

Acknowledgements

Microthermometry, Raman and microprobe analyses were undertaken at the Laboratory of Lithological Characterization of the Department of Geosciences at Universidad Nacional de Colombia, Campus Bogota, as part of a bachelor project. Sector Resources Colombia is acknowledged for the financial and logistical field support as well as for providing some samples and field information for the study.

References

Geological and structural evolution of the Madenköy gold occurrence in Bolkar Mountains (Niğde-Turkey): preliminary results

Duygu İŞBİL, Hayrettin KORAL, Nurullah HANİLCİ, Hasan EMRE
Istanbul University-Cerrahpasa, Faculty of Engineering, Department of Geological Engineering, Turkey

Abstract. Madenköy village of Niğde Province is located in eastern edge of the Central Taurus Belt. The region is geologically in an area where the Anatolide-Tauride Belt and the Kırşehir Massif are adjoined to each other. Paleozoic-Cenozoic aged rocks which are different in origin and types outcropped in this area. The characteristic feature which makes the area geologically significant is a karstic cave system developed in the Triassic-Jurassic aged carbonates and placer gold deposits which are present within these karstic caves. The subsurface placers gold deposit is the only known instance in Turkey and is also a rare situation in the world.

1 Geological overview of the Madenköy (Niğde)

The Madenköy placer gold deposit is located to the south of Niğde Province in Madenköy village. In N/NE side of the study area there are two different tectonic units. They are the Anatolide-Tauride Platform and the Kırşehir Massif which were juxtaposed with each other following the upper Cretaceous collision (Okay & Tüysüz, 1999; Fig.1).

Investigation area and its vicinity contain many geological features due to its long history of geological evolution from the Paleozoic to Present. In the study area where the subsurface placer gold deposit is located, there are two different rock units. First is “Basement Units” that consist of low-grade metamorphosed carbonates of the Triassic-Jurassic and the Neotethyan ophiolitic rocks/mélange of the Cretaceous. Second is here called “Cover Units” and includes sedimentary rocks of the Paleocene-Eocene up to Miocene. The sedimentary rocks unconformably overlie the basement units (Fig. 2).

Figure 1. Map illustrating main geological features of the study area and its vicinity (Study area is indicated by a yellow star; map is from Okay & Tüysüz, 1999).

Figure 2. Generalized stratigraphic section of the study area.

Magmatic rocks in these areas occur as a stock, dyke or sill in the carbonates, yielding some primary mineralization (e.g., lead, iron). The known ages of magmatic units nearby, such as the Horoz Granodiorite located to the east of the study area, fall into Paleocene and Eocene (Engin, 2013; Gürer, 2016). Placer gold occurrences are however present in caves of these carbonates. Although no definitive mechanism is available so far, it is considered that there were some erosional/geological processes after the magmatic activity, so that primary ores were transported, enriched and deposited in karstic caves.

2 Structural and geochemical properties of the Madenköy (Niğde) area

2.1 Structural features
The study area and its vicinity, where principally two different tectonic units are juxtaposed, contain various structural features of the Paleotectonic and Neotectonic tectonic periods. In order to determine tectonic evolution of the region, a detailed geological structure map has been prepared and field data on foliation, bedding, fault and fracture were collected. Foliations in the low-grade metamorphosed unit have an N60-75°E'ly orientation. Those in the mélange occur in N40°-50°E and N35°-45°W'ly directions. Bedding planes of the Tertiary unit are N40°-60°E oriented. However, dykes and sills of the magmatic rocks have an E-W'ly orientation range (Fig 3a-h).

Figure 3. Rose and pole diagrams a-f show overall strikes of beds/foliations measured in the Basement and Cover Units; g-h illustrate the orientation of dykes and sills (Diagrams are prepared by using Rocscience-Dips programme).

2.2 Geochemical characteristics of the magmatic units

Previous studies did not evaluate the relationship between the magmatic activity and mineralization in the region (Çalapkulu, 1978; Alan ve dğ., 2007; Karaoğlan 2016). Therefore, geochemical properties of seventeen selected magmatic samples collected during field studies were determined by ACME Laboratories (Vancouver, Canada).

The mean value of SiO₂ is %73.79 (min: %64.37; max: %79.22); K₂O is %4.20 (min: %1.64; max: %7.03) and Na₂O is %0.64 (min: %0.02, max: %3.53). According to the results of geochemical analysis, the mean values of ore minerals vary between 0.001 ppm and 0.08 ppm for gold and is in ranges of 0.07 ppm-0.6 ppm for silver. Whereas, gold values up to several gr/ton and even more for silver are said to have been obtained in the karstic placer gold occurrences.

3 Conclusion

In the light of field studies and observations, at least 3 different tectonic episodes have been determined in the study area where the subsurface placer gold deposit is located. They are namely contractional, extensional, and transtensional tectonic episodes, all of which are related to the still ongoing Alpine Orogeny.

The contractional tectonic episode is linked to ophiolite obduction due to the closing of the Inner Tauride Ocean, hence juxtaposition of the southerly Tauride Platform with the northerly the Kırşehir Block during Campanian-Maastrichtian times (Engin, 2013). The extensional episode is related to a period of collapse in the orogeny and formation of semi-closed basins during lower Eocene (Seyitoğlu et al, 2017). The translational episode is associated with the southwesterly extrusion of the Anatolian Platelet in Neo-tectonic history of the Anatolia during Miocene.

It is suggested that hydrothermal fluids which were associated with the magmatic units were not rich enough to form gold/silver bearing primary mineralization. The mineralization was by other water circulation mechanism in karstic caves after the intrusions of the magmatic bodies. It is expected that there will be more details about which stage of the tectonic episodes was responsible for bringing gold bearing magmatic bodies and which one for karst formation as the geochronology of sub-magmatic intrusions are determined.

Acknowledgements

This study was financially supported by the Scientific Research Foundation of Istanbul University-Cerrahpasa (Project Numbers: 25569, 30125).

References

Karaoğlan F (2016), Tracking the uplift of the Bolkar Mountains (south-central Turkey): evidence from apatite fission track
https://www.rocscience.com/software/dips
Structural controls of orogenic gold in Northern Ireland: implications to orogenic gold genetic models

James I. Shaw, Taija M. Torvela, Robert J. Chapman
University of Leeds

Mark R. Cooper
Geological Survey of Northern Ireland (GSNI)

Steven P. Hollis
Irish Centre for Research in Applied Geosciences (iCRAG), Geological Survey of Ireland (GSI)

Cian O’Meara
Dalradian Gold Ltd.

Abstract. Orogenic gold genetic models (e.g. crustal continuum model) are based entirely on gold emplacement during the final stages of orogenic shortening, coincident with a shift from compressional to transpressional deformation. Despite this, the final stages of orogenesis are often dominated by extensional tectonics, and an increasing number of gold deposits are now inferred to have been emplaced during orogenic extension. Here we propose that orogenic gold in Northern Ireland, including the world-class Curraghinalt gold deposit, was emplaced by transtensional shear zones syn-kinematic with the final stages of SE-directed thrusting. The structural orientations (E-W, N-S) and kinematics (normal-dextral, sinistral) of these conjugate shears is interpreted to be the result of localised strain partitioning during the thrusting of metasediments over an accreted arc-ophiolite complex. The strike of the shear zones in respect to NW-SE orogenic compression directly influenced the accommodation space created for mineralising fluids, and therefore, the structural geometry and grade of the gold deposits.

1 Introduction

The Sperrin Mountains of Northern Ireland (NI) have been the most prospective area of the British Isles for precious metals since the 1980s. In the Sperrin Mountains, the Grampian Terrane of the Caledonides hosts significant gold deposits of economic potential at Cavanacaw (0.46 Moz; Galantas Gold Corp 2014) and Curraghinalt (>6 Moz Au; Dalradian Resources 2018), with minor occurrences also reported at Alwories, Cormavarrow, Creevan Burn, Erganagh Burn, Glengowana, Glenmaccoffer, Golan Burn, Glenlark, Rylagh Burn, and Scotch Town (Fig. 1a). The quartz vein-hosted gold mineralisation shows many features typical of orogenic gold, including being spatially and temporarily related to a convergent, terrane-bounding structure; the NE-SW-striking Omagh Thrust Fault (OTF; Fig. 1a).

Though the exact source(s) of the gold-bearing fluids remains debated, the temperature, salinity, and CO₂ content ranges of the mineralising fluids are within the range ascribed to orogenic gold (Rice et al. 2016). The mineralising fluids also have a similar geochemical and isotopic signature on both a deposit- and regional-scale, which has been used to infer extensive fluid flow events by previous studies (Parnell et al. 2000; Earls et al. 1996). Recent geochronological dating (Re-Os, ⁴⁰Ar-³⁹Ar) of the gold mineralisation at Curraghinalt has confined the emplacement of these mineralising fluids to a ca. 10 Ma interval in the lower Late Ordovician (462.7 – 452.8 Ma), postdating peak greenschist facies metamorphism and coincident with the final stages of orogenic deformation (Rice et al. 2016). Despite the regional-scale similarities in the mineralising system described above, it is notable that the deposit-scale structural controls on the gold mineralisation differ significantly along the same NE-SW orogenic strike. For example, the vein array structures at Cavanacaw and Curraghinalt dominantly strike NNE and WNW with sinistral and normal-dextral kinematics, respectively (Fig. 1b, 1c; Cliff & Wolfenden 1992; Shaw et al. in prep*). This study will investigate the structural setting of these second- and third-order accommodation structures, linking them to the tectonic evolution of the Grampian Terrane in NI. We will propose an overarching genetic model which accounts for these contrasting structural settings, also discussing the implications that this has on existing and widely advocated orogenic gold genetic models (e.g. crustal continuum model, Groves 1993).

2 Geological setting

Orogenic gold mineralisation in the Sperrin Mountains is hosted by the metasedimentary rocks of the Dalradian Supergroup in the Grampian Terrane (NW of study area; Fig. 1a). The metasediments were deposited on the Laurentian passive margin in the mid-Neoproterozoic to
early-Ordovician (ca. 800 to 500 Ma; Cooper & Johnston 2004). This was terminated in the early to mid-Ordovician by the collision and accretion of a lower Palaeozoic oceanic arc-ophiolite complex, which outcrops in the SE of a study area as the ophiolitic and arc-related rocks of the Tyrone Igneous Complex (ca. 470 Ma; Fig. 1a; Cooper et al. 2011). This resulted in the onset of the Grampian Orogeny (ca. 470 – 465 Ma; Hollis et al. 2013), which was followed by the formation of major SE-facing isoclinal folds and upper greenschist facies metamorphism in the Dalradian Supergroup (D2 phase; Fig. 1a; Aslop & Hutton 1992a). The final compressional phase of the orogeny (D3) resulted in the oblique-dextral thrusting of the Dalradian Supergroup over the Tyrone Igneous Complex along the OTF (ca. 465; Fig. 1a; Aslop & Hutton 1993b). The orogeny was reportedly followed by the collapse of the hangingwall pile, resulting in exhumation and extensional tectonics between ca. 465 to 450 Ma (Aslop & Hutton 1993a, Rice et al. 2016). The OTF was subsequently reactivated during the Variscan Orogeny, resulting in the SE-directed thrusting of the Dalradian over Devonian and Carboniferous rocks (ca. 300 Ma; Fig. 1a; GSNI, 2004).

3 Structural setting of orogenic gold in NI

The terrane-bounding OTF appears to have had an integral role in emplacing gold mineralisation in NI, with deposits and occurrences all found within <10-km of the faults trace. The first-order structure was most likely able to focus gold-bearing fluid flow from depth into shallower, lower-order accommodation structures. The deposit-scale structural controls on orogenic gold can be split into two groups based on the orientation, kinematics, and geographical locations of the vein array structures: (1) Curraghinalt Trend; (2) Cavanacaw-Rylagh Trend. These are described in detail below, as well as their relationship to the first-order OTF:

3.1 Curraghinalt Trend

Since its discovery in the 1980s, the Curraghinalt gold deposit (>6 Moz Au) has been developed into one of the largest undeveloped gold mines in the world by grade (Dalradian Resources Inc 2018). The high-grade mineralisation (15.01 g/t Au) is hosted by twenty-one quartz-carbonate-sulphide veins that generally strike WNW-ESE and dip moderately to steeply to the NE (Fig. 1b; Dalradian Resources Inc 2018). The quartz vein-hosted gold mineralisation is cross-cut by two reactivated brittle-ductile shear zones (Kiln and Crowsfoot), which strike E-W and dip near vertically to the N (Fig. 1b). Recent underground geological mapping suggests that normal-dextral movement (oblique-slip, N-side down) on the shear zones was responsible for emplacing the vein system, forming a syn-kinematic extensional-shear fracture network in which the gold-bearing mineralisation was synchronously emplaced (Fig. 2; Shaw et al. in prep*). The geometry of the vein system is also strongly indicative of gold emplacement under normal-dextral kinematics, with WNW-striking and moderately NNE-dipping shear-laminated veins connected by right-stepping, NW-striking and steeply NE-dipping extensional jogs (Fig. 2; Shaw et al. in prep*). On a regional-scale, the Curraghinalt vein system can currently be traced along-strike to Golan Burn (4-km to WNW) and Alwories (4-km to ESE), forming an 8-km along-strike structural corridor (hereafter the Curraghinalt Trend;
Fig. 1a; Dalradian Resources Inc 2018). The Curraghinalt Trend is intersected by a 1-km wide belt of E-W-striking shear zones with normal-dextral kinematics (oblique-slip, N-side down), which extend along strike for several kilometres (continuations of the Kiln and Crowsfoot shears, Fig. 1a, GSNI 2004; Shaw et al. in prep). The shear zones are notably aligned with an E-W re-entrant in the trace of the NE-SW-striking OTF, where the strike of the thrust footwall swings by ~50° (Fig. 1a). At the E-W re-entrant, a high-strain zone is marked by intense imbrication of mylonitised metasediments with black shales along S to SE-directed thrusts, which are associated with overturned to recumbent S-verging folds (also reported in Earls et al. 2003).

3.2 Cavanacaw-Rylagh Trend

Until recently, the Cavanacaw (‘Lack’) gold deposit (0.46 Moz Au) was the only operating gold mine in the United Kingdom and Ireland, commencing operation in the late 1990s (Galantas Gold Corp 2014). The gold deposit is primarily hosted by brecciated quartz-carbonate-sulphide veins (7.71 g/t Au) that strike N-S and dip near vertically (Fig. 1c; Galantas Gold Corp 2014). The mineralised veins are hosted within co-planar sinistral strike-slip shear zones, which are intersected by minor NW-SE-striking extensional veins to form a sinistral strike-slip reidel array (Fig. 1c; Cliff & Wolfenden 1992). At Rylagh Burn (~10-km to the NE of Cavanacaw; Fig. 1a), similar N-S-striking structures and near vertically dipping quartz-carbonate-sulphide veins are hosted by co-planar and transtensional shear zones, with sinistral and top down to W kinematics (Parnell et al. 2000). The genesis, orientation, and location of the N-S-striking mineralised veins at Cavanacaw and Rylagh (hereafter the Cavanacaw-Rylagh Trend) is thought to be controlled by a N to NNE-striking deep seated, crustal lineament, known as the Omagh Lineament (Fig. 1a; Parnell et al. 2000; Earls et al. 1996; Cooper et al. 2013). The pre-Caledonian lineament (up to 1800 Ma) is largely inferred from an abrupt ‘knee-bend’ swing in the strike of the Dalradian metasediments (NE-SE to NNE-SSW; Fig. 1a; Cooper et al. 2013). To the SSE of Rylagh Burn (~5-km), geological mapping has also identified an N-S swing (30°) in the trace of the OTF (Fig. 1a). The swing in the thrust footwall is also marked by a high-strain shear zone, where the Dalradian metasediments are imbricated with black shales and chloritic tuffs from the Tyrone Volcanic Group. Within the shear zone, multiple examples of recumbent folds with N-S-striking axial planes have been identified, potentially indicating that the Dalradian metasediments were folded against the N-S margin of the OTF footwall.

4 Preliminary structural model for orogenic gold in NI

Here we propose a new structural model to explain the differences in the orientations and kinematics of the vein array structures at Curraghinalt and Cavanacaw/Rylagh. We interpret the E-W-striking (normal-dextral) and N-S-striking (sinistral) transtensional shear zones responsible for gold emplacement at Curraghinalt and Cavanacaw/Rylagh to be conjugate (Fig. 3). The transtensional shear zones may have formed by strain partitioning during late SE-directed thrusting (D3), with the orientations and kinematics of the shears controlled directly by the topology of the underlying arc in respect to NW-SE orogenic compression (Fig. 3). In addition to this, the strike of the transtensional shear zones in respect to the orogenic compression also appears to have directly influenced the resulting accommodation space for mineralising fluids, with NW-SE orientated veins at both Curraghinalt and Cavanacaw notably having extensional and dilational ore textures (Fig. 2, 3; Shaw et al. in prep).

Figure 2. Plan view geometry of the Curraghinalt vein system (simplified from Shaw et al. in prep)

Figure 3. Preliminary structural model for orogenic gold in the Sperrin Mountains of Northern Ireland

The geometry of the OTF provides some insight into the topology of the underlying basement, with the E-W and N-S-striking transtensional shear zones aligned parallel to 40 and 30° swings in the strike of the thrust footwall (Fig. 1a). These swings extend to depth and are observable on magnetic and electromagnetic geophysical surveys of the area (GSNI 2004). In the field, high-strain zones are found along the E-W and N-S swings in the thrust footwall, with the Dalradian metasediments folded parallel to the swings and imbricated intensely with Tyrone volcanics along SE-directed thrusts. It is notable that this preliminary model places gold mineralisation prior to reported orogenic collapse (ca. 465 to 450 Ma; Aslop & Hutton 1993b),
which has been previously inferred to have formed the accommodation structures and emplaced the gold mineralisation at Curraghinalt by geochronology (462.7–452.8 Ma; Rice et al. 2016). If the geochronology is correct, this could indicate that the final stages of SE-directed thrusting continued later than previously thought (ca. 465 Ma; Aslop & Hutton 1993a).

5 Implications to orogenic gold genetic models

The structural setting of orogenic gold in the Sperrin Mountains of NI shows some similarities to that outlined in orogenic gold genetic models (e.g. crustal continuum model; Groves 1993). For example, gold emplacement is genetically related to a convergent, terrane-bounding structure, which most likely acted as a primary pathway for auriferous fluids to enter shallower, lower-order accommodation structures through stress fluid-pressure cycling. In addition to this, second- and third-order accommodation structures are orientated obliquely (30 – 40°) to the general orientation of the first-order structure (Fig. 1a; Groves et al. 2018). These lower-order accommodation structures are aligned parallel to bends/jogs in the trace of the first-order structure, with high-strain zones indicative that the lower-order structures accommodated ‘bending’ during orogenic shortening (Groves et al. 2018). However, there are a number of fundamental differences between the structural setting of orogenic gold in NI and that outlined in genetic models. The most notable of these is that the lower-order accommodation structures responsible for gold emplacement are related to transtensional deformation during that final stages of orogenesis rather than compression/transpression (Fig. 2, 3). The geometry of the vein zones at Curraghinalt is highly indicative of emplacement under normal-dextral (oblique-slip, NE-side down) kinematics, with high-grade gold mineralisation hosted by steeply dipping extensional jogs rather than in low angle faults bends as typical in convergent orogenic systems (Fig. 2; Robert & Poulsen 2001).

Over the past decade an increasing number of gold deposits have been linked to episodes of orogenic extension (Warren et al. 2015). Previous studies have primarily linked the extensional deformation to (1) stress heterogeneities created around granitic plutons, and (2) pre-existing structures controlling sites of local extension (Warren et al. 2015). Here we hypothesise that localised transtensional deformation induced by arc-continent collision can also express orogenic gold mineralisation.

Acknowledgements

JIS is funded by a Natural Environmental Research Council (NERC) CASE PhD studenthip with Dalradian Gold Ltd (DGL) and the Geological Survey of Northern Ireland (GSNI). DGL and GSNI are acknowledged for financial and logistical support as well as access to company/government information. JIS is a recipient of the Graduate Student Fellowship award from the Society of Economic Geologists Foundation. JIS would in particular like to express gratitude to Orla McKenna (DGL) for her ongoing support.

References

Alsop GI, Hutton DHW (1993a) Major southeast-directed Caledonian thrusting and folding in the Dalradian rocks of mid-Ulster: implications for Caledonian tectonics and mid-crustal shear zones. Geol Mag 130:233–244. doi: 10.1017/S0016756800009882


Recent developments on the origin of gold mineralization in East Kazakhstan

Marina Mizernaya, Asel Akylbaeva
D. Serikbayev East Kazakhstan State Technical University, Ust-Kamenogorsk, Kazakhstan

Joyashish Thakurta, Evangelia Murgia
Western Michigan University, Kalamazoo, MI, USA

Abstract. Metallic mineral deposits in East Kazakhstan are oriented along the NW-SE trend of the Central Asian Mobile Belt. The Rudno-Altai, Kalba-Narim, West Kalba and Zharma-Saursky are the major metallic ore belts which formed on the Hercynian structural floor of the region. Many polymeric mineral deposits in these mineralized belts contain significant quantities of gold. Although most of these deposits are small with ore reserves less than 100 tons, the grades are substantially high to justify mining. Base metal and gold deposits are found in zones of tectonic convergence and compression, particularly along fault zones, fold belts and in association with shallow granitic to intermediate plutonic bodies. In the Hercynian structural floor, several gold-polymetallic sulfide ore zones are found hosted within Devonian volcanic rocks which include some of the most well-known gold deposits in the world such as, the Ridder-Sokolnoe deposit. Quartz-vein and stockwork type gold deposits are found hosted within metasomatic and hydrothermally altered sedimentary and volcaniclastic sequences as seen in the Bakyrchik deposit. Quartz, pyrite-vein associated porphyry copper-gold type deposits are found within fault-controlled small igneous intrusions such as the Ashaly deposit in the Zharma-Saurskaya Belt.

1 Introduction

The Republic of Kazakhstan is well-known for metallic mineral deposits. East-Kazakhstan is uniquely endowed with substantial reserves of base metals such as Cu, Pb, Zn and precious metals such as Au and Ag. There has been a rising interest in the re-evaluation of existing deposits and exploration for new mineral deposits in order to replenish the steadily declining stockpile of metallic reserves. The discovery of several small gold deposits in the region has also led to a revival of interest in the exploration for precious metals.

Most gold deposits of East Kazakhstan are located in West Kalba, Chingiz-Tarbagatai and South Altai region. The mode of occurrence for most of these deposits is quartz-vein type. Akzhal, Kazan-Chunkur, Dzhumba, Sentash, Kuludzhun and Laily are some of the known deposits. New examination and re-evaluation of these deposits are critically important to increase the reserve estimate for gold. This article highlights the recent developments in the understanding of gold mineralized zones in East Kazakhstan.

2 Locations of mineralized zones

The mineralized belt in East Kazakhstan is located along the Central Asian mobile belt, at the junction of Kazakhstan and Altai geological structures. The following four major ore belts have been identified (Figure 1) on the Hercynian structural floor based on metallogenic zoning: (1) the Rudno-Altai copper-polymetallic belt; (2) the Kalba-Narym rare metal belt, (3) the West Kalba gold ore belt and (4) the Zharma-Saursky multi-metal belt. These four belts form a single metallogenic structure in the Big Altai (BA) area (Dyachkov et al. 2016). The Gornoltaiisk metallogenic province (in the north-east) and Chingiz-Tarbagataiisky ore belt (in the southwest) are two subsidiary belts. Gold deposits were formed in various geodynamic settings and ore-magmatic systems. These are characterized by an uneven distribution in metallogenic zones, oriented in a linear geographical trend. Gold mineralization in the region span a large section of geological time from Precambrian to Mesozoic-Cenozoic, but the main events of gold mineralizations were recorded during specific regional geotectonic events (Table 1).

<table>
<thead>
<tr>
<th>Tectonic setting</th>
<th>Host rocks</th>
<th>Ore type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceanic rift</td>
<td>Hyperbasite amphibole-gneissic</td>
<td>Au-Hg listvenite</td>
<td>Chara group Maralikha</td>
</tr>
<tr>
<td>Rift-related island arc</td>
<td>Basalt-andesite-rhyolite</td>
<td>Pyrite-related</td>
<td>Ridder-Sokolnoe Maleevskoe</td>
</tr>
<tr>
<td>Early-collision</td>
<td>Gabbronodiorite-granodiorite</td>
<td>Vein-type porphyry Cu-Au</td>
<td>Kyzyl-Kain Bugaz group</td>
</tr>
<tr>
<td>Late-collision</td>
<td>Gabbronodiorite-diabasic</td>
<td>Magmatic Cu-Ni</td>
<td>Maksut</td>
</tr>
<tr>
<td></td>
<td>Gabbrodiorite-granodiorite</td>
<td>Au-telluride</td>
<td>Sekisovskoe</td>
</tr>
<tr>
<td></td>
<td>Plagiograrnite-granodiorite</td>
<td>Au-sulfide-quartz, Au-As</td>
<td>Suzdalskoe Bakyrchik</td>
</tr>
<tr>
<td>Continental rift</td>
<td>Au-bearing formations</td>
<td>Au-bearing weathered rocks</td>
<td>Zhana, Suzdalskoe Mukur</td>
</tr>
<tr>
<td>Alpine Neotectonics</td>
<td>Placer Au formations</td>
<td>Placer</td>
<td>Kurchum Valley B. Boukon</td>
</tr>
</tbody>
</table>
3 Tectonic settings of ore deposits

In the Big Altai region, the Precambrian basement rocks host several primary Cr, Ni, Cu, Co ore deposits. These deposits are often characterized by the prevalence of metamorphic-hydrothermal gold-listvenite and gold-mercury associations. These ore mineralizations are confined within deep faults, shear and thrust zones, melange structures, often in association with serpentinized hyperbasite protrusions and blocks of metamorphic rocks (e.g. Irtysh, Chara zones). It is interpreted that these deposits formed in a compressional tectonic setting at the mid-Hercynian stage during the convergence and collision of the Kazakhstan and Siberian continental lithospheric plates and blocks (possibly terranes). This phase of tectonism led to regional metamorphism and consequent hydrothermal mobilization and concentration of metallic ore minerals. Small ore deposits of mercury and gold have been found in association with serpentinized hyperbasites.

The Caledonian ore-bearing formations are overlapped by the Hercynian structural floor on the BA territory. These are best developed in the Chingiz-Tarbagatay belt, which was formed along the active continental margin of the Balkhash Plate. But there are several pyrite-gold-copper and gold-polymetallic deposits which were formed in rift and island arc settings in basaltic volcanic rocks (e.g. Mizek Kosmurnskaya-gold-copper-pyrite zone). The orientations of these deposits are controlled by near-vertical faults and localized centers of magmatism at the intersections of these faults. Such intrusive rock massifs often occur as ring dikes and are composed of rocks such as gabbro-diorite-granodiorite and granodiorite-plagiogranite. Many of these intrusions are associated with gold-sulfide and gold-quartz deposits. Rocks with high concentrations of gold are commonly found in fold-belts, in strong association with magmatic
intrusions. These gold-enriched zones often encompass multiple rock types and the depositional veins crosscut lithological boundaries. For instance, gold-enriched ore-zones are found in calcareous rocks, black shales and basaltic volcanic flows.

The most important gold deposits of the region are hosted within the Hercynian basement rocks, although the gold deposits themselves were formed at different times and under different geotectonic settings.

The Rudny Altai polymetallic belt lies in the NW-SE trending Altai Mountain Range which defines an active continent-continent collisional margin. In this belt there are Devonian volcanic rocks composed of basalt-andesite-ryholite. Some of the most commercially valuable gold deposits of East Kazakhstan are hosted in these rocks (Chekalin and Dyachkov 2013). The common mineral associations in these ore zones include gold-chalcopyrite-pyrite, and gold-polysulfide (e.g. Ridder-Sokolnoe, Tishinskoe, Maleevskoye, Orlovskoye). These deposits are located in several geochronological levels of the Devonian volcano-sedimentary stratigraphic succession. The highest quantities of gold are found in the lower-Ridder-Zmeinogorskoy-Sokolnoe level, which is known for its unique gold-silver-barite-polymetallic association. The Ridder-Sokolnoe deposit is also notable because more than 500 tons of gold have been mined from this deposit over many years.

Gold deposits were formed in the middle stage of Hercynian orogenic process under collisional geodynamic conditions as a result of horizontal displacement at the junction of Kazakhstan and Siberian lithospheric plates. This area of tectonic interaction corresponds to the Zaisan suture zone, in the axial part of which the arcuate shaped Charsko-Gornostaevsky ophiolite belt is located. This belt is oriented along the general northwesterly alignment of Great Altai.

According to available subsurface geological and geophysical data, the Zaisan suture in its deep section is characterized by a shaft-like uplift of the upper mantle rocks and a system of conical crustal faults in different directions (under Rudny Altai in the northeast and in the direction to Central Kazakhstan in the southwest). It is evident that the faults acted as channels for the transport of ore-bearing fluids from mantle depths.

4 Characteristics of major ore belts

Apart from gold and silver, the Rudny Altai Belt is also known for iron, manganese, copper and lead. It has been proposed (Dyachkov et al. 2009) that the ores were formed under submarine conditions with the hydrothermal emanations of mineralizing fluids from the sea-floor. There are two modes of occurrences of the metallic ores: sedimentary stratiform and hydrothermal metasomatic (Dyachkov et al. 2018). The former is characterized by rhythmic occurrences of ore in the volcaniclastic sedimentary layers (e.g. Ridder-Sokolnoye, Verkh-Ubinskoe, Nikitinsky). The latter is associated with changes in volcaniclastic rocks and fluid-porphyry complexes along the path of ore-bearing fluids (e.g. Zyranyovskoye, Maleevskoe, Belousovskye).

The West Kalba Belt is the most important gold-bearing district in East Kazakhstan with more than 450 deposits. Most of the gold deposits in this region are associated with small intrusions and dikes of the Kunushsky, Saldyrminsky and Katoy Complexes. The following types of mineralogical associations have been observed in the gold deposits: (1) gold-listenitic (e.g. Maralakha deposit); (2) gold-sulfide (e.g. Suzdalskoe, Mirage, etc.); (3) gold-quartz (e.g. Kuludzhun, Sentash, Kystav-Kurchum); (4) gold-quartz beresit (e.g. Baladzhal, Manka); (5) gold-arsenic-carbonaceous (e.g. Bakyrchik, Bolshevik); (6) crust weathering (e.g. Zhanan, Mukur) and (7) gold-placer (e.g. West Kalba, the South Altai). The Bakyrchik deposit is the largest world-class “black shale type” gold deposit with zones of gold-arsenic-carbon mineralization and vein silicification (Narseev et al. 2014). Ore bodies are lenticular and ribbon-like in shape hosted within hydrothermally altered black shales with stockworks and veins of quartz and an abundance of disseminated lenses of gold-bearing pyrite and arsenopyrite. The thickness of the ore zones varies from 0.6 to 20 m. The average gold content is 8–9 g/t.

The Zharma-Saurskaya Belt is known for porphyry-copper, sulfide copper-nickel and gold mineralization. The Maksut deposit is genetically associated with stratified intrusions and dike-like bodies which are controlled by deep faults. Quartz-vein and stockwork-type gold ore-deposits are hosted within these small igneous intrusions (e.g. Ashaly, Daubai, Chang).

References


Rafailovich MS, Mizernaya MA and Dyachkov BA (2011) Large gold deposits hosted in black shales: formation conditions and signs of similarity. Almaty, 272 p (English translation by CERCAMS NHM London, 2012:177.)
Bismuth and antimony mineralization in deposits of the Zarmitan gold ore zone (Uzbekistan)

Anna Krivosheeva, Rustam Koneev
National University of Uzbekistan, Tashkent
Oybek Tursunkulov
Centre for Advanced Technologies, Tashkent

Abstract: The ores of Zarmitan, Urtalik, Gujumsay deposits were studied. The development of /Au-W/Au-Bi-Te/Au-As/Au-Sb-Ag/ ore types has been established. Bismuth mineralization is represented by maldonite, tellurides and bismuth sulfosalts; antimony mineralization is represented by aurostibite, Pb, Fe, Ag sulfoantimonides. Deposits of Zarmitan zone belong to orogenic Au-Bi-Te-W type associated with intrusive.

1 Introduction

Zarmitan gold ore zone is located in the North-Nurata mountains of Western Uzbekistan and includes three deposits: Zarmitan, Urtalik Gujumsay. The most studied is Zarmitan or Charmitan deposit (Bortnikov et al. 1996; Graupner et al., 2007, 2010), which was considered as "gold-quartz" or as "granitoid - hosted gold deposit" (Abzalov, 2007). The deposit belongs to large objects with reserves of more than 200 tons of gold. Four to six stages of mineralization are distinguished at the deposits of Zarmitan zone. Bortnikov and co-authors (1996) identified five stages of mineralization: I. quartz-scheelite-feldspar; II. quartz-telluride; III. quartz-arsenopyrite; IV. quartz-sphalerite-sulfoantimonite; V. quartz-carbonate-antimonite. II-III stages are productive for gold. The objectives of our research included the study of mineralogy and geochemistry of gold ores in order to determine the type of deposits, the elements of zonality, mineralogical and geochemical criteria for finding hidden objects of a similar type.

2 Methodology

Studying of ores of deposits Zarmitan, Urtalik, Gujumsay was carried out on polished thin sections and briquettes with concentrates isolated from gross samples. They have the highest probability of occurrence of gold, tellurides and other "rare" minerals. The studies were performed on a JXA Superprobe 8800R electron probe microanalyzer at the Institute of Geology and Geophysics, Carl Zeiss electron microscope (SEM-EDX) at the Center for Advanced Technologies, Tashkent. Methods developed for nanomineralogical and nanogeochemical studies were used (Koneev et al., 2010).

3 Geology

Zarmitan gold zone is located in the western part of the South Tien Shan orogenic belt (Goldfarb et al., 2013) or Turkestan Accretionary Complex (fig. 1), Kyzylkum-Nurata segment (Dolgopolova et al., 2017). Tectonically, the zone is confined to the intersection node of the sub latitudinal Karaulkhona-Zarmitan fault with the north-east, hidden Zirabulak-Koshrabad fault (Khamroev, 2007). The deposits are located in the southern endocontact of the Koshrabad granitoid intrusion and partly in the sand-shale sediments of the Jazbulak suite (S1) (fig. 2). The intrusive age is 283 Ma, the age of pyrite mineralization is 286 Ma (Dolgopolova et al., 2017). Samples of gold-quartz ores are shown on fig. 3.

Figure 1. a) Tectonic setting of the Altaids collage; b) Location of key mineral deposits in the Tien Shan with relations to major terranes (after Seltmann et al., 2014).

Figure 2. Geological map of the Zarmitan gold zone. 1 – Koshrabad multiphase massif (C2); 2 – 2 - sand and shale rocks (S1dzh); 3 - gold zones; 4 - faults; 5 – dikes (Atlas, 2010)
4 Research results

It was previously established that As-Te-Bi-Au-Sb-Pb-W-Hg (Koneev et al., 2010, 2015) are geochemical leaders in the ores of Zarmitan, Urtalik, Gujumsay deposits. Gold ores with Au:Ag ratio in ores 2:1 and gold-silver ores with Au:Ag ratio in ores of 1:12. The main vein minerals are quartz, albite, chlorite, sericite, carbonates. Ore minerals are represented by scheelite, pyrite, arsenopyrite, chalcopyrite, sphalerite, galena, tetrahedrite, bismuthinite, and antimonite. Sulfides make up 0.5-15%. Gold standard is 980-850 in the ensemble with bismuth minerals, 750-850 with antimony. Values from 700 to 350‰ associated with Au-Ag mineralization occur. Studies on a microanalyzer have shown that, in addition to native gold, maldonite (Au2Bi) and aurostibite (AuSb2) are found. Maldonite forms micro-nano-ensembles with tellurides, sulfotellurides, Bi sulfosalts, aurostibite with Sb, Pb, Fe, Ag sulfosulfides (Table). Bismuth mineralization is released in pyrite, arsenopyrite, quartz (fig. 4, I), antimony also in antimonite, galena (fig. 4, II).

5 Discussion

As a result of the conducted research, it was established that the Au-W, Au-Bi-Te, Au-As, Au-Sb-Ag and Au-W deposits are developed in the Zarmitan, Urtalik and Gujumsay fields with a weak gold-bearing ore type. Au-Bi-Te mineralization is represented by tellurides, sulfotellurides, Bi-sulfosalts. This type of ore is the main productive gold and developed in all deposits. Au-Sb-Ag is inferior to Au-Bi-Te and its amount increases from Zarmitan to Gujumsay.

The most obvious sign of different types of gold ores is the presence of maldonite (Au2Bi) or aurostibite (AuSb2). According to its geochemical, mineralogical composition, age of magmatism and ore, the deposits are close to Muruntau. The widespread development of Au-Bi-Te mineralization, the presence of scheelite, placement in the granitoid intrusive, allow us to classify objects of the Zarmitan gold ore zone to the orogenic type of deposits (Groves et al., 1998) associated with intrusives (Baker et al., 2005). Apparently, deposits with Au-Sb mineralization should also be attributed to this type. Graupner (2007), Bortnikov (1996) consider that fluids of different origin, including fluids from the mantle and the lower crust, are involved in the formation of Zarmitan deposit.

Thus, the conducted studies allowed to correct the schemes of the staged formation of deposits of the Zarmitan gold ore zone. The following types of ores are distinguished: 1 - Au-W, quartz-scheelite-feldspar pre-ore type, 2 - Au-Bi-Te quartz-gold-bismuth-telluride (table, Sb minerals), 3 - Au-As quartz-pyrite-arsenopyrite with the minerals Ni and Co, 4 - Au-Sb-Ag quartz-antimonite-sulfosalts (table, Sb minerals), 5 - Au-Hg quartz-cinnabar. Au-Bi-Te and Au-Sb-Ag are the main gold-producing types and are developed in all ore bodies. Graupner (2007), Bortnikov (1996) do not give chemical analysis of bismuth and antimony minerals as the main productive associations; they distinguish quartz-pyrite-arsenopyrite. The identified mineralogical and geochemical features of the ores of the deposits of the Zarmitan zone are direct signs of a search for hidden orogenic deposits associated with intrusions.

Figure 3. Samples of ores deposits of Zarmitan gold ore zone. A - quartz-sulfide ore with scheelite; B - quartz-sulfide ore in modified granosyenites, Gujumsay.

Figure 4. Micro-nano-ensembles of gold (Au, Ag), bismuth (I) and antimony (II) minerals in arsenopyrite (Aspy), pyrite (Py), galena (Gal) and boulangerite (Bul).
### Table 1. The chemical composition of the minerals of bismuth and antimony of the deposits of Zarmitan gold zone (mass, %)

<table>
<thead>
<tr>
<th>Минерал</th>
<th>Au</th>
<th>Bi</th>
<th>Sb</th>
<th>Pb</th>
<th>Ag</th>
<th>Fe</th>
<th>As</th>
<th>Te</th>
<th>Se</th>
<th>S</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bi minerals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maldonite Bi$_4$Te$_3$ Au$_2$Bi</td>
<td>66.60</td>
<td>38.61</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
<td>99.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hedleyite Bi$_4$Te$_3$</td>
<td>-</td>
<td>77.15</td>
<td>0.35</td>
<td>-</td>
<td>0.57</td>
<td>-</td>
<td>21.08</td>
<td>0.27</td>
<td>0.48</td>
<td>99.90</td>
<td></td>
</tr>
<tr>
<td>Tsumoite Bi$_4$Te$_3$</td>
<td>-</td>
<td>78.00</td>
<td>0.41</td>
<td>-</td>
<td>0.71</td>
<td>-</td>
<td>19.63</td>
<td>0.18</td>
<td>0.35</td>
<td>99.56</td>
<td></td>
</tr>
<tr>
<td>Tellurobismuthite Bi$_4$Te$_3$</td>
<td>-</td>
<td>51.69</td>
<td>0.73</td>
<td>1.96</td>
<td>-</td>
<td>46.00</td>
<td>-</td>
<td>0.44</td>
<td>98.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Josètie Bi$_4$Te$_5$S$_2$</td>
<td>-</td>
<td>74.62</td>
<td>0.72</td>
<td>-</td>
<td>-</td>
<td>22.29</td>
<td>0.30</td>
<td>2.82</td>
<td>100.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volynskite Bi$_4$Te$_5$S$_2$</td>
<td>-</td>
<td>74.37</td>
<td>0.83</td>
<td>-</td>
<td>-</td>
<td>22.81</td>
<td>0.16</td>
<td>2.81</td>
<td>101.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Matildite AgBi$_2$S$_3$</td>
<td>-</td>
<td>55.13</td>
<td>2.11</td>
<td>0.90</td>
<td>28.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.75</td>
<td>99.13</td>
<td></td>
</tr>
<tr>
<td>Treasureite Ag$_2$Pb$_2$Bi$_2$S$_8$</td>
<td>-</td>
<td>50.24</td>
<td>1.29</td>
<td>20.14</td>
<td>9.69</td>
<td>0.17</td>
<td>0.72</td>
<td>-</td>
<td>16.49</td>
<td>98.74</td>
<td></td>
</tr>
<tr>
<td><strong>Sb minerals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aurostibite AuSb$_2$</td>
<td>45.93</td>
<td>52.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100.46</td>
<td></td>
</tr>
<tr>
<td>Berthierite Fe$_3$Sb$_2$</td>
<td>-</td>
<td>57.98</td>
<td>0.31</td>
<td>12.71</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29.57</td>
<td>100.57</td>
<td></td>
</tr>
<tr>
<td>Plagioclase Fe$_3$Sb$_2$</td>
<td>-</td>
<td>36.51</td>
<td>40.89</td>
<td>-</td>
<td>0.37</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>22.60</td>
<td>100.48</td>
<td></td>
</tr>
<tr>
<td>Jamesonite Pb$_2$Sb$_2$S$_7$</td>
<td>-</td>
<td>37.18</td>
<td>40.47</td>
<td>-</td>
<td>0.25</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>21.71</td>
<td>99.84</td>
<td></td>
</tr>
<tr>
<td>Owyheite Pb$_2$Fe$_2$Sb$_5$</td>
<td>-</td>
<td>35.61</td>
<td>38.11</td>
<td>0.30</td>
<td>3.25</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>21.70</td>
<td>99.18</td>
<td></td>
</tr>
<tr>
<td>Agbouliangerite Pb$_2$Sb$_2$S$_5$</td>
<td>-</td>
<td>55.85</td>
<td>38.79</td>
<td>0.37</td>
<td>3.09</td>
<td>0.89</td>
<td>-</td>
<td>-</td>
<td>21.01</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

### Acknowledgements

The research was supported by OT-F8-01 and IZ-0929142 grants of the Ministry of Innovation Development of the Republic of Uzbekistan. These funds were used for field work and analytical research. Special thanks to the chief geologist of the Zarmitan expedition I.Sh. Turopov. for assistance in conducting field work and Deputy Director of the Center for Advanced Technologies R.A.Khalmatov for assistance in conducting analytical research.

### References

Atlas of models of ore deposits of Uzbekistan (2010) State Committee of the Republic of Uzbekistan on geology and mineral resources. Tashkent, Uzbekistan. 100 (In Russian)


Gold chalcogenides natural occurrence in Maletoyvayam (Kamchatka, Russia) - an experimental approach

Marek Tuhý*1,2, Anna Vymazalová1, Nadhezda D. Tolstykh3, Jakub Plášil4, František Laufek1,
1Czech Geological Survey, Czech Republic
2Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Czech Republic
3Sobolev Institute of Geology and Mineralogy, SB RAS, Russia
4Institute of Physics ASCR, v.v.i., Czech Republic

Abstract. The Au-Te-Se system was experimentally studied based on a field research performed in the Maletoyvayam ore field at the Kamchatka peninsula located in the Eocene-Oligocene central Kamchatka volcanic belt. Gaching – Maletoyvayam is a high sulfidation type of epithermal deposit where two ternary phases Au₂TeSe and Au₆Te₆Se₄ were proved there and characterized in terms of crystal structure, solid solutions, stable associations and thermal stability. The phase Au₂TeSe is stable up to 462 °C and the phase Au₆Te₆Se₄ is stable up to 447 °C. Experimental results revealed phase relations in the system at 400 °C. The ternary phase Au₂TeSe coexists with gold and AuSe, calaverite (AuTe₂) and gold, AuSe and Se. The phase Au₆Te₆Se₄ forms stable association with Au₂TeSe and Se, Au₂TeSe and calaverite, calaverite and gold. Calaverite dissolves up to 6.7 at. % Se. Coupling mineralogical study and experimental investigations, formation temperature of this Au-bearing mineralization is considered to be below 450 °C.

1 Introduction

The aim of this research is to investigate the selenium-tellurides of gold using experimental techniques. Tolstykh et al. (2017) and (2018) recently documented previously undescribed natural Au-Te-Se phases. In particular, the Au-rich chalcogenide mineralization was described at the Gaching - Maletoyvayam ore field located in the Eocene-Oligocene central Kamchatka volcanic belt (Fig.1) in southwestern part of the Koryak Highland, Far East, Russia. The precious metals in Gaching ores are hosted in (Au, Ag) - tellurides. Gold-silver mineralization in the Maletoyvayam ore field belongs to high-sulfidation epithermal type. Gold and Se-rich minerals are characteristic for this ore association that implies special conditions for their formation: an abundant source of Au and Se and high oxidizing environment. Therefore, selenides are formed under these conditions. The vein and disseminated mineralization in the ore field include pyrite, native gold and Au-Ag-tellurides in association with various sulfosaltas of Cu, Fe, and Zn in quartzites and quartz-alunite altered rocks (Okrugin et al. 2014). Within this unusual mineralization two unnamed ternary phases in Au-Te-Se system were found. The ternary phases are intergrown with Au-Ag alloys and Au-tellurides. These associations are related to the main stage of ore mineralization which is stable at 250 °C in log/Se₂ range of −12.4 and −5.7. A further increase of f/O₂ leads to oxidation of Au-tellurides to Au₄Ag(Sb,As,Te,S) oxides and formation of mustard gold (Tolstykh et al. 2018).

This ternary system has been preliminarily experimentally studied by Wang (2000). Our experimental study in the system Au-Te-Se has been performed in order to better understand the formation processes and to determine the mineralogical properties of these unnamed Au-Te-Se phases at the Maletoyvayam ore field.

Figure 1. Geological and geographical setting of Maletoyvayam ore field. Adapted from Tolstykh et al. (2018).

2 Methodology

2.1 Experiments

Within this research the experiments were performed in the Au-Te-Se system. All syntheses were made in the Laboratory of Experimental Mineralogy of the Czech Geological Survey in Prague. To prevent any unwanted reactions with the atmosphere, calculated portions of pure reactants were placed in sealed evacuated quartz tubes. Afterwards samples were heated in the horizontal tube-furnace up to 4 months until the load has completely reacted. Temperature was set according to the predicted natural forming conditions: 200-400 °C. The experiments took place under constant pressure of 1 bar. Once during the experiment, the samples were quenched using cold water bath, run products were homogenized in acetone, evacuated,
2.2 Analyses of experimental products

Experimental products were examined using the powder-XRD using Bruker D8 Advance diffractometer equipped with LynxEye XE detector in Bragg-Brentano geometry and using CuKα radiation. Single-crystal XRD studies were carried out using a Rigaku SuperNova single-crystal diffractometer with Atlas S2 CCD detector and monochromatized MoKα radiation situated at the Institute of Physics, ASCR.

Differential thermal analyses (DTA) measurements were performed at the Institute of Geology of the Czech Academy of Sciences using Thermal Analyzer SDT 650 (TA Instruments) - weighed sample (app. 20 mg) was heated linearly (up to 1000 °C) with the step of 2.5 °C/min in argon atmosphere to prevent any unwanted reactions.

Products were analyzed in polished sections using reflected light microscopy, electron microscope (FEG-SEM observations), and electron microprobe WDS analyses using CAMECA SX-100 electron probe microanalyzer in a wavelength-dispersion mode using an electron beam focused to 1-2 μm. SEM pictures and performed analyses that have been done clearly show that the prepared analogues exhibit good crystallinity, chemical homogeneity and corresponds to natural phases.

3 Results and discussion

The system Au-Te-Se was previously studied by Wang (2000) who preliminary determined the phase relations at 400 °C. We proved the existence of two ternary compounds Au₂TeSe and Au₃Te₆Se₄ in the system. Unlike Wang (2000) investigations our experiments proved the existence of solid solutions in the ternary system. The phase Au₂TeSe forms a broad solid solution while Au content is constant Se and Te are substituting in the range of Au₀.₉₅Te₀.₇₃ - Au₂Te in which Au₃Te₆Se₄ and the phase Au₂Te₆Se₄ in the range Au₂.₈₆Te₅.₉₁Se₃.₆₁ – Au₂.₈₅Te₅.₉₆Se₃.₇₁. Crystal structures were determined: the phase Au₂Te₆Se₄ is triclinic, space group P-1 and the phase Au₂TeSe is orthorhombic space group Cmca. The natural analogue Au₃Te₆Se₄ (Fig. 2a) reported for the first time in nature in the Gaching ores (Tolstykh et al. 2018) was submitted to be approved as a new mineral species to the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA). Among the binary phases the phase AuTe₂, analogue of calaverite, dissolves up to 6.7 at. % Se at 400 °C.

Based on differential thermal analyses the melting point of the phase Au₂TeSe is 462°C. The melting point of the phase Au₃Te₆Se₄ was defined to 447°C. This knowledge gives us the overall information about the temperature conditions reigning during forming of the mineralization. We might assume that the forming temperatures of this mineralization could be deduced from the melting point of the phase therefore must be lower than 460 °C.

The phase diagram of the system Au-Te-Se at 400 °C is shown in Fig. 3. Experimental results have proved that the ternary phase Au₂TeSe coexists with gold and AuSe, AuSe and Se, calaverite (AuTe₂) and gold. The Au₃Te₆Se₄ phase coexists with the phase Au₂TeSe and Se, Au₂TeSe and calaverite (AuTe₂), calaverite and gold (Fig. 3). The phase relations in the lower part of the diagram are just predicted due to ongoing experimental work. Such parageneses were also observed among natural compounds, including the supposed relations between the Au₃Te₆Se₄ and Te-Se solid solutions (Fig. 2b).

Figure 2. BSE micrograph of natural Au₃Te₆Se₄ grain (a) and the same phase intergrowing with other minerals (b).

Figure 3. Ternary diagram showing the phase relations in the system Au-Te-Se. Two broad solid solution ranges of ternary phases are shown. The relations in the lower part of the diagram have not been clearly defined yet.
4 Conclusions

Two ternary phases $\text{Au}_2\text{TeSe}$ and $\text{Au}_3\text{Te}_6\text{Se}_4$ were proved and characterized in terms of crystal structure, solid solutions, stable associations and thermal stability. Both ternary phases form broad solid solutions, the phase $\text{Au}_2\text{TeSe}$ in the range $\text{Au} : 48.35-49.46$ at. %, $\text{Te} : 22.90-33.32$ at. %, $\text{Se} : 17.61-28.14$ at. % and the phase $\text{Au}_3\text{Te}_6\text{Se}_4$ in the range $\text{Au} : 21.53-22.67$ at. %, $\text{Te} : 45.44-48.93$ at. %, $\text{Se} : 27.76-32.47$ at. %. Calaverite dissolves up to 6.7 at. % Se at 400 °C. The phase $\text{Au}_2\text{TeSe}$ is stable up to 462 °C and the phase $\text{Au}_3\text{Te}_6\text{Se}_4$ is stable up to 447 °C. The ranges of solid solutions also reflect the variability of natural phases.

Stable phase associations in the system Au-Te-Se were assessed at 400 °C. Most of the associations are in agreement with the natural findings in the Gaching - Maletoyvayam ore field and can be expected to be found elsewhere, under similar conditions. The appearance of the phase $\text{Au}_3\text{Te}_6\text{Se}_4$ suggests mineralization forming temperature lower than 450 °C. Described associations can be expected at conditions of abundant source of Au and Se and high oxidizing environment such as at the Gaching - Maletoyvayam ore field.

Acknowledgements

This research was supported by the Grant Agency of the Czech Republic (project No. 18-15390S). The authors would like to thank Dr. Šárka Matoušková for DTA measurements and Dr. Zuzana Korbelová for EPMA analyses, Institute of Geology ASCR, v.v.i.

References


Synthetic study of the sources and origin of the gold deposit in the western Hoggar prospect (South of Algeria)

Ismahane Chaouche, Mohamed Talbi
University of Houari Boumediene. Algiers. Algeria

Abstract. The gold deposits of the Iskel terrane (Western Hoggar) are orogenic type and they are localized along the connected terranes deformed during the Pan African collision. The gold occurrences are present in tourmaline-rich quartz veins.

The general structure of tourmaline determined by using electronic microprobe and Mossbauer spectrometry shows the coexistence of ferric iron Fe\(^{3+}\) with ferrous iron Fe\(^{2+}\) in the Y site. This represents "deprotonated" tourmaline. Having divalent iron and trivalent iron simply reflects the redox conditions (\(\delta F_O\)) at a given temperature of the formation of tourmaline. While the phenomenon of deprotonation (dehydroxylation) indicates a much later oxidation of the tourmaline. The presence of gold seems to be related to a late phase of the hydrothermal process and is associated either to the second stage of tourmalinization or to the alteration of the sulfides (chalcopyrite).

The results of these mineralogical and geochemical analyses, allow us to establish guidelines prospection for the big area like the Hoggar and finally understand the relationship between the gold veins and geological hosted formations.

1 Introduction
Tourmaline is frequent in gold bearing quartz veins and in associated hydrothermal fields (Slack and Trumbull 2011). Determination of its crystal-chemistry is a good tool for a better understanding of the conditions of formation of the gold deposits (Slack and Trumbull 2011).

As the crystal-chemistry of tourmaline reflects the conditions (e.g. T, \(\delta F_O\)) prevailing during their formation it is an important tool for a better understanding of the genesis of the gold deposits and help for exploration in the big area like a Hoggar shield.

2 Geology setting
The Iskel terrane, which is part of the occidental Hoggar, is an exotic bloc in the center of the "Hoggar" shield (Black et al. 1994).

Two major tectonic structures, the 4°50 and the 4°30 lineaments are the limits of the Iskel Terrane on the west and on the east. The basement in this region is formed of conglomerates, greywackes, pelites and marbles, with intercalated basaltic sill and pyroclastic beds that are attributed to Pharusian I and II (Fig1). This basement is intruded by three large complexes of Panafrican age: a pre-orogenic poorly differentiated complex (Afedafeda) of dominantly calco-alkaline composition (868-840 Ma) (Caby et al. 1982), a syn-orogenic calco-alkaline granites group (583 Ma) (Bertrand and al. 1986) with granitoids, quartz diorites and tonalite (Immezarene type) and a late granitic complex (520 Ma) named Taourirt.

The auriferous quartz veins are mainly located along the shear-zones or in second faults order showing the same orientations as the main structures. Two dominant directions N-S and NE-SW are present.

Figure 1. Geological Map of Iskel gold prospect

3 Tourmaline study

3.1 Petrography
Quartz in the veins was deposited during two different stages: first deposited is the quartz1 shows deformation whereas posterior deposited is the quartz2 occurs as filling of the fractures in quartz1.
There are also two generations of tourmaline. The first one is intensively brecciated (Fig 2). It is associated with quartz2 and muscovite in the fissure of the quartz1. The second one is the tourmaline2 (appears as needles), where it fill the fractures in tourmaline1 and is associated with sericite.

3.2 Gold mineralization

Gold occurs as xenomorphic grains (from 5.1 up to 147.9 µm) or as small needles. It is disseminated in the quartz matrix or appears as inclusions in tourmaline and chalcopyrite (Fig3).

3.3 Mineralogy and crystallochemistry of tourmalines

Tourmalines of Iskel prospects have been previously studied in the Scanning Electron Microscope (SEM), which revealed their chemical variation depending on the types and generations. This variation has been confirmed by the results of the electronic microprobe and Mössbauer Analyzes (Fig. 3).

Based on the analytical results (Table1) and calculated structural formulas (Table 2), it can be observed that tourmalines from different veins exhibit similar compositions and show intermediate position in the solid solution series schorl-dravite (Figs. 4a, b), with relatively constant Fe/Mg ratios, varying between 0.82 and 0.98. 

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Seld1</th>
<th>Seld2</th>
<th>Seld3</th>
<th>Seld4</th>
<th>Seld5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyzes</td>
<td>10</td>
<td>7</td>
<td>10</td>
<td>10</td>
<td>16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Seld1</th>
<th>Seld2</th>
<th>Seld3</th>
<th>Seld4</th>
<th>Seld5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>36.74</td>
<td>37.19</td>
<td>36.92</td>
<td>36.75</td>
<td>36.49</td>
</tr>
<tr>
<td>Al2O3</td>
<td>29.01</td>
<td>30.02</td>
<td>31.76</td>
<td>31.41</td>
<td>31.35</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.32</td>
<td>0.20</td>
<td>0.28</td>
<td>0.24</td>
<td>0.20</td>
</tr>
<tr>
<td>FeO</td>
<td>12.06</td>
<td>10.44</td>
<td>9.63</td>
<td>9.93</td>
<td>9.61</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.05</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>6.10</td>
<td>6.07</td>
<td>5.84</td>
<td>5.66</td>
<td>5.78</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.04</td>
<td>0.08</td>
<td>0.04</td>
<td>0.04</td>
<td>NA</td>
</tr>
<tr>
<td>CaO</td>
<td>0.67</td>
<td>0.65</td>
<td>0.69</td>
<td>0.57</td>
<td>0.60</td>
</tr>
<tr>
<td>Na2O</td>
<td>2.36</td>
<td>2.26</td>
<td>1.94</td>
<td>1.93</td>
<td>1.90</td>
</tr>
<tr>
<td>K2O</td>
<td>0.04</td>
<td>0.23</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>F</td>
<td>0.07</td>
<td>0.01</td>
<td>0.02</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>Total</td>
<td>87.51</td>
<td>87.24</td>
<td>87.23</td>
<td>86.74</td>
<td>86.06</td>
</tr>
</tbody>
</table>

Table 2. Average structural formulas of Iskel tourmalines (Structural formulas are calculated based on 24.5 oxygens)

This tourmaline is a solid solution between the schorl and the dravite. The structural formula can be written as follows.

\[
\begin{align*}
(0.27\text{Na}_{0.611}\text{Ca}_{0.106}\text{K}_{0.004})\text{(Mg}_{1.427}\text{Mn}_{0.004}\text{Fe}^{2+}_{1.048}\text{Fe}^{3+}_{0.177}\text{Fe}^{3+}_{0.288}\text{Sb}_{0.001}\text{Cr}_{0.003}\text{Ti}_{0.024}\text{Al}_{0.120})\text{Al}_{6}\text{Si}_{6}\text{O}_{18}\\(\text{BO}_{3})_{3}\text{(OH)}_{3}\text{(OH)}_{0.992}\text{F}_{0.008}
\end{align*}
\]
Figure 4. Composition of the two generations of Tourmalines plotted in terms of:
(a) $\text{Fe}_{\text{oct}}/(\text{Fe}_{\text{oct}}+\text{Mg})$ versus Ca/(Ca+Na)
(b) $\text{Fe}_{\text{oct}}/(\text{Fe}_{\text{oct}}+\text{Mg})$ versus Na/(Na+Ca)

Figure 5. Analyzes spectrum obtained from Mössbauer spectrometry

The Mössbauer Analyzes result (Table 3) shows that Fe$^{2+}$-Fe$^{3+}$ and intervalent charge transfer Fe exists in the Y site.

- The value of the chemical drift (isomer shift=$\delta$) characterizes the valence (2, 3 or Intervalent, in the above table)
- The value of the quadrupole splitting ($\Delta$). Characterizes the type of site in which iron is located.
- The surface of each area attributed to every doublet is said to be representative of the percentages of each doublet to total iron.

<table>
<thead>
<tr>
<th>Doublet</th>
<th>$\delta$ isomer shift</th>
<th>$\Gamma$/2 width</th>
<th>$\Delta$ quadrupole splitting</th>
<th>% Iron total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doublet 1</td>
<td>1.097(1)</td>
<td>0.160</td>
<td>2.462(2)</td>
<td>52.3%</td>
</tr>
<tr>
<td>Doublet 2</td>
<td>0.585</td>
<td>0.270</td>
<td>0.64(1)</td>
<td>21.6%</td>
</tr>
<tr>
<td>Doublet 3</td>
<td>0.828(2)</td>
<td>0.264</td>
<td>1.40(4)</td>
<td>12.8%</td>
</tr>
<tr>
<td>Doublet 4</td>
<td>0.986(2)</td>
<td>0.190</td>
<td>1.93(2)</td>
<td>12.4%</td>
</tr>
</tbody>
</table>

- Doublet 1: Fe$^{2+}$ present in the octahedral site Y (Burns 1972; Pieczka et al. 1997)
- Doublet 2: Fe$^{3+}$ in the octahedral site Y (Burns, 1972; Pieczka et al. 1997)
- Doublet 4: Fe$^{2+}$ attributed to a distorted Y site (Pieczka, 1997) or to Z site (Burns 1972, Fuchs and Maury 1995, Bosi 2008).

4 Discussion

Unlike tourmalines from some gold-bearing boron-silicates hydrothermal systems, such as those of Lincoln Hill, NV and Jack Creek, Montana in the USA, or the gold-bearing Uranium deposits of Ben Lomond, Queensland, Australia and Novas, Berg masques Alps, Italy (Gade et al. 1987; Fuchs 1989; Foit et al. 1989; Fuchs et al. 1995), that show great chemical variations, the studied tourmalines are homogenous in their chemical composition.

The observed occupation deficiency of X site is moderate, varying between 10 and 30%. However, all analyzed samples plot below the representative line of charge compensation because of the lack in alkaline cations in X site caused by R$^{3+}$ element excess in Y site. This suggests that, for various analyzed samples, it is convenient to add to the sum $\Sigma=\text{[Y]}\text{Al}^3++4/3\text{[Y]}\text{Ti}^4+$ some of iron present in the form of Fe$^{3+}$. Based on the Mössbauer spectrometry results (Fig. 6) of Iskel tourmaline, the total $\Sigma=\text{[Y]}\text{Al}^3++4/3\text{[Y]}\text{Ti}^4++\text{YFe}^{3+}$ was recalculated. It is then observed that this sample (figure 4) plots to the right, above the compensation line of charge deficit. This is explained by the effects of substitution with charge compensation, in addition to deprotonation effects (Foit and Rosenberg 1977).

Chemical analyses performed by SEM, EMP and Mössbauer techniques allow to precise the different types of tourmaline on the basis of their composition and structure. The tourmaline of the gold occurrence of the Iskel terrane shows an evolution of a solid solution between the schorl and the dravite types with a moderate vacancy in X site. This vacancy is often compensated with an excess of electric charge either by trivalent cations that could occupy site Y or by deprotonation of the central OH.

Whereas the tourmaline has a higher Fe$^{3+}$ content...
reflecting the more oxidizing condition prevailing in the outer zone of the hydrothermal system with lower temperatures.

The presence of gold seems to be related to a late phase of the hydrothermal system and it also associated to the 2nd generation of tourmaline.

Figure 6. Diagram of tourmalines deprotonation

5 Conclusions

Many authors report that gold deposition seems to be related to the late hydrothermal stage, at the example of the Humboldt Range, Nevada (Fuchs and Maury, 1995) or at Guibaré and Fété Kolé (Bukina Faso) (Beziat et al. 1999), Iron rich tourmaline showing evidence of late oxidation and deprotonation processes is often present (Béziat et al. 1999. Fuchs et al. 2002, Baksheev et al. 2011).

Further studies and experimental synthesis are in progress to emphasize the importance of the tourmaline and tourmaline oxidation process in the deposition of gold. The results of these forthcoming researches would be useful for the exploration of potentially gold bearing paleo hydrothermal systems.

Acknowledgements

We are particularly grateful to Professor J. Linarès Laboratoire de Magnétisme et d’Optique de l’Université de Versailles-Saint Quentin for his help in the realization of Mössbauer Spectrometry operations and Analyses. To Mr. Michel Fialin in charge of microprobe analytical developments at the laboratory CAMPARIS (University Pierre et Marie Curie) for the Analyses made with Microprobe Analyses SX 50. To Mr. Omar Boudouma, in charge of the SEM

A particular acknowledgement for Professor Fuchs Y (Laboratoire Géomatériaux Environnement, Institut Francilien des Sciences Appliquées (IFSA), Université Paris-Est Marne la Vallée, France) for his contribution to this work, for carrying out the analyses, for his pertinent remarks and for the enrichment of the present work.

References

Single and Multiple Weathering-Erosion Cycles in Supergene Ore Genesis

Paulo M. Vasconcelos
The University of Queensland, Australia

Abstract. Supergene ore deposits form when the relative tempo between weathering and erosion favors the formation and preservation of deep chemically stratified weathering profiles. If erosion outpaces weathering, weathering profiles are incipient or the surface is stripped to bedrock, and no supergene metal concentration occurs. If erosion and weathering occurs at comparable rates, metals chemically enriched at the Earth’s surface are physically eroded, preventing the formation of supergene deposits. When chemical weathering is fast but chemical erosion slow, shallow weathering profiles devoid of enrichment blankets form because undesirable elements are not removed fast enough. Therefore, the ideal conditions for the formation and preservation of supergene ore deposits are relatively fast chemical weathering and erosion but slow physical erosion at the local scale, and relatively fast physical erosion, drainage incision, and lowering of the water table at the regional scale. Determining absolute ages of weathering profiles and rates of chemical and physical weathering and erosion for landsurfaces at local and regional scales is one of the primary challenges in quantifying supergene ore genesis and a necessary approach for identifying areas likely to host significant supergene ore deposits.

1 Introduction

Supergene processes (i.e., processes associated with the transport and deposition of chemical elements by meteoric water at the earth’s surface) account for the formation or the economic viability of numerous ore deposits currently mined. Bauxites, channel iron deposits (CIDs), Ni-laterites, lateritic gold, and supergene manganese deposits illustrate the economic importance of weathering and erosion in ore genesis. The absolute enrichment of porphyry copper deposits or the relative enrichment of hydrothermally altered banded iron-formations improves their economic viability. In the first case, surficial processes drive ore formation; in the later, ore enrichment.

Major advances in supergene ore genesis understanding require identifying the agents (chemical vs physical, organic vs inorganic) and quantifying the processes responsible for the formation or enrichment of supergene ore deposits. A classification scheme helps to identify the nature and categorize the sequence of processes involved in the formation of particular supergene ore deposits. To quantify each process and identify major controlling factors, novel geochronological methods, cosmogenic isotope studies, and geochemical modeling are necessary.

2 Supergene Ore Genesis

Supergene ore genesis encompasses a variety of chemical and mechanical processes, often biologically mediated, that promote the concentration of a desirable mineral commodity to economic grade at the earth’s surface. Chemical and physical weathering release an element of interest from its host lithology. Chemical and physical erosion separate the element of interest from gangue elements and minerals, leaving the valuable element residually enriched. Alternatively, the valuable element is physically or chemically transported to a suitable trap, where a combination of chemical, physical, or biological sedimentation promotes its re-deposition in an enriched or purified form (Figure 1).

If an element or mineral liberated by weathering processes is re-precipitated and enriched within the weathering profile, it forms an autochthonous supergene deposit (AUSD). In AUSDs, if the enrichment process occurs by the loss of relatively mobile gangue elements and minerals, where the partial or total retention of the ore element promotes an increase in its concentration with respect to the parent rock, it constitutes relative enrichment. If the enrichment process occurs by the removal of the ore element or mineral from its original site, its downward transport within the weathering profile, and its re-precipitation in concentrated grades at a lower horizon, it constitutes absolute enrichment.

If an element or mineral released from its host lithology is transported away from the original parent rock by chemical and mechanical erosion, and it is re-deposited at a distance from its source (Figure 1), it forms an allochthonous supergene deposit (ALSD). In ALSDs, the depositional process may be chemical, physical, or organic sedimentation (Figure 1). This depositional process ultimately controls the location, size, grade, and composition of the supergene ore deposit.

Finally, in the interplay between weathering and erosion, there maybe a single cycle of bedrock exposure, weathering, and supergene enrichment, forming single-cycle supergene ore deposits (SCSOD, Figure 1a). Alternatively, previously enriched profiles may be partially eroded, truncated, and re-weathered; or the eroded component may be physically transported, deposited elsewhere and re-weathered. These later scenarios characterize multi-cycle supergene ore deposits (MCSOD, Figure 1b). Distinguishing SCSODs from MCSODs is essential for differentiating among the various processes that may have contributed for the formation of an ore deposit and for determining the rates of these processes.

For example, basalts deeply weathered in situ may
form Fe-duricrusts (goethite cemented) at the surface and Al-rich duricrusts (gibbsite-cemented) between the Fe-rich horizon at the surface and a clay-rich saprolite at depth; this constitutes a single-cycle bauxite deposit. Erosion may remove the Fe- and Al-duricrusts, exposing the clay-rich horizons, depleted in iron, at the surface. Renewed weathering of the partially truncated and iron-depleted profile will preferentially remove aqueous silica, leaving a gibsite-cemented duricrust at the surface; this constitutes a multi-cycle bauxite deposit (Figure 1b).

Another example of bauxites formed by more than one cycle of weathering interrupted by an erosive event is provided in terrains where deeply weathered granites or gneissies are partially or completely eroded. During physical transport, iron oxides, quartz, and clay minerals (often kaolinite) removed from the weathered profile may be mechanically sorted and re-deposited as transported duricrusts, sand, and clay beds. Renewed weathering of clay-rich sediments will form bauxites. Deposits where more than one period of weathering are separated by a significant erosive event are MCSODs (Figure 1b).

3 Quantifying rates of weathering and erosion

Quantifying rates of weathering and erosion through time is possible through a combination of weathering geochronology and cosmogenic isotope studies. Weathering geochronology provides ages of supergene minerals enriched in situ, or precipitated away from the source. Geochronology also permits identifying minerals that were eroded, transported, re-deposited, and partially re-weathered at the depositional site. Similarly, cosmogenic isotopes permit differentiating among minerals that formed and were continuously exposed at the Earth’s surface, from minerals that formed at the surface, were eroded, transported, deposited, and re-exposed. This combination of weathering geochronology and cosmogenic isotopes is a powerful tool in unraveling the sequence of processes, and their rates through time, responsible for supergene ore genesis.

For example, dating of supergene Mn oxides and K-bearing sulfates by 40Ar/39Ar geochronology yields rates of weathering front propagation within a profile (e.g., Carmo and Vasconcelos 2006). (U-Th)/He geochronology of supergene goethite also helps quantifying rates of weathering front propagation (Heim et al., 2006; Monteiro et al. 2018). Cosmogenic 3He concentrations in hematite and goethite yield long-term exposure ages for weathered profiles and supergene enrichment zones (Shuster et al. 2012; Monteiro et al. 2014, 2018a,b; Vasconcelos et al. 2019). These isotopes also permit quantifying rates of erosion for supergene deposits (Monteiro 2018a,b; Vasconcelos et al. 2019). Combining these measurements with 26Al and 10Be concentrations in quartz and 36Cl in carbonates yield exposure ages or short-term erosion rates for the landsurfaces hosting supergene ore deposits (Vasconcelos et al. 2019). In addition, concentrations of these isotopes in sediments permit determining their depositional ages (Monteiro 2018a,b; Vasconcelos et al. 2019). Combination of these approaches at a regional scale yield timing of exposure and/or rates of weathering and erosion for exposed land surfaces, and timing of deposition and age of re-weathering of the transported material (Monteiro 2018a,b; Vasconcelos et al. 2019).

Figure 1. Diagrammatic illustration depicting the relative contributions of weathering and erosion in the formation of single-cycle vs multi-cycle supergene ore deposits.

4 Processes and rates of formation of supergene iron deposits in Brazil and Australia

Iron deposits form the largest and most valuable global mineral resources. Therefore, their genesis matters. As Brazil and Australia host the largest and richest supergene iron deposits on Earth, I concentrate on their origin by comparing and contrasting the processes and rates of formation of these deposits in these two distinct environments. The largest and most valuable iron deposits in Brazil and Australia are SCSOD formed by relative Fe enrichment during weathering of hydrothermally altered banded iron-formations (BIFs) or MCSOD formed by erosion of deeply weathered BIFs, deposition of detrital iron in aggraded rivers, and re-weathering of the detrital material to form CIDs. Supergene iron deposits in both regions result from weathering processes that initiated at least ~80 Ma in Western Australia (Heim 2006) and ~70 Ma at Carajás (Shuster et al. 2005; Monteiro et al. 2018a), Urucum (Vasconcelos et al. 2019), and the Quadrilátero Ferrífero (Monteiro et al. 2018b). Interestingly, despite the similar
tectonic and geomorphological settings between the iron deposits in Brazil (Carajás, Quadrilátero Ferrífero, Urucum) and Australia (Tom Price, Paraburdoo), CIDs appear to only have formed in Australia.

Differences in climatically controlled relative rates of weathering and erosion likely account for the abundance of CIDs in Western Australia and their absence in Brazil. Rates of propagation of weathering fronts in Brazil were ~7–8 m.Ma\(^{-1}\), while in Western Australia they were ~3–4 m.Ma\(^{-1}\) during the formation of the weathering profiles. Erosion rates derived from cosmogenic isotope concentrations, on the other hand, suggest that the summits of the plateaus in Western Australia erode at a higher rate (~1 m.Ma\(^{-1}\)) than their counterparts in Brazil (< 0.1.Ma\(^{-1}\)) (Fujioke et al. 2010; Shuster et al. 2012; Monteiro et al. 2018a,b). Vegetation and microorganisms appear to play a major role in the iron cementation that gives the duricrusts their resilience (Monteiro et al. 2014; Levet et al. 2016). In contrast, transition to arid climates in Western Australia sometime between 45–35 Ma (Vasconcelos et al. 2013) or more recently (Danisik et al. 2013) promoted the erosion of previously formed duricrusts, their deposition in aggrading river channels, and their re-weathering and iron cementation during the prolonged Neogene aridification of Western Australia. Transition from humid to arid and persistence of semi-arid to arid climates through the late Cenozoic promoted the formation and preservation of CIDs in Australia. The persistence of relatively continuous wet conditions in Brazil throughout the Neogene most likely accounts for the absence of CIDs in the iron producing regions of South America.

The approaches applied to iron deposits are also suitable in the study of the genesis of other supergene ore deposits (e.g., Vasconcelos 1999; Hautmann & Lippolt 2000; Mote et al. 2001; Colin et al. 2005; Aranciba et al. 2006; Li et al. 2007; Reich et al. 2009; Deng et al. 2014; Bonnet et al. 2016;). Ongoing studies of these deposits confirm the importance of climatically controlled alternating periods of weathering and erosion in supergene ore genesis.

Acknowledgments

The author thanks the Australian Research Council for funding the \(^{40}\)Ar\(^{39}\)Ar laboratory (A39531815 and LE0882818) and weathering geochronology research at UQ (ARC DP06666925, DP160104988, LP140100805).

References


Carmo IO, Vasconcelos PM (2006). \(^{40}\)Ar\(^{39}\)Ar geochronology on late Miocene weathering rates in Minas Gerais, Brazil. EPSL 241:80–94.


Monteiro, HS, Vasconcelos, PMP, Farley, KA (2017) A combined (U-Th)/He and cosmogenic \(^{39}\)He record of landscape arming by biogeochemical iron cycling. JGR 123, 298–323.


Vasconcelos PM, Heim JA, Farley KA, Monteiro HS, Waltenberg KM (2013) \(^{40}\)Ar\(^{39}\)Ar and (U-Th)/He – \(^{39}\)He/\(^{40}\)He geochronology of landscape evolution and channel iron deposit genesis at Lynn Peak, Western Australia. GCA 113:283–312.

Mineralogy and chemistry of Ni-phyllosilicates in the Wingellina Ni-Co laterite deposit (Western Australia): alteration processes of mafic to ultramafic lithologies

Francesco Putzolu¹, Maria Boni¹, Nicola Mondillo¹, Jens Najorka², Giuseppina Balassone¹, Piergiulio Cappelletti¹, Fabio S. Graziano³, Licia Santoro⁴
¹DiSTAR “Federico II”, Napoli, Italy
²Core Research Laboratories, The Natural History Museum, London, UK
³Dipartimento di Farmacia, Università degli Studi di Napoli “Federico II”, Napoli, Italy
⁴Earth Sciences Department, The Natural History Museum, London, UK

Abstract. Ni-phyllosilicates are the main phases in the saprolite zone of the Wingellina Ni-Co laterite deposit (Western Australia). In this study, we analysed the mineralogy and chemistry of the clay fraction of the saprolite from two different zones of the deposits. Our results highlight that the mineralogy, chemistry and general paragenesis of clays reflect the heterogeneity of the underlying bedrock, as well as the different alteration histories recorded in two drill cores.

The mineralogy of the saprolite zone lying on the gabbro bedrock is dominated by dioctahedral smectite clays (montmorillonite), which developed directly from the weathering of pyroxenes and plagioclases. On the contrary, the alteration of olivine resulted in the precipitation of Fe-(oxy)-hydroxides. The early stage alteration of the ultramafic unit (peridotite) involved the serpentinization of the ferromagnesian minerals. This process was followed by a Fe-(oxy)-hydroxides/quartz and smectite precipitation stage, with the latter mineral belonging both to the tri- and di-octahedral types (saponite and nontronite). The last local alteration process resulted in the formation of Ni-rich mixed-layers minerals, such as talc/smectite (T/S) and chlorite/smectite (C/S). The genesis of chlorite/smectite could be potentially due to the low temperature diagenetic process that occurred after the main lateritization phases.

1 Introduction

Mafic to ultramafic terrains weathered in tropical areas have been the subject of several studies, as their alteration produces the enrichment of metallic elements in Ni-laterite soils (Freyssinet et al. 2005; Butt and Cluzel 2013). The Ni mineralogy in laterites varies broadly and, according to such diversity, Ni-laterites have been subdivided into oxide- and phyllosilicate-types (Freyssinet et al. 2005). Oxide-type laterites are characterized by economic concentrations of Ni and Co within the ferruginous saprolite unit, in association with Fe- and Mn-(oxy)-hydroxides. Phyllosilicate-type deposits show the highest Ni-grades in the lower zones of the regolith. Nickel-bearing phyllosilicates have been the subject of several studies in past years as their mineralogy and chemistry are sensitive to the main controlling factors of the ore- and soil-forming processes: parent rock lithology and chemistry, climate, drainage, degree of hydrothermal serpentinization, chemistry of soil solutions and syn-pedogenetical tectonics. Consequently, several studies dealing with the composition and mineral transformation of phyllosilicates in soils derived from ultramafic bedrocks have been already carried out, especially where their formation is intimately related with the accumulation of Ni ores. The studies conducted on Australian ultramafic systems mainly focused on the weathering profiles in Queensland, in the Kalgoorlie district (Western Australia) and in the Murrin Murrin deposit (Western Australia). Nevertheless, there is a lack of knowledge about the pedogenesis of similar lithologies cropping out in the Musgrave Province (Western Australia), where the chemical weathering resulted in the genesis of the Wingellina laterite deposit. Here, we briefly report the results of a study on the phyllosilicates-rich horizons of the Wingellina deposit, to assess the weathering dynamics that controlled crystallographic and chemical variations during the saprolitization of the Giles Suite intrusions.

2 Geological setting

The Wingellina Ni-Co laterite deposit (Fig. 1) derived from the weathering of the olivine-rich mafic to ultramafic layered intrusion of the Mesoproterozoic Giles Complex (Putzolu et al. 2018, 2019). The weathering profile comprises an oxide-dominated zone, with high Ni and Co concentrations, and a phyllosilicate-bearing section (i.e. saprolite), which occurs as a subordinate unit. The laterite profile is characterized by a high degree of lateral variation due to the lithological heterogeneity of the magmatic bedrock, which consists of gabbro/gabbronorite and serpentinite (ex-peridotite).
3 Materials and analytical methods

This study was conducted on samples collected from two saprolite zones developed from different protoliths: samples from drillcore W12 lie above a gabbro/gabbronorite bedrock, whereas samples from W19 lie on a serpentinite (deriving from the alteration of the peridotite bedrock). The specimens have been studied through X-ray powder diffraction on clay fraction (XRPD), One-dimensional X-ray diffraction modelling and Electron MicroProbe Analyses (EMPA). XRPD analyses were conducted at DiSTAR (Italy) with a Bruker D2 Phaser diffractometer. The data were acquired with a CuKα radiation of 30 kV and 10 mA. The Randomly Oriented patterns were collected at the Natural History Museum (UK) with a Panalytical X’Pert PRO MPD diffractometer equipped with an Xcelerator PSD detector with a CuKα radiation, operating at 45 kV, and 40 mA. One-dimensional simulation XRPD was performed with the NEWMOD software, to assess the presence of disordered mixed layers. EMPA was performed at the NHM (UK), using a Cameca SX100 equipped with five Wavelength Dispersive Spectrometry Bragg spectrometers (beam current of 20 nA, accelerating voltage of 20 keV and a spot size of 1 µm).

4 Results

4.1 XRPD on clay aggregates

Saprolite samples from W12 (Figs 2a,b) are predominantly formed by ~15 Å to ~17 Å swelling phyllosilicates (i.e. smectites). In this drillcore, the detection of the regular sequences of the d001 reflections, together with the absence of systematic deviations of the d002, d003 and d005 reflections of smectite in EG conditions from their overall nominal positions, suggests the presence of pure phases, rather than mixed-layer clays. The uppermost sample of W12 also contains kaolinite. The RO (Fig. 2b) patterns show that the 06l reflections of smectite fall within a d-spacing diagnostic of dioctahedral Al-bearing smectites, in this case corresponding to montmorillonite.

Also the saprolite intersected by W19 is dominated by swelling clays (Fig. 3a), but in this unit the broadening of the d001 reflections of smectite and the absence of superlattice reflections and the detection of irrational d00l series suggest the presence of disordered mixed-layer minerals. In addition, the typical reflections of disordered talc and serpentine occur at 10 and ~7 Å. The RO pattern (Fig. 3b) highlights the presence of both di- (d001: 1.511 Å) and tri-octahedral (d001: 1.542 Å) phases, as well as the potential occurrence of ilb chlorite (d204: 2.254 Å and d204: at 2.030 Å).

4.2 One-dimensional XRPD modelling

The modelling of samples from W12 showed good fitting by using a Dismectite-2Gly (d001: 16.75 Å, 0.6 < Fe < 1.2, N: 1-8, delta: 4) and kaolinite (d001: 7.15 Å, N: 1-30, delta: 15), occurring as discrete phases. The NEWMOD analysis showed that in a few samples from W19 the trioctahedral forms disordered mixed layers with turbostratic talc and with chlorite. The former mixed layer has been modelled with a talc/Trisme-2Gly (95 –5 relative proportion, R: 0.5), whereas the chlorite-smectite mixed layer has been modelled with a di,tri-chlorite and tri-smectite structure (90–10 proportion, 1.45 < Fe < 1.75, R: 0.5). The serpentinite bedrock is characterized by the occurrence of discrete di-smectite and serpentine, modelled through Dismectite-2Gly (d001: 16.7 Å, N: 1-6) and serpentinite (d001: 7.26 Å, N: 1-4, Fe = 1.5).
4.3 Textures and paragenesis

Montmorillonites in the gabbro bedrock (W12) are replacing and enclosing pyroxenes and plagioclase grains (Fig. 4a). The olivine crystals in the bedrock are not altered to phyllosilicates, but are crosscut by veins filled by Fe-(oxy)-hydroxides (Fig. 4b). The saprolite zone deriving from the gabbro bedrock is almost entirely composed of smectite, which occurs as pelitomorphic masses (Fig. 4c).

The petrographic study of the bedrock of drillcore W19 revealed a different early stage alteration style. In this drillcore the femic phases are pseudomorphed by mesh serpentinizations enveloping micro-aggregates of quartz and Fe-hydroxides (Fig. 4d). The uppermost section of the local saprolite is characterized by the progressive neo-formation of tri- and di-smectite that directly replaces serpentine (Fig. 4e). In their turn, tri-smectites are locally replaced by massive chlorite-smectite mixed-layers (Fig. 4e). In the uppermost section of the local saprolite, a total loss of the original magmatic texture is observed. Here, fine-grained talc-smectite is the major phyllosilicate (Fig. 4f).

4.4 Phyllosilicate mineral chemistry

Montmorillonites forming from the gabbro bedrock are close to the Al- and Fe-rich end members; starting from the bottom of the local saprolite up to its top, a general loss of Mg paired to an enrichment of dioctahedral cations (i.e. Fe and Al) has occurred (Fig. 5). The Ni gain has been observed mainly in the montmorillonites from sample WPDD0012-16 (values of 0.56 apfu).

In drillcore W19 (Fig. 6), serpentines show the lowest Ni concentrations in the local bedrock, whereas they are relatively Ni- and Fe-enriched toward the uppermost section of the saprolite (Ni up to 0.15 apfu, Fe up to 0.90 apfu). Smectitic clays with a nontronitic and saponitic chemistry are found mainly in the saprolite zone developed directly above serpentine, with the latter showing the highest Ni concentration (up to 0.48 apfu).
highest Ni grades have been observed in chlorite/smectite, with Ni concentrations up to about 1 apfu, whereas talc-smectite has up to about 0.5 apfu Ni.

5 Discussion and conclusions

For the formation of thick clay units in Ni-laterites, similar to those observed at Wingellina, it is essential to have limited cation leaching as well as the existence of an impeded drainage (Gaudin et al., 2004). At the same time, the nature of the newly-formed phyllosilicates is controlled by the mineralogy of the parent rocks and by the activity of the diverse species in solution.

At Wingellina the pedogenesis of the mafic units resulted in the development of a thick secondary plasmic system, in which montmorillonite totally obliterated the original rock texture. The initial alteration stages involved the conversion of pyroxenes and plagioclases to clays, which is consistent with the observation of Eggleton (1975), whereas olivine was converted into Fe-(oxy)-hydroxides. The uppermost zone of the local saprolite is characterized also by the presence of kaolinite, which can be the result of the transformation from montmorillonite to kaolinite. This process has been widely recognized during chemical weathering, and considered a proxy for the transition from “immature” to “mature” soil systems, related to the acidification of meteoric solutions in surficial environments (Altschuler et al. 1963). The saprolitization process recorded in clay minerals observed in W19 was more complex. According to the observed paragenesis three evolutionary stages could be established:

(i) Serpentinite formation: this is the early post-magmatic alteration stage, during which olivine and pyroxenes are converted to lizardite through hydrothermal processes.

(ii) Fe-(oxy)-hydroxides/silica aggregates and smectite stage: this is the first weathering stage, in which Fe-(oxy)-hydroxides and silica formed as pseudomorphs of the still unaltered olivine. This process commonly represents the initial stage of the ferralitic alteration at tropical latitudes (Delvigne et al. 1979). Concurrent with the FeO/OH+quartz formation, oxidative weathering resulted in Mg leaching from serpentine and Ni gaining in neo-formed tri- and bi-smectite (Hseu et al. 2007). Although no textural association between di- and tri-smectites has been detected, it is possible to infer that Fe-rich smectite formed from the transformation of Mg(Ni)-smectite due to a local increase of the drainage conditions and of the leaching degree.

(iii) Mixed-layers stage: mixed-layers were identified either as overprints on tri-smectite (as chlorite/smectite) or as total replacements of serpentine textures, thus highlighting that their formation was linked to late stage processes during saprolitization. The late precipitation of C/S and T/S could reflect a local post-lateritization process resulting from low temperature diagenesis and/or authigenic processes (Beaufort et al. 2015).

Acknowledgements

This contribution is part of the ongoing PhD of Francesco Putzolu at the DISTAR. The authors are indebted to Max Maczurad (Metals X Ltd.) for field assistance and to John Spratt (Natural History Museum of London, UK) for technical help during EMPA analyses. This study has been funded by "Programma per il finanziamento della ricerca di Ateneo 2016 -Progetto CEB", granted by Università degli Studi di Napoli Federico II (Italy) to Dr. Nicola Mondillo.

References


New data on the Francevillian manganese ore from Bignomi plateau, Gabon

Alexis NDONGO, Norbert ONDO ZUE ABAGA, Benjamin MUSAVU MOUSAOU, Simplice M. NDONG ONDO
Université des Sciences et Techniques de Masuku, Département de Géologie, Franceville, Gabon

Kalle KIRSIMAE
University of Tartu, Geology department, Tartu, Estonia

Abstract. Manganese deposits in the Franceville basin have largely been studied thanks to the discovery and exploitation of worldclass manganese ore of Bagombe. The results from these studies on the Bagombe plateau are commonly generalized to all deposits in the Franceville basin. We present here new data from Bignomi deposit located in the south of the basin. As in Bangombe, the profile shows five horizons of massive ore (H1), platy ore (H2), transition layer (H3), pisolith (H4) and humic layer (H5). However, unlike in Bangombe where the most enriched layer is H2, the high grade horizon (44% Mn) in Bignomi is the Massive horizon (H1). This Mn enrichment of the lower part of the profile could be linked to the karstic and fractured system which allowed Mn-rich fluids to flow in channels towards the lower horizons. That is showed by the occurrence of manganese oxides in fractures, cavities and pores. Furthermore, X-ray diffraction (XRD) reveals that material from massif Horizon (H1) consists of a mixture of different poorly crystalline Mn-oxyhydroxides which were impossible to quantify. This result suggests that the massif horizon of the Bignomi deposit can be considered, unlike in Bangombé, as a recently precipitated material.

1 Context of the study

Manganese deposits in Franceville basin have been known since the 19th century (Barrat 1895). Previous work carried out in the basin since the 1960s has highlighted several manganese rich plateaus located in Moanda, Franceville and Okondja. These include, Bagombe, Okouma, Bafoula and Yeye in Moanda area and Menai, Bordeau, and Biniomi in Franceville (Weber 1969; Pambo 2004).

Bagombe plateau contains the largest manganese deposit in Franceville basin evaluated at 20 million tons before exploitation. This deposit has been in operation for some 30 years by the COMILOG Company owned by Eramet group.

Bagombe plateau contains the largest manganese deposit in Franceville basin evaluated at 20 million tons before exploitation. This deposit has been in operation for some 30 years by the COMILOG Company owned by Eramet group.

Located southeast of the Franceville city, the Biniomi plateau contains one of the minor manganese deposits in the basin. This deposit is currently operated by Nouvelle Gabon Mining Company and has been estimated at 35 million tons. As Bignomi deposit is of small importance compared to Bagombe, it has not been the subject of any scientific study to date.

The numerous scientific studies carried out on the manganese deposits in Bagombe plateau, have made it possible to establish a synthetic log of the mineralized layer, to identify mineralizations types and to know the geochemical and metallogenic composition of the deposit (Bouladon 1963; Weber 1969; Azzibrouck Azzilet 1986; Pambo 2004).

Studies on the Bagombe plateau have often been generalized in Franceville deposits, but smaller deposits must also be studied in order to better constrain the paleogeochimical and paleoclimatical processes that led to manganese accumulation in the basin.

We have been working since 2017 on the Bignomi deposit with the aim of understanding the geological and paleoatmospheric evolution of manganese precipitation in the protore, to characterize the mineralogical core and to determine the geochronological age of the manganese enrichment of the deposit.

We present here preliminary results obtained by meso to microscale studies of manganese profile as well as bulk XRD, XRF analysis and SEM mapping of two samples (Bi01 and Bi02) from massive horizon (H1) of Bignomi deposit. XRD, XRF and SEM mapping where performed at the University of Tartu in Estonia.

2 Geological background

Bignomi deposit is located in the eastern part of the Franceville basin. This basin was opened during the Paleoproterozoic as an intracratonic basin. The opening of the basin was led by two major fault sets such as (1) N–S-transverse faults and (2) longitudinal normal faults that run parallel to the overall NW–SE trend of the basin. Those faults combined to open the Franceville basin (Gauthier-Lafaye, 1986; Pambo et al., 2006; Bouton et al., 2009a, Ndongo et al., 2016).

The Franceville Basin has been extensively studied thanks to the discovery and exploitation of worldclass manganese resources (Pambo 2004) and uranium deposits (Weber 1969). This basin which lies in the Haut Ogooué region of south-eastern Gabon, is hosted by the Francevilian series. The stratigraphic column of the Francevilian series has been defined into five stratigraphic units FA, FB, FC, FD, and FE (Weber 1969), arranged into two sedimentation cycles (Parize et al., 2013). The FA (Francevilian A) forms the base of the series which is made up of coarse sandstones and conglomerates interbedded between pelitic layers at the base and the alternating coarse to medium sandstones and silt-sandstones toward the top. According several
authors, the FA formation could correspond to a large Paleoproterozoic delta system (Gauthier-Lafaye 1986; Pambo et al., 2006; Deynoux and Duringer 1992; Ndongo et al., 2016). The FB (Francevillian B) is made up mostly of marine black shales and organized into two stratigraphic subunits, FB1 and FB2 (Weber 1969). The FB1 subunit is mainly composed of black shales with dolomite and manganese rich layers in the upper part (Weber 1969; Azzibrouck Azziley 1986; Gauthier-Lafaye 1986; Pambo 2004). The FB2 is about 100 meters thick and is made up mostly of Poubara sandstones (FB2a) and black shales (FB2b) which have been associated with turbidites (Parize et al., 2013). The FC (Francevillian C) comprises massive dolomites, ribbon chert, andstromatolitic jaspes. The following Formations FD and FE (Francevillian D-E) are prominent in the northern part of the Francevile Basin and in the Okonja Basin (Bouton et al., 2009a), but they are poorly documented in terms of their depositional environments. FD-FE are composed of black shales and sandstones associated with volcano-sedimentary deposits (Weber 1969 Gauthier-Lafaye and Weber 1989; Thiéblemont et al., 2014).

The first geochronological data have shown that the Francevillian group formed between c. 2100 and 2000 Ma (Ruffenach et al., 1976; Bros et al., 1992; Horie et al., 2005) but the youngest age reported on zircon from FA and FB around Ngoutou volcanic complex, is 2191± 13 Ma (Sawaki et al., 2016).

3 Manganese deposits in Franceville basin

Manganese deposits in the Franceville basin form a superficial layer that outcrops in several plateaux (Bagombe, Okouma, Bafoula, Menai-Oyali, Bordeau, Biniomi) at 600 meters altitude around Moanda, Franceville and Okonja cities (Weber 1969; Pambo 2004). Bagombe plateau is the most important deposits with 19 km² and 200 million of tones before exploitation. This deposit is still exploited by the COMILOG Company and constitutes the base of all studies done on the manganese in Franceville basin.

The synthetic log of the manganese profile described on the Bagombe plateau has five main horizons, including mineralized base layers topped by a humic horizon. This profile rests on the manganese hosted black shales (FB1) with manganese content varying between 5 and 30% (Weber 1969; Pambo 2004). These manganese black shales are considered to be the protore of the deposit. Several authors have shown that the mineralization of the Bagombe plateau is the result of the meteoric weathering process which has led the replacement of manganese carbonates (Mg, Ca, Mn)CO₃ by manganese oxide/hydroxide, on the manganese-rich black shales (Bouladon et al., 1965; Weber 1973; Nziengue Mapangou 1981; Beauvais 1984; Azzibrouck Azziley 1986; Pambo 2004).

4 The Manganese deposit of Bignomi plateau

The Bignomi manganese deposit is located in the southeast of Franceville city, in a landscape of a succession of hills varying sizes along West-East trend. Bignomi plateau is part of deposits acquired by the Nouvelle Gabon Mining Company which exploited the plateau since 2017.

4.1 Synthetic log of the Bignomi deposit

The studied profile is about 5 meters thick with lateral extension exceeding a hundred meters. It rests directly on the black shales attributed to the top of FB1 (Francevillian series). We have identified five horizons in Bignomi plateau (H1, H2, H3, H4, and H5). According to the data from the Company, manganese content in the profile ranges from 35% at the base of the profile (H1) to less than 10% at the top (H5).

**Massive horizon (H1)** is directly in contact with FB1 black shales. This horizon is mainly made up of a massive manganous layer (30-40% Mn). Massive layer evolves laterally toward complex forms including cavities, stalactites or lens concretions. **Platy horizon (H2)** overlies the massive horizon and is mainly composed of platy associated to clay with 25 to 30% Mn content. Careful analysis of this horizon showed that platyies are randomly distributed in the horizon and are affected by fractures which are filled or not by manganese oxides. **Transition horizon (H3)** rests on platy level. Its thickness varies between 0.1 and 0.5 meters. This horizon is formed by a mixture of pisoliths and platies. **Pisolith horizon (H4)** is mainly composed of pisoliths of variable sizes. The upper part of the horizon is constituted of massive blocks of pisolith aggregates. **Humic horizon (H5)** is made of soil rich in clays and sandstones including some pisoliths (<10% Mn), where vegetation develops.

4.2 Litho-geochemical description of the Massive horizon of Bignomi deposit

Detailed study of the massive horizon (H1) reveals that the ore is associated with varying sized cavities where Mn features as lenticular, botryoidal and stalactite shapes. Cavities are usually coated by manganese oxides. Small scale botryoidal bodies are associated with lens and stalactite shape in the cavities.

Two samples were respectively taken on stalactite shapes (Bi01) and crust covered cavities (Bi02). Those samples were analyzed by XRD, XRF and SEM mapping at the University of Tartu (Estonia). XRF shows that Bi01 and Bi02 samples are mainly made of Mn oxides ranging from 43 to 44 %. Manganese oxides are associated with several other oxides such as SiO₂ (5-8%), Al₂O₃ (7%), Fe₂O₃ (<1%). Other elements like Ca, K, Ti, P, S, occur as traces. These results demonstrate that the high grade manganese horizon is the massive horizon, which is different in Bagombe where the platy horizon holds the highest Mn content (Azzibrouck Azziley 1986; Pambo 2004). XRD reveals that material from massif Horizon (H1) consists of a mixture of different poorly crystalline Mn-oxhydroxides which were impossible to quantify. This result suggests that the massif horizon of Bignomi deposit can be considered as a recently precipitated material, they are either amorphous or too finely
crystalline to produce a discernible diffraction pattern via XRD (Zhang and Karathanasis 1997; Johnson et al., 2016).

SEM imaging was obtained on a polished cross section (2.5 cm wide) of a stalactite manganese concretion (Bi01 sample). As shown by Fig. 1a, this concretion consists of dark gray small scale concretions embedded in the light grey matrix. However, there is no significant distinction between concretions and matrix in terms of texture and composition (Fig. 1d, e). Texture is mainly porous with small cavities randomly distributed in the section (Fig. 1d, e). EDS element map shows a typical composition of Bi01 sample made of Mn, Al, Si and Fe which are distributed according to the texture. As shown in EDS element map (Fig.1), Mn and Al, the main phases, are abundant in the vicinity of pores and cavities. This particular distribution is probably the result of Mn and Al rich fluids circulation and subsequent precipitation within the pores and cavities (Zhang and Karathanasis 1997).

Massive Horizon (H1) also displays two fracture types which cut through the massive ore. They are completely filled by manganese oxide or not. When not completely sealed, the fractures sides are often covered by manganese oxides.

We therefore suggest that Mn enrichment of Massive horizon of Bignomi deposit is linked to the karstic and fracture system which allowed Mn-rich fluids to flow channels toward the lower horizons. That is shown by the occurrence of manganese oxides in fractures, cavities and pores.

Acknowledgements

We are grateful for manuscript comments and analytical support the University of Tartu all of those who has contributed in this study. We acknowledge Nouvelle Gabon Mining Company which allows us to work and sample in Bignomi open pit.

References


Parize, O., Feybesse, J.L., Guillocheau, F., Mulder, T., 2013. Were the 2.1-Gyr fos-sil colonial organisms discovered in the Francevillian Basin (Palaeoproterozoic, Gabon) buried by


Characterisation of the nonsulphide zinc ore at Huoshaoyun, Northwestern China, and its genetic aspects

Wenbin Jia, Fengyue Sun
College of Earth Science, Jilin University, China
Guangsheng Yan
China Geological Survey, Beijing, China

Abstract. The Huoshaoyun carbonate-hosted nonsulfide Zn deposit, in the Sanjiang-Tethys metallogenic belt of west China, is a newly discovered world-class deposit. Two ore bodies occur in the Longshan Formation limestone, in which the ore textures are mainly developed as laminated, banded, and brecciated. The metal minerals of the Huoshaoyun deposit are dominated by smithsonite and cerussite, with subordinate amounts of galena and siderite. Ore mineralization of this deposit is distinguished into three stages: sulfide stage, oxidation stage, and post-oxidation stage. Unlike most supergene Zn-Pb deposits, the Huoshaoyun orebody shows comparable ore grades for both Pb and Zn with an inverse supergene chemical zoning. Zinc is most abundant at the top of the deposit, whereas lead increases with depth. These two elements have different mobilities in solution, which implies that the primary source of zinc in the Huoshaoyun nonsulfide mineralization was originally located not far from the primary galena mineralization, the remnants of which are present in situ. Supergene zinc mineralization was derived from the dissolution of primary sphalerite hosted in the now-eroded rocks above the Huoshaoyun mine site. Zinc-rich solution migrated through the sedimentary host rocks, precipitated Zn minerals in pore spaces, and replaced detrital and hydrothermal alteration minerals.

1 Introduction

The Himalayan-Zagros orogenic system (Fig. 1), which formed by the India-Eurasia and Arabia-Eurasia collisions, is a classic example of a young and active continent–continent collisional orogenic system (Yin and Harrison 2003; Spurlin et al. 2005; Hou et al. 2011). The system hosts a world-class polymetallic metallogenic province that extends along strike for 10,000 km and includes some carbonate-hosted Pb-Zn deposits. Among them, clusters of Zn-Pb mineralization occurring in the Sanjiang-Tethys Belt of the Tibetan Plateau in China (Hou et al. 2008; Deng et al. 2014b; Deng and Lin 2015), and the Sanadaj-sirjan Zone in Iran (Rajabi et al. 2012; Mirnejad et al. 2011).

The Huoshaoyun is a newly discovered world-class Zn-Pb deposit located in the west Sanjiang Belt. The deposit (with more than 19.6 million tons of Zn+Pb at grades of 23.6% Zn and 5.6% Pb) (unpublished data) is the largest known and the only currently mined deposit in China (Dong et al. 2015). Moreover, Huoshaoyun is the first discovered nonsulfide deposit in China, and study of the nonsulfide Zn deposit is still a blank space in China.

![Figure 1. Sketch map of India- Ouya Block (a) and sketch tectonic map of the Tibetan collision belt and locations of the study zones (b). After Spurlin et al. (2005).](image)

2 Ore deposit geology

The Huoshaoyun deposit is situated in the southern part of the Tianshuihai basin, which lies in the west of the Sanjiang-Tethyan Metallogenic Belt. The Proterozoic metamorphic basement (Tianshuihai Group) consists mainly of metasandstone, phyllite intercalated with limestone, and unconformably overlain by Paleozoic strata. The Paleozoic and Mesozoic strata includes seven formations: Qiaoerti, Kongkashan, Heweitan, Keleqinghe, Longshan, Hongqilapu, and Tielongtan (Fig. 2). Mineralization is hosted by the Longshan Formation, which consists of bioclastic limestone and sandstone. The Longshan Formation includes four members: (1) the lower member consists of thick sandstone (~100 m thick), (2) the middle member hosting the ore-bodies, consists of micrite and bioclastic limestone (100~200 m thick), (3) the middle member consists of mudstone and argillaceous rocks (50~200 m thick), (4) the upper member containing metal mineralization, consists of limestone (20~300 m thick). All the mineralization occurred in the carbonatite and extended stably in the Huoshaoyun deposit area.

The fault structures in the area are simple. The NEE trending fault (F10, F11) and NWW trending fault (F6) are normal faults, which dislocated the ore bodies and strata (Fig 3). The ore-controlling regional structures in the mine area are the Qiaoertianshan fault, the Heweitan fault and their secondary faults (Fig. 3).


2.1 Ore body

According to the pattern of distribution and position, the ore bodies can be divided into two sections: no. II and III (Fig. 3). These two orebodies are developed nearly parallel, the average grade of Zn and Pb is 23.6% and 5.7%, respectively. No. II ore body is about 260 m long, 160 m wide, and located in the upper part of the fourth member of Longshan formation. The No. III ore body is the main mineralized layer, which is located in the second member of the Longshan formation. The ore body is about 2280 m long, 1400 m wide and 25~55 m high, which is controlled by the carbonate.

Orebodies in the Longshan Formation mainly occur as laminated, banded, and brecciated ores. The metal minerals of the Huoshaoyn deposit are dominated by smithsonite and cerussite, with subordinate amounts of galena and siderite. The gangue minerals comprise calcite, dolomite and gypsum. Due to the content of Fe and Mn, smithsonite of different colors, such as brown, reddish and light-brown, can appear in the same stratum and thin section. The cerussite is mainly white, with massive, layered and brecciated structure.

2.2 Mineralization stages

Based on the mineral paragenetic association of the deposit, three stages of hydrothermal mineralization are established (Fig. 4).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sulfide stage</th>
<th>Oxidation stage</th>
<th>Post-oxidation stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphalerite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smithsonite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anglesite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron oxides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cerussite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrozincite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sulfide stage: A number of metallic sulfides were developed in this stage, such as pyrite, galena, and
sphalerite (Fig. 5a). At present, galena is commonly rimmed by anglesite that contains abundant sub-size galena inclusions (Fig. 6a). Anglesite forms an armour around galena, protecting it from direct contact with oxidising reagents (Fig. 6b).

Oxidation stage: this stage is a subordinate economic stage characterized by breccia matrix composed of disseminated cerussite and minor smithsonite (Fig. 5b). Black cerussite contains abundant relics of galena (Fig. 5c). The smithsonite precipitates as massive botryoidal layers (Fig. 5d) or as a fine-crystalline matrix of carbonate breccia in the limestone host rocks (Fig. 6c and 6d).

Post-oxidation stage: the main economic stage, consisting of white cerussite, smithsonite, hydrozincite and anglesite. The purest nonsulphide zinc ore, locally referred to as “calamine”, has formed typically at the uppermost levels of the carbonate rocks by rhythmic replacement of cerussite and as joint fillings (Fig. 5e and 6e). In addition, some of the cerussite aggregated as the massive ore (Fig. 5f and 6f).

Figure 5. Photographs of the orebody in the Huoshaoyun deposit. (a) residual sulfide minerals after oxidation; (b) breccia matrix composed of disseminated cerussite and minor smithsonite; (c) black cerussite contains abundant relics of galena; (d) the smithsonite precipitates as massive botryoidal layers; (e) The nonsulphide zinc ore rhythmic replacement of cerussite and as joint fillings; (f) the massive ore consists of cerussite. Gn=galena, Sm=smithsonite, Cer=cerussite,Hdr=hydrozincite, Anl=anglesite.

During the oxidation and post-oxidation stages, oxidation, fractionation, and precipitation processes that formed the supergene nonsulphide ore, through a distinct progress of geochemical evolution. Moreover, the replacement textures between sulphide and non-sulphide ore at different scales, strongly suggest that the predominant mass of nonsulphide ore has been formed by in-situ oxidative leaching of the sulphide ore, multistage replacement and re-precipitation with weak metal fractionation or secondary zinc enrichment only.

Figure 6. Photomicrographs of representative metal minerals in the Huoshaoyun deposit. (a) the galena is commonly rimmed by anglesite that contains abundant sub-size galena inclusions; (b) banded smithsonite in the post-oxidation stage; (c) and (d) cerussite and smithsonite under transmitted and reflected light; (e) banded smithsonite developed in the margin of calcite, in a backscattered electron image; (f) residual galena granule in the center of a circle of cerussite after oxidation. Gn=galena, Sm=smithsonite, Cer=cerussite, Cal=calcite.

3 Possible genetic type

The Zn-Pb mineralization in the Huoshaoyun deposit occurred at 26.6 ± 1.7 Ma (unpublished data), suggesting that metallogenesis of the Huoshaoyun deposit directly relates to the India-Eurasia collision. The late collision between the Indian plate and Eurasian plate happened at about 40~25 Ma based on the magmatic zircon results from north Tibet (Chung et al. 1998; Hou et al. 2006; Zhai et al. 2009). Before the Zn-Pb mineralization at Huoshaoyun, the Trassic-Jurassic limestone strata thickened and folded due to the large-scale regional thrusting. This not only provided favourable lithological and structural traps for fluids, but drove basin brines carrying ore-forming metals over a long distance. Therefore, the late Paleogene was a significant period for carbonate-hosted deposits. Such as Jinding deposit (Deng et al. 2017, Leach et al. 2016), Mohallaheng deposit (Liu et al. 2015, Liu et al. 2011), Duocaima deposit (Song et al. 2015), and this period is marked by a series of continental collisional events (Yin and Harrison, 2003; Deng et al., 2014a, 2014b).

Because there is no apparent genetic association with igneous activities, we classify the Huoshaoyun Zn-Pb deposit as a sediment-hosted Pb–Zn deposit. The Huoshaoyun deposit shows some syngenetic
characteristics that are typical of MVT deposits, e.g. host rock, mineralogy, alteration, deposit morphology, ore textures, temperature (Leach et al. 2005), although the Huoshaoyun deposit occurs in a compressional fold and thrust belt associated with the Tibetan plateau orogen, which is an unusual tectonic setting for MVT deposits (Liu et al. 2011). Different from other MVT Pb-Zn deposits in China, the geotectonic setting within the overriding plate of the active convergent plate of Tibet provided long term uplift, erosion, rapid exhumation of the sulphide protore, and exposure to oxygenated surface waters (Daliran and Borg 2005). And paleoclimatic conditions prevented the nonsulphide solutions from being flushed out of the system. Oxidation processes may have been additionally promoted by a regional high heat flow due to the young geothermal activities. Smithsonite and cerussite were probably formed by mixing of the CO$_2$ rich meteoric waters with the hydrothermal fluids. In all, we conclude that the Huoshaoyun deposit is a MVT deposit, which is a new discovered nonsulfide type in China.

Acknowledgements

This study was jointly supported by the National Key R & D Program of China (Grant No. 2018YFC0603704) and the Geological Survey Project of the China Geological Survey (DD20160050).

References


884 Life with Ore Deposits on Earth – 15th SGA Biennial Meeting 2019, Volume 2
Mineralogy and geochemistry of black beach sands along the coastline of Milos and SW Kimolos Islands, Greece

Marianthi Anastasatou, Michael Stamatakis
National and Kapodistrian University of Athens, Greece

Aristomenis Karageorgis
Hellenic Centre for Marine Research, Greece

Abstract. ‘Heavy-mineral sands’ are deposits of heavy minerals hosted by sediments of sand, silt and clay in coastal environments. Their formation begins inland and these sands are deposited through various physico-mechanical processes in the coastal environment. Heavy-mineral sand can be of high economic importance as they include valuable metals. Twenty-six samples were collected along the entire coastline of Milos Island and one sample from Kimolos Island Samples were analyzed for their mineralogical composition and also trace element analysis was performed (PXRD, SEM/EDS and XRF). Most of the samples studied indicate their origin as weathering products of mainly volcanic rocks, barite and polymetallic deposits. Among the samples, several are significantly enriched in titanomagnetite, ilmenite and barite. Moreover, the geochemical analysis revealed that samples from the coastal areas of Milos Gulf, Triades (west Milos Island) and Ellinika (SW Kimolos Island) are enriched in elements such as Ag, As, Mn, Pb, Sr, Zr, V, W and REE.

1 Introduction

The term ‘heavy-mineral sands’ is commonly referred to deposits of heavy minerals hosted by sediments of sand, silt and clay in coastal environments (Van Gosen et al. 2014). Heavy sands are deposited and redistributed through multiple physico-mechanical processes in various environments, such as deltas, the beach face, offshore, dunes, barrier islands and tidal lagoons (Cronan 2003). Igneous and metamorphic rocks are a significant source of the heavy minerals that are deposited in coastal environments and often contain ilmenite, rutile, zircon, garnet, monazite and kyanite (Van Gosen et al. 2014).

The coastline of the Mediterranean Sea is rich in heavy-mineral sands of volcanic origin, where several volcanoes are still active (Braccini et al. 2018). In the case of Greece, a few studies exist regarding heavy-mineral coastal sands. These studies focus on the following areas: the coastal area of Kavala (Ioakeim 2016), Sithonia Peninsula at Chalkidiki (Papadopoulos et al., 2015), Touzla Cape near Thessaloniki (Fillipidis et al. 1997), Nisyros Island (Tzifas et al. 2017) and selected islands of the Atticocycladic zone (Papadopoulos 2018). However, the economic importance of the Greek heavy-mineral coastal sands is unevenly studied.

For the first time, heavy mineral sands are identified along the entire coastline of a Greek island. Mineralogical analysis of some of the beach sands of Milos was recently implemented by Kotschenreuther (2018). The aim of the present study is to investigate and evaluate the mineralogical and geochemical composition of heavy-mineral coastal sands along the coastline of Milos Island and the nearby SW Kimolos Island coast, Greece. In addition, the study makes an attempt to identify the origin of specific heavy minerals and element enrichments in each particular case studied.

2 Geological setting of Milos Island

Milos Island along with the neighbouring islands of Kimolos and Poliegos belongs to the central part of the active volcanic arc of the Aegean Sea, which has an age of Middle Pliocene to Recent (Hoffman and Keller 1979, Fytikas et al. 1986). Milos Island mainly hosts volcanic lavas and tuffs which cover most of its surface. Upper Miocene sedimentary rocks occur in the south part of the island, whereas there is only limited exposure of the metamorphic basement rocks, mainly in the SE part of the island (Hoffman and Keller 1979; Fytikas et al. 1986; Valsami-Jones et al. 2005).

Milos is comprised mainly of Late Pliocene and Pleistocene volcanic, pyroclastic and volcanoclastic rocks of dacitic, andesitic and rhyolitic composition (Fytikas et al. 1986; Hein et al. 2000) (Fig. 1). The island hosts a wide range of mineral deposits some of which were mined in the past, including Pb-Zn sulphides, Mn oxides, epithermal gold, barite, alunite, sulphur, diatomite, kaolin, zeolite tuff, obsidian, whereas current mining activity is on bentonite, perlite, pozzolanic tuffs, and silica (Stamatakis et al 1996; Hein et al. 2000). Kimolos Island also hosts industrial minerals, some of which are currently exploited, whereas there are ancient and old mining activities for the extraction of mixed sulfides and silver (e.g. Lykakis and Kilias 2010).
3 Materials and methods

3.1 Sampling
Twenty-six representative beach (subaerial) samples of black sand were collected manually along the entire coastline of Milos Island, as shown in Fig. 2. One representative beach (subaerial) sample of black sand (ELL 1) was collected from the SW part of Kimolos Island (Fig. 2) as it was detected in the past that, similar to Milos, black sands occur there and the island is part of the Milos-Kimolos-Poliegos volcanic island complex (Tsokas et al. 1995).

The samples were collected from a specific black horizon, extracted from the upper 20cm layer (Figs 3 and 4).

3.2 Analytical methods
Mineralogical analysis was carried out using a powder X-Ray Diffractometer (PXRD) of Siemens D 5005 type, with copper tube and graphite monochromatographe, in combination with the DIFFRACplus software package at the laboratories of the Department of Economic Geology and Geochemistry (DEGG), Faculty of Geology and Geoenvironment (FGG), National and Kapodistrian University of Athens (NKUA). In addition, representative samples were examined under a JEOL JSM-5600 Scanning Electron Microscope (SEM) equipped with a backscatter electron detector (BSE) combined with a microanalyzer Energy Dispersive System (EDS) OXFORD LINK ISIS 300, with ZAF correction quantitative analysis software at the laboratories of DEGG, FGG, NKUA. The system was operated at 20KV, 0.5nA and 50sec dead time.

Trace elements (i.e. Ag, As, Ba, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, Ga, Ge, Hf, Hg, I, La, Mn, Mo, Nb, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Te, Th, Ti, U, V, W, Y, Yb,
Zn, Zr) as well as, CaO, Fe₂O₃ and TiO₂ were measured with the X-Ray Fluorescence (XRF) method. XRF analysis was performed in a Philips PW-2400 X-ray wavelength spectrometer in pressed powder pellets at the Hellenic Centre for Marine Research (HCMR).

All samples were homogenized, dried and all coarse impurities (sea shells, seagrass etc.) were removed.

4 Results and discussion

Field observations indicate a diverse degree of enrichment in each beach and even in the same beach there are irregular spots of heavy mineral concentrations. It has been detected that in coastal areas (e.g. Ellinika on Kimolos Island), the enrichment is temporal/seasonal and the initial deposition follows the current coastline. Moreover, despite the complex path of sediment transport, it is documented that ilmenite is carried from a host rock for long distances (tens of kilometres) by fluvial transport (Van Gosen et al. 2014).

Qualitative mineralogical analysis (PXRD) was carried out for all twenty-seven samples and the results of the bulk samples are shown in Table 1.

Table 1. Qualitative mineralogical composition of selected black beach sands samples from Milos and Kimolos Islands.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TR1</th>
<th>FYR1</th>
<th>ADA2</th>
<th>ACH4</th>
<th>ELL1</th>
<th>EMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pl</td>
<td>MJD</td>
<td>MD</td>
<td>TR</td>
<td>MD</td>
<td>MD</td>
<td>n.d.</td>
</tr>
<tr>
<td>Mag</td>
<td>MD</td>
<td>MD</td>
<td>MJ</td>
<td>MJ</td>
<td>MJ</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ilm</td>
<td>n.d.</td>
<td>TR</td>
<td>n.d.</td>
<td>TR</td>
<td>n.d.</td>
<td>MJ</td>
</tr>
<tr>
<td>Brt</td>
<td>TR</td>
<td>MD</td>
<td>n.d.</td>
<td>MD</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>MgHbl</td>
<td>MJ</td>
<td>n.d.</td>
<td>MD</td>
<td>n.d.</td>
<td>MD</td>
<td>n.d.</td>
</tr>
<tr>
<td>Dol</td>
<td>MD</td>
<td>MD</td>
<td>TR</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ill</td>
<td>TR</td>
<td>TR</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>


Magnetite and quartz were identified as major minerals in most of the samples (e.g. Fig. 5b). Plagioclase revealed as crystalline phase of medium content (Table 1). Ilmenite and hematite occur mostly as accessory minerals. Sample EMP is enriched in magnetite, ilmenite, barite and magnesio-hornblende, as any other mineralogical phases are absent (e.g. Fig. 6a,b). Magnesio-hornblende appears as a medium to major crystalline phase at the samples from Triades are and Milos Gulf (TRI and ADA). Barite is detected in some areas, such as Triades and Milos Gulf. Clay minerals are almost absent in most of the samples. Olsson and Kärland (2009) identified discrete heavy mineral particles, such as Ti-bearing minerals (e.g. rutile) and Fe-bearing minerals (e.g. magnetite and hematite/maghemite) in bentonite tuffs at the NE part of Milos Island. Samples with enriched presence of ilmenite, magnetite and hematite (e.g. Adamas) are correlated with enrichment in REE (e.g. Fig. 5b). This fact according to Moustafa et al. (2011) and Olsson and Kärland (2009) indicate their volcanic origin.

SEM/EDS analysis indicates the presence of barite (Fig. 5a) and Sr-rich barite (Fig. 6b). According to Marschik et al. (2010), the Sr signature of barite in the wider Triades area is suggestive of a seawater hydrothermal system and fluid/rock interaction (Fig. 6b). The enrichment of As, Ag, Pb, Sb, Te and REE content (i.e. Adamas and Triades area) are indicative of such an association. Moreover, barite is present in kaolin deposits, which are widespread on Milos Island. Triades area’s samples are located at western part of Milos Island and present a high content of Ba (~ 8%) and As (~ 825ppm). Interestingly, Pb and Zn show a degree of enrichment, but not the highest values among the studied black sands. In Triades area, Pb - Zn - Ba (Ag – Au) mineralization is hosted in pyroclastic rocks (Marschik et al. 2010). Sample ELL1 from Kimolos Island presents enrichment in Sn, Pb, Zn, related to the presence of polymetallic type of deposit. According to Hauk (1988), in the Unit of Milos-Kimolos-Polyegos exist Kuroko type polymetallic deposits, which are countered as the youngest (Plio-Pleistocene) worldwide. In general, Kuroko-type deposits are strata-bound polymetallic sulfide-sulfate deposits, genetically related to felsic volcanism in island arc systems (Sato 1977; Sawkins 1984). The samples KYR, AGS and KAN, which were collected from the beaches Agia Kyriaki, Agios Sostis and Kanavas, respectively show the highest content of chromium. At these beaches, the basement rock is mainly Mesozoic schists.

Figure 5. SEM microphotographs of ADA2 black sand sample from Milos Isl. with EDS data. a) barite (Brt) crystal (BaSO₄) and b) titanomagnetite crystal with monazite-(Ce) [Mnz – (Ce)] inclusions.

Figure 6. SEM microphotographs of EMP black sand sample from Milos Island along with EDS data. a) ilmenite (Ilm) grain with halite (Hl) crystals and b) strontian barite (Sr - Brt) crystal.

Inside Milos Gulf, samples present significant enrichment in TiO₂, Fe₂O₃, Mn and V. According to Karageorgis et al. (1998), chemical analysis of underwater sediments from Milos Gulf similarly show high values for Mn, Pb, Zn, Cr, and Sr. Especially, sample
ADA2 (Adamas) exhibits higher levels of As, Ba and LREE, such as La, Ce and Nd. Achivaldolimni (Milos Gulf) sample ACH4 presents high Mo relative to other samples. Mo presence is related to apatite as SEM/EDS microanalysis reveals (Mo-rich apatite). Samples ACH3 and ACH4 exhibit high Zr, Mo, W, Hf and Ga values, indicative of the presence of higher temperature metallic deposits in that part of the island.

5 Conclusions

The majority of the studied samples are the weathering products of the nearby volcanism. The black sands chemistry is controlled by their mineralogical composition. Barite is associated with and without Sr. Feldspar, quartz, carbonates, and clay minerals are of various origins, such as Neogene sediments, lahar, volcanic and metamorphic rocks. Iron is not exclusively associated with Ti, as titanium occurs in various percentages within magnetite, but also forms ilmenite. REE content is also related to volcanism. Coastal sands with adjacent hinterland composed of metamorphic rocks present a lower heavy mineral content, while samples inside Milos Gulf, Triades area (west Milos Island) and Ellinika (SW Kimolos Island) present an enriched heavy mineral content and are promising for further exploration. Differences in heavy mineral content among the same deposits in that part of the island.

Acknowledgements

The authors would like to thank Mr Chris Branse, MSc, Nurnberg-Erlangen University, for his assistance regarding sampling and photos on site after the guidance of Prof. M. Stamatakis. Thanks are also expressed to Mr Vasilis Skounakis, NKUA, for helping with SEM/EDS analysis.

References


Characterization and origin of the industrial minerals and rocks of NE Kimolos Island, Aegean Sea, Greece

Michael Stamatakis, Marianth Anastasatou, George Tselepis
National & Kapodistrian University of Athens, Greece

George Kotsis
Bentomite SA, Greece

Abstract. In the northeast of Kimolos Island, zeolitic tuffs occur as the underlying formation to a white bentonite deposit that is dipping at an angle of 30° towards the NE. Off-white pumiceous tuffs are developed as a thick cover of the bentonite deposit. The aim of the present research is to characterize these industrial rocks, and to define their genetic relationship. Representative bulk samples were examined by XRD, XRF and SEM techniques. Three major rock type zones were defined, the mordenite tuff, the bentonite, and the pumice tuff. The predominant mineral phases in the zeolite tuff are mordenite, opal-CT (a poorly crystalline silica polymorph), and feldspars, whereas smectite phases predominate in bentonite, and volcanic glass in the pumice tuff. Clinoptilolite occurs only in the bentonite, whereas barite randomly occurs in all zones. All samples are poor in trace elements, except of barium, whereas bentonite shows the highest content of magnesium. Transition zones between mordenite tuff-bentonite and bentonite-pumice tuff were identified. The irregular development of the mordenite zone and the irregular variation of mordenite/smectite content within it, suggest a diagenetic origin dominated by high-heat flow and hot spots. Bentonite was probably formed at a late stage, at the expense of the unaltered pumiceous tuff.

1 Introduction

Significant deposits of bentonite, zeolite tuff, pozzolans and perlite occur on the island of Kimolos, central Aegean Sea. Several models and theories for the genesis of bentonites and zeolite tuffs have been presented on a global scale, some of which suggest a genetic relationship between them (Christidis et al. 1995; Hay 1987; Hay and Sheppard 2001; Pe-Piper and Tsolis-Katagas 1991; Stamatakis 1989; Stamatakis et al. 1996; Utada 2001). The aim of the present research is to characterize the bentonite, zeolite tuff and glassy tuff which coexist in Prassa area, NE Kimolos, and to define their origin and genetic relationship. In total, 24 bulk samples were extracted and analysed by XRD, SEM and XRF techniques.

2 Geological setting

Kimolos along with Milos and Poliegos islands comprises a unit within the South Aegean Volcanic Arc. The volcanic activity in the unit can be divided into two main periods (Fytikas and Vougioukalakis 1992, Francalanci et al. 2007). Basaltic to rhyolitic pyroclastic deposits and pyroclastic rocks were erupted during the 1st period, whereas rhyolitic pyroclastic deposits and perlite lava domes characterize the 2nd period (Francalanci et al. 2007). The rock composition belongs to the calc-alkaline and high-K calc-alkaline series. In the NE part of Kimolos Island, in the Prassa area, greenish zeolitic tuffs are located as underlying rocks south-southwest of a white bentonite deposit that is dipping with an angle of 30° towards the NE, oriented in a NW-SE general direction. Towards the bentonite deposit, the zeolite tuffs are turning to white in colour, via an interval of irregular mixing of white and greenish tuff bodies. Off-white pumiceous tuffs partially cover the bentonite deposit. The glassy tuff retains its original pumiceous nature, whereas the bentonite and zeolite tuffs are fine-grained and homogenous. South of Prassa active bentonite quarry, off-white bentonite also occurs, having loose lapilli tuffs as overburden. This bentonite deposit was exploited before 1965 [Bouras Quarry], whereas borehole data in the area of Prassa reveal the presence of more bentonite bodies, covered by glassy tuffs, having thickness ranging from 25 to 55m (Kanaris 1993). The succession of the zeolitized tuffs, the white bentonite and the white glassy pumiceous tuffs belong as an undivided formation to the Prassa Ignimbrite or Prassa Tuff, which has an age of 2.0-1.7 M.a. (Fytikas and Vougioukalakis 1993; Lykakis and Kiliaris 2010).

3 Fieldwork and rock sampling

Even though there have been a series of publications on the bentonite and zeolite tuffs of Kimolos and neighbouring islands, there is as yet no complete model for the formation of these industrial minerals and rocks, and their relationship with the almost unaltered glassy tuff which overlies the bentonite deposit (Marcopoulos and Christidis 1989; Francalanci 1997; Godelitsas et al. 2010; Kanaris 1993). To identify the relationship in between the zeolite tuffs, bentonite, glassy pumiceous tuff and the dark volcanic breccio-conglomerate, as well as the neighbouring geological formations, a total of 20 samples were obtained from these raw materials, as well as 2 samples from the neighbouring bentonite deposit of Bouras Quarry and 2 more from the neighbouring tuffaceous formations of Vromolimni and Monastiria (Fig. 1). Intense active tectonics is present in the Prassa area, as documented by Louis et al (2003) and Francalanci et al. 2007. The significant dip of the currently mined bentonite towards the NE, contrary to the other bentonite deposits in the Prassa area (see Kanaris 1993), is due to
neotectonic faults.

**Figure 1.** a. Geological map and b. sampling sites in the Prassa area, NE Kimolos (Lykakis and Kilias 2010). PT: Prassa Tuff/Rhyolitic pumice flow units with ground and ash cloud surges, GL: Geronikola Lavas/Basaltic-andesitic lava flows and scoriae fall deposits, VT: Vromolimni Tuffs/Shallow marine pumice flow deposits, PT2: Prassa Tuff reworked/Epiclastics.

4 Analytical techniques

Twenty-four bulk rock samples of 5kg each were milled to <100μm using an agate mill. They were mineralogically and chemically analysed by XRD and XRF techniques. Textural examinations and microanalyses were performed by SEM/EDS.

5 Results

The XRD analysis suggests that the volcanic succession of the Prassa Ignimbrite can be subdivided at a macro-scale into three distinct zones: i) the zeolite tuff zone, ii) the bentonite zone and iii) the glassy tuff zone. The zeolite zone is mainly composed of mordenite, opal-CT and high sanidine, the bentonite zone is almost exclusively composed of smectitic clays, and the glassy zone is mostly composed of volcanic glass. The zeolite zone is the most irregular one, as white smectite-rich irregular patches of some meters occur within the greenish mordenite tuff, whereas mordenite was detected in traces, even in the glassy zone. Clinoptilolite occurs in trace amounts in the bentonite and in the transition zone of bentonite to glassy zone. It was noticed that there exist two transition zones, one in between zeolite tuff and bentonite, and another in between bentonite and volcanic glass. In the transition zones, mixture mineral phases occur. Southwards, the bentonite of Bouras Quarry contains higher amounts of clinoptilolite, compared with Prassa Quarry, but not mordenite. In Bouras Quarry, the glassy tuff has been eroded and the bentonite overburden is mostly loose volcanic sand and gravel. The tuff samples collected from the neighbouring areas of Vromolimni and Monastiria (Fig. 1) belong to other Prassa Ignimbrite formations and are free of authigenic silicates.

Under the SEM, the zeolitized tuffs are mainly composed of cryptocrystalline groundmass and only locally occur in fissures and pores, curved hair-like mordenite crystal assemblages formed, with opal-CT lepispheres (Fig. 2). Successive deposition of mordenite mineral assemblages, directly replacing volcanic glass is common. It is suggested that most of mordenite was formed by a solid-solid inversion mechanism of the volcanic glass. Euhedral authigenic K-feldspar crystals, indicative of the existence of high heat flow rates during the formation of authigenic aluminosilicates and silica polymorphs, were detected in the zeolite zone, sometimes replacing early formed mordenite and/or plagioclase (Fig. 3).

The bentonite beds are composed of massively stacked montmorillonite flakes (Fig. 4). In addition, another zeolite, clinoptilolite was detected in euhedral mineral assemblages in the bentonite zone and the transition zone of bentonite to volcanic glass of Prassa and the Bouras quarries. Interestingly, some of clinoptilolite was formed at the expense of a mordenite precursor (Fig. 5a). It is known that clinoptilolite is formed at lower temperatures than mordenite in hydrothermal systems (Pe-Piper and Tsolis-Katagas 1991; Tsolis-Katagas and Katagas 1989). The general trend of the clinoptilolite crystal growth is as a late stage deposition, developed above mordenite aggregates in the intermediate zone of bentonite to volcanic glass. Silicified worm-like trace fossils and microbial assemblages occur in bentonite, in both Prassa and Bouras Quarry (Fig.6a,b). Samples from the glass zone are composed almost exclusively of vesicular volcanic glass particles (Fig. 5b).

Chemical analysis revealed that the succession studied is poor in trace elements, except of barium, whereas EDS microanalysis showed that smectites are rich in MgO, and mordenite and feldspars are rich in K2O.
6 Diagenetic implications

In the west of Kimolos Island, diagenetic alteration of volcanic glass to zeolites has been found in porous clinoptilolite tuffs and hard massive mordenite tuffs (Fragoulis et al. 1997). In the NE of Kimolos, according to the recent findings on the distribution of authigenic silicates in the field, the laboratory results and literature data, we conclude that in the Prassa area, an original pumiceous glassy tuff belonging to Prassa ignimbrite formation, was partially and irregularly transformed to K-rich mordenite, K-feldspar-bearing tuff, under high heat flow rates, originated from multiple hot spots. Louis et al. (2003) (Fig. 7) had already detected in south Prassa a field of high heat flow rates, with multiple centres which were assumed to have been more intense during late Pliocene-Pleistocene volcanism. At a later stage, part of the unaltered pumice tuff, but also part of the mordenite tuff were transformed to smectite clays, opal-CT and clinoptilolite, under different pore fluid chemistry which was Mg- and Na-dominated, and under lower temperature conditions. Vesicular volcanic glass shards sometimes occur in the bentonite zone and scantly in the mordenite zone, indicating a common pumice tuff precursor.

The diagenetic reactions took place in an open hydrological system by the action of alkaline groundwater, under conditions of high and moderate heat flow rates. Measurements and observations during mining operations and drillings in Bouras Quarry revealed the existence of upwelling warm water with temperatures of 35°C at the surface, and 52°C at 50m depth (Louis et al. 2003). The same authors suggest that there was a very significant geothermal anomaly in the past. The intense tectonism in the area promoted the circulation of hot groundwater, especially close to the fractured surfaces. This model explains the diverse content of the authigenic minerals in the mordenite zone, even in samples that were collected less than 1m from one another. It is assumed that the fluids responsible for mordenite formation were probably higher temperature than those of clinoptilolite due to high heat flow rates originating from the emplacement of lavas in their vicinity. The presence of trace fossils within the tuffs is a new finding and suggests a specific fluid composition and temperature during deposition and early diagenesis. Clinoptilolite is more abundant in the southern outcrops of bentonites (Bouras Quarry), even though the transformation of the volcanic glass to smectite clays is immature and mordenite and authigenic K-feldspar are absent. It is concluded, therefore, that the Prassa ignimbrite was influenced by fluids of diverse chemistry and temperature, most likely in repeated periods since the Upper Pliocene. The presence of multiple hot spots is proved by the irregular development of mainly the zeolite, the hottest zone, and subsequently the bentonite zone which varies in size and shape.
Figure 5. SEM microphotograph of (a) euhedral clinoptilolite blade crystals replacing early formed mordenite in bentonitic groundmass /transition zone of bentonite to glassy tuff and (b) unaltered volcanic glass shard, developed in the glassy tuff zone.

Figure 6. SEM microphotograph of (a) silicified trace fossils developed in the bentonite zone and (b) silicified worm-like trace fossils developed in the bentonite zone.

Figure 7. Heat flow rates in the south Prassa area (after Louis et al. 2003).

Acknowledgements

The authors would like to thank Mr. Vasilis Skounakis, NKUA, for helping in the SEM/EDS analysis.

References


Constraints on gem opal formation: a case study of Ethiopian opals

Boris Chauviré
ISTerre (UMR-CNRS 5275), Université Grenoble Alpes, Grenoble, France

Benjamin Rondeau
Laboratoire de Planétologie et Géodynamique (UMR-CNRS 6112), Université de Nantes, France

Abstract. Unlike other gems like diamond and corundum, opal is not forged in the heat and pressure of the earth, but at the surface. Composed of silica, which is by far the most abundant constituent in the earth’s crust (and other terrestrial planets), the opal’s specific microstructure is the origin of its striking beauty. The alteration of silicate by aqueous fluid releases the constituting silica, which is then transported by fluids until physical or chemical changes induce the precipitation into opal. Identifying the exact source of silica and the physical and chemical conditions required for gem opal formation remains challenging. Using the case of Wegel Tena, we demonstrate how to identify the process involved in gem opal formation. Petrological examination of opal host-rocks provides significant hints to understand the context for opal precipitation. Geochemical signatures of opal inform on the silica source and chemical conditions during fluid transportation. An improved genetic classification of gem opal is also proposed.

1 Introduction

Opal is the hydrated amorphous variety of silica formed from the precipitation of silica-supersaturated fluids. Two types of opal have been categorized according to their atomic structure using X-ray diffraction: opal-A is purely amorphous silica whereas opal-CT is poorly crystallized, (disordered cristobalite and tridymite; Jones and Segnit 1971; Elzea and Rice 1996). Both types of opal can be gems. Among gem opals, precious opal displays a play of colour, an optical phenomenon exhibiting patches of pure spectral colours moving over the stone, whereas common opal does not. The regular arrangement of silica spheroidal units of 150-300 nm in diameter is responsible for this play-of-colour (Sanders 1964; Darragh and Sanders 1965).

On Earth, opal forms in various geological environments: deep-ocean to lacustrine sediments (Murata and Randall 1975; Hein et al. 1978; Rice et al. 1995), geothermal sites (Jones and Renaut 2003), weathering profiles (Thiry and Milnes 2017) and volcanic to volcano-sedimentary host-rocks (Berlo et al. 2018). In all cases, opal formation is due to water circulation that alters silicates constituting the crust releasing silica in the fluid. A change in the chemical and/or physical condition will trigger the silica precipitation into opal. Three distinct processes for opal genesis have been identified: biological precipitation, continental weathering, and hydrothermal activity. Even if microorganisms (e.g. diatoms and radiolarians) are the main opal producers on Earth (DeMaster 2014), no gem opal has been documented to form through biological precipitation. Gem opals are thus associated with either hydrothermal activity or continental weathering. The main challenge of gem opal geology is to identify which of these two processes is involved.

The aim of this paper is to show how petrological examination and geochemical investigation provide significant information for reconstituting the geological history of gem opal formation.

2 Petrology of opal deposits

Precious opal deposits are known all over the world but remain scarce. Australian opals are found in Cretaceous sandstones and shales (Senior et al. 1977; Dutkiewicz et al. 2015). Opal is embedded in volcano-sedimentary rocks in Slovakia (Rondeau et al. 2004), Indonesia (Sujatmiko et al. 2005), Mexico (Gaillou 2006), or at the interface between sedimentary and magmatic intrusions in Brazil (Bartoli et al. 1990). In these deposits, the process responsible for gem opal formation (hydrothermal activity or continental weathering) is not always clear. Here, we focus on the petrological features specific to the Wegel Tena Ethiopian deposit as an efficient example to identify the genesis process.

2.1 Wegel Tena deposit (Ethiopia)

The Wegel Tena deposit was discovered in 2008 in the Oligocene volcanic traps in the North of Ethiopia (Rondeau et al. 2009). Gem opal is extracted from horizons hundreds of metres wide and tens of metres thick, stratigraphically conforming to the rhyolitic ignimbrite sequence (Rondeau et al. 2012; Chauviré et al. 2017a). Opal-bearing horizons are highly weathered compared to sterile ignimbrite. These field observations indicate a formation by weathering occurring between the depositions of volcanic rocks.

A petrographic examination reveals a microgranular microstructure cemented by opal, with granules composed by clays, and illuvial clays coating the opal-filled porosity (figure 1; Chauviré et al. 2017a). These features are typical of pedogenesis, that develops when rhyolitic rocks are exposed to meteoric water that alter the constituting minerals (especially glass and feldspar) releasing a large amount of silica. Chauviré et al. (2017a) proposed that isolation of the weathered layer by the
deposition of the following ignimbrite might trigger the precipitation of gem opal. However, weathering of volcanoclastics is a very common process on Earth. It commonly generates precipitation of common opal and very rarely precious opal, although the geological context does not display obvious, specific characters for precious opal deposits. One critical observation is that precious opal nodules or masses are often found in the immediate vicinity of masses of common opal, or empty cavities, at the centimetre scale. Therefore, the specific conditions required for precious opal genesis are encountered altogether in a given cavity when missing in the neighbouring cavities filled by common opal. Such local variations may be induced by poorly circulating underground waters, separating evolution of neighbouring cavities in terms of chemical and physical conditions for silica spheres growth and precipitation. Regional conditions enhancing local variations of confinement at the centimetre to meter scale may be key for gem opal to form in general.

3 Geochemistry of opal

Minor and trace elements can be used to trace the source of silica and the chemical conditions of opal precipitation. Geochemistry of opal has been intensively investigated on Australian opal (Brown et al. 2004; Dutkiewicz et al. 2015), demonstrating that silica originates from the weathering of sedimentary and volcanic rocks. The global study of Gaillou et al. (2008) has shown strong variations in the geochemical signature of opal, each reflecting the composition of its host-rock.

3.1 Minor and trace elements

Wegel Tena opals exhibit a clear correlation between Ba, Sr and Eu (figure 2; Chauviré et al. 2019), which are the typical substituting elements in feldspar (Icenhower and London 1996). Therefore, even if volcanic glass is one the main silica provider during the weathering of volcanic rocks (Gislason et al. 1996), feldspar may have participated in the silica-enrichment of the fluid. Moreover, two samples are much enriched in minor and trace elements, suggesting a higher degree of weathering. Trace element composition is strongly variable from one sample to another in the deposit, consistent with the assumption of a local environment specific for each opal.

REE patterns of Ethiopian opal provide information for the source of silica. In volcanic rocks, Eu anomaly is usually due to the feldspar fractionation during magmatic differentiation, explaining the negative Eu anomaly of Wegel Tena ignimbrite (Ayalew et al. 2002). We proposed that positive Eu anomaly measured in opal is due to a preferential weathering of feldspar compared to glass. The Ce anomaly, commonly related to variations in redox conditions (Braun et al. 1990), is observed in opal. Ce may be used as a proxy for chemical conditions during the fluid transportation. The high variability of geochemical signature in Wegel Tena opals suggests that source of silica and conditions of precipitation strongly vary from a cavity to another, underlying the role of local confinement in the formation of precious opal.

3.2 Oxygen isotope

Oxygen isotope in silica is a powerful tool to trace the forming fluid and/or the temperature of formation. Silica precipitating at high temperature have a lower δ¹⁸OSMOW (from 3 to 23 ‰) than silica forming at low-temperature (from 25 to 32 ‰: Sharp et al. 2016 and references therein). In the case of Wegel Tena opals, the δ¹⁸OSMOW ranges from 26.5 to 31‰ (Chauviré et al. 2019). Isotopic measurement can be used to calculate the temperature of precipitation of opal, by assuming the isotopic composition of the forming fluid. The hypothesis most consistent with paleoecological studies (e.g. Abbate et al.
Supergenes, gems and non-metallic ores 895

2014) suggest that Wegel Tena opals precipitated between 18 and 21 °C, an ambient temperature in agreement with the pedogenetic model.

4 Toward a genetic classification

In the literature, especially in the gemological literature, many studies distinguish between “sedimentary opal” and “volcanic opal” (i.e. Smallwood et al. 2008; Dutkiewicz et al. 2015) with reference to the nature of the host-rock. Indeed, many gem opal deposits are hosted in sedimentary and volcanic rocks (e.g. respectively in Australia and Mexico). However, many others are hosted in volcano-sedimentary rocks, which makes uncomfortable the distinction between “sedimentary” and “volcanic” opals. More importantly, one could extrapolate that opal in sedimentary rocks are formed by weathering and volcanic opal related to hydrothermal activity. However, several cases demonstrate that this assumption is not correct: Coenraads and Zenil (2006) show that precious opal in fresh basalt formed through continental weathering of overlaying volcanoclastics, and the similar case of Tirtriya Mine in Ethiopia (Chauviré et al. 2017a).

To avoid any confusion, we propose to use the terms "hydrothermal opal" and "weathering opal", which are the basis of a genetic classification. A careful examination of the petrography and geochemical signatures is required to characterize precisely the process of genesis. In the case of the Wegel Tena deposit, petrological examination of the opal deposit, petrological features point toward a pedogenetic origin, and oxygen isotopes point toward low temperatures of precipitation. All this lead to ascribe a pedogenetic origin to these opals, a process belonging to the wider family of continental weathering processes.

5 Perspective: water configuration

Opal contains up to 15 wt. % of water (Adams et al. 1991). Water occurs in two main species: molecular water that can be trapped in the porosity or adsorbed at the silica surface, and hydroxyl groups attached to silicon atom (silanols). Both species and their possible configurations can be discriminated by near infrared spectroscopy (Langer et al. 1974). Recently, Chauviré et al. (2017b) has demonstrated that hydrothermal opal and weathering opal differ by the shape of near infrared absorption bands (figure 3). A geometrical criterion, called CRC (for Concavity Ratio Criterion), has been created to quantify the shape difference and efficiently discriminate hydrothermal and weathering opal.

The water configuration has recorded the chemical and/or physical conditions of opal precipitation. However, the exact control of the geology in this variation (temperature, pH) remains unknown.

6 Conclusion

Opal is one of the rare gem minerals that forms very close to the surface, enabling to record specific supergene conditions during its precipitation. In the case of Wegel Tena opal deposit, the combination of petrological examination and geochemical signature was required to assess the exact geological process involved. All observations and measurements confirm the pedogenetic model, a particular case of weathering, for Wegel Tena gem opal deposit.

The identification of the process involved is a key for gem opal exploration. Therefore, pedogenesis may have been occurred all over the Oligocene Ethiopian Traps. Chauviré et al. (2017a) observed several opal-bearing horizons one above the other, multiplying the potential for opal extraction.

Other precious opal deposits worldwide suffer of uncertainties on their geological conditions of formation. This is sometimes due to a lack of studies, sometimes due to the difficulty to interpret data into an unambiguous way. One recent way investigated to constrain the geological origin of opals is the interpretation of infrared spectral features (Chauviré et al. 2017b). This already proved powerful on Earth, although spectral criteria are still under development. This may also be powerful to reconstruct geological history on Mars, as hydrothermal activity and continental weathering tell so contrasting stories (Pineau et al. 2018).

Acknowledgements

Authors thank F. Mazzer and D. Ayalew for their help for Ethiopian expedition and samples collection. A. Alexandre greatly helped authors for isotopic measurements and interpretations.

References


The origin of sapphires in alluvial and marine placers from the Loire river, France

Gaston Giuliani1,2, Anthony E. Fallick3, Adrian J. Boyce3
1Université Paul Sabatier, France
2Université de Lorraine, France
3Isotope Geosciences Unit, S.U.E.R.C., East Kilbride, Scotland, UK

Abstract. Gem sapphire deposits from the basaltic Cenozoic magmatism of the French Massif Central were eroded by the Loire River and its tributaries. New placers formed downstream up to the beach of Brétignolles-sur-mer on the Atlantic Ocean.

1 Introduction

Alluvium and colluvium gem sapphires are common in the basaltic fields of the French Massif Central (Lacroix, 1901). These deposits have been exploited since the Middle Age (Forestier, 1993) and are constantly panned by enthusiasts of mineralogy. The Loire, the longest river in France with a length of 1006 km, with its tributary the Allier, drains a large fraction of the French Massif Central (FMC). Placer deposits are located on both rivers within the volcanic areas of the Chaîne de la Sioule, Chaîne des Puys, and Velay (Fig. 1). In 2002, Goujou described a marine placer at the beach of Brétignolles-sur-mer, on the Atlantic Ocean, located at around 100 km south of the estuary of the Loire River (Fig. 1). In 2003, a sapphire placer was discovered on the Loire, at the city of Gien, located about 100 km downstream from its confluence with the Allier (Perinet, 2010).

The present contribution compares the mineralogy and geochemistry of sapphires from the FCM, Gien and Brétignolles-sur-mer in order to discuss the ability of the Loire River to transport corundum from the central part of France to its estuary at the Atlantic Ocean, prior to the construction of dams.

2 The placers of sapphires from the Loire and Allier rivers to the Atlantic Ocean

2.1 The placers

In the FMC (Fig. 1), volcanic sapphires generally occur in placer deposits (Sioulot in the Puy de Dôme, Riou Pezzoulou-Espaly, Le Puy and Taulhac in the Haute Loire), and occasionally in colluvium formed on the slopes of the strombolian cones of Mont Coupet and Mont Croustet (Giuliani et al., 2009; Gaillou et al., 2010). Xenocrysts of sapphire have also been found in magmatic phreatic tuffs, strombolian tuffs and lavas as in the Menet trachyte Quarries and in the Mont Croustet cone (occurrences of Croustet, Denise, Bilhac, Vialette, Taulhac, Vissac).

The Chambon-le-Château sapphire occurrences are related to isolated basaltic cones intruding the Margeride granite. The volcanic rocks are alkali basalts and basanites containing peridotite, pyroxenite, amphibolite, and neplelinitite xenoliths. The blue sapphires are found in colluvium and alluvium sediments. The strombolian cone of Chomelix intrudes the Velay granite and the sapphire occurs in the alluvium fans of a creek that crosscuts the basanites. A number of zircons associated with sapphires have been dated using the U-Pb method by laser-ablation ICP-MS (Paquette et al., 2009). Zircon and sapphire occurred at various times, from 20.3 ± 0.5 Ma in the Limagne to 956 ± 11 ka in the Velay, indicating a continuous magmatic process throughout the volcanic history of the FMC.

Figure 1. Distribution of the placers of sapphires along the Loire and Allier rivers, and the Atlantic Ocean. The source of sapphire deposits (1) is located in colluvium and alluvium of the French Massif central, and in the Loire and Allier rivers: (1) Le Puy, Espaly, Taulhac, Le Mont Croustet, Chromelix at the North of Espaly; (2) Le Mont Coupet; (3) Chambon-le-château; (4) Les Monts Dore with Le Puy de St Sandoux; and (5) la Chaîne des Puys with Le Sioulot. The placer of Gien (6) is located 100 km downstream of the Allier river confluence with Loire. The marine placer (7) is located at Brétignolles-sur-mer. Typical blue sapphires from the different areas are also presented.
The marine placer of Brétignolles-sur-mer was reported in the 90’s (Goujou, 1992) and has been described by Goujou (2002). It concerns heavy fine-grained sands formed by reddish garnet, ilmenite, magnetite, staurolite, rutile, zircon, and rare tourmaline, epidote, amphibole, kyanite, apatite, anatase, limonite and sapphire.

The placer of Gien was discovered in 2003 by panning after an exceptional annual period of low flow and high flood of the Loire River (Périnet, 2010). The sapphires were located in highly supplied alluviums in large flint elements, ferruginous nodules, and volcanic rocks mixed with black sands.

2.2 Mineralogy of sapphires

The sapphires of the FMC have a size between 1 to 7 mm, and the colours are generally in the blue, yellow or green with different shades.

Sapphires of Mont Coupet (Mazeyrat-Crispinhac and Saint-Eble localities) present different morphologies and colours (blue, green, pinkish greyish). The sapphire crystals have an elongated, barrel-shaped habit and most of them are rounded and corroded. They are bounded by hexagonal dipyramidal $\omega$ {14 14.3} or $z$ {22.1} faces combined with the basal pinacoid $c$ {00.1}. The crystals frequently present the prismatic {11.0} faces and rarely the additional hexagonal dipyramid $n$ {22.3} faces described by Lacroix (1901). The other main features are: (i) triangular stairs as found on the Sioulot sapphire (see Fig. 1) developed on the basal pinacoid $c$ {00.1}; (ii) the presence of grooves parallel to the pinacoid $c$ which result from piling up of several crystals formed along the same axis (iii) the basal pinacoid faces {00.1} sometimes present a deep blue colour with six whitish star-like arrays developed from the centre towards the corners between the faces. The solid inclusions in sapphires are ferrocolombite, pyrochlore, oligoclase, zircon, thorite, ilmenite, rutile, hercynite, Nb-bearing rutile, and magnonate (Simonet, 2000; Gaillou 2003).

The sapphires of Gien have been studied by Périnet (2010). The crystals present a size less than 1 mm (90%) and between 1 to 3 mm (10%). The colours are mainly in the blue and green, and sometimes milky or whitish. The crystals are either euhedral, clear, and with shiny faces (20% of the production) or broken crystals which present sometimes blunt and gleaming surfaces. The habits of the preserved crystals are similar to those from the FMC (Fig. 1) and presented in Figure 2.

Solids in sapphires are ilmenite, ferrocolombite, Nb-bearing rutile, hercynite, plagioclase, zircon, plagioclase, pyrochlore, oligoclase, zircon, apatite, chlorite, pyrrhotite, chalcopyrite (Denis, 2008).

The sapphires of Brétignolles-sur-mer are around 1 mm in size and their colour is light to deep blue, light to deep green, colourless and rarely yellow. The crystals have suffered transport by the ocean currents, and specially wear due to rising and falling tides and the devastating wave force. The crystals are either broken or transformed in dull and glossy grains. Among the grains that have retained their habits, four main forms are observed that are those described in the FMC and Gien placers (Goujou, 2002). The solid inclusions have not been identified but the study is in progress.

2.3 Chemistry of sapphires

The sapphires from the different sites were analysed by EPMA (Simonet, 2000, for the MCF sapphires; this work for the Gien sapphires) and LA-ICP-MS (Gaillou et al., 2010, for the FMC sapphires). The analyses for sapphires from Brétignolles-sur-mer are in still in progress (Giuliani et al., in preparation). All the data point of the analysis represent the average for one crystal. The analyses plot in the chemical field of sapphires associated in alkali basalts (Fig. 3) defined in the FeO - Cr$_2$O$_3$ - MgO - V$_2$O$_3$ vs. FeO + TiO$_2$ + Ga$_2$O$_3$ classification diagram proposed by Giuliani et al. (2014). The representative points of the sapphires from Menet in the FMC that are found in xenoliths of anorthoclases, and those from Sioulot, plot in the field of syenite. The other representative points are in the field of metasomatic - metamorphic corundum defined by Giuliani et al. (2014). In that case, the origin of the

2.4 Oxygen isotope composition of sapphires

The $\delta^{18}$O values of sapphires from the FMC placers range between 4.4 and 13.9‰ (Fig. 4).
The chemical distribution of sapphires from Gien is scattered between the fields of metasomatic- and syenite-bearing corundum. It illustrates the mingling of the different sources and origin of sapphires from the FMC, and transport by Allier and Loire rivers up to Gien. The placer is a mixed concentration of corundum of magmatic and metamorphic origins.

The O-isotopic composition of sapphires from the FMC (Fig. 4) were discussed by Giuliani et al. (2009): (i) a magmatic origin was proposed for the blue-green-yellow sapphires (4.4 < δ18O < 6.8‰, n= 22) which suggest that these sapphires crystallized from felsic magmas under upper mantle conditions; (ii) a metamorphic origin for sapphires with δ18O values between 7.6 and 13.9‰ (n= 9) formed under amphibolite or granulite facies conditions.

The δ18O values of three sapphires from Gien, between 4.0 and 7.2‰, fall within the δ18O range of values defined for sapphires in syenite, plasmatic and mafic gneiss (Giuliani et al., 2014). The presence of inclusions of ferrocolombite and Nb-bearing rutile in these three blue and green sapphires provide a strong additional argument for a magmatic origin. As a result, the δ18O value of 4‰ would extend the worldwide range of δ18O values defined for sapphires in syenites.

The δ18O values of three sapphires from Brétignolles-sur-mer, between 6.5 and 7.5‰, fall within three possible sources: syenite, biotite in gneiss and plasmatic. In the absence of chemical analysis, the source may be approached considering the habit described for the blue sapphire, i.e., characterized by the combination of the tabular prism (11.0) and pinacoid (00.1) faces, and modified by the rhombohedron (10.1) and hexagonal dipyramid (22.3) faces (Fig. 2d), which is a very common feature of all the blue sapphires from the FMC and Gien, and for which the O-isotopic signature indicates a magmatic origin.

During the Pleistocene (Nehlig, 2010), the Loire River was divided into: (i) Paleo-Loire flowing north, and (ii) Loire Atlantique with its source towards Gien and then flowing westward. At the Middle Pleistocene (0.8 to 0.4 Ma), the junction of the two rivers produced the current Loire river. Marine levels related to Quaternary
Eustatic variations were, 18,000 years ago, more than 100 meters below current levels. The Loire reached the Ocean through a drainage system consisting of three main valleys, 30 km long, 0.7 to 4 km wide and 60 m deep, that disappear 50 km from the current coast. The central and south valleys were located at the West of Noirmoutier Island (see Fig 1). At that time, the volcanism of the Chaîne des Puys was still active and the Allier and Loire Rivers were eroding and carrying sediments (with sapphires) from the FMC down to the Atlantic Ocean. The location of the Central and South valleys of the Loire can explain the formation of placers at Brétignolles-sur-mer, located only at 50 km south-east from Noirmoutier Island, and with marine currents oriented NW-SE.

4 Conclusions

The present study has shown that the sapphire placers of Gien and Brétignolles-sur-Mer, were formed by the erosion of sapphire-bearing colluvium and alluvium placers in the French Massif Central, by the Loire and Allier rivers and their several small tributaries, and consequent transport by the Loire River down to the coasts of the Atlantic Ocean.

Acknowledgements

The authors thanks Messrs. Pégère, Périnet and Goujou for providing sapphires from, respectively, the French Massif Central, Gien and Brétignolles-sur-mer. Thanks to the Muséum National d'Histoire Naturelle of Paris (MNHN) for providing samples from the FMC.

References

Simonet C (2000) Géologie des gisements de saphir et de rubis. L’exemple de la John Saul mine, Mangari, Kenya. Thèse de Doctorat, Université de Nantes, France
**Geology of the La Pava emerald mine, Colombia**


*Technological Development Centre for the Colombian Emerald (CDTEC)*

**Abstract.** This paper includes the main results of an integrated geochemical and structural study of the La Pava emerald mine. Despite several works having been carried out dealing with the unusual genesis of the Colombian emeralds, limited information is available about the geological features of this mine. Through a detailed mapping and stratigraphic approach, we determined the predominant mineralogy of the enclosing rocks and black shales and state how the circulation of sodium and calcium–rich solutions modified the sedimentary rocks. Additionally, we evidenced a fault propagation that played a key role in focusing the circulation of the mineralizing hydrothermal fluids.

1 Introduction

Colombia has been a major emerald producer for more than 1000 years. Nowadays, it occupies the third place in terms of emerald production, after Zambia and Brazil. The Colombian mineralization style is remarkably different from the rest of the world. The main contrast is related to the composition of the host rock and the absence of magmatism. Emeralds are typically found in metamorphic aureoles or pegmatitic veins in countries like Zambia, Brazil, Pakistan or Ethiopia; whereas in Colombia, the host rocks are sedimentary (organic–rich black shales, calcareous mudstones, limestones, and evaporitic siltstones) and the mineralizing processes are similar to those found in sediment–hosted Pb–Zn or Mississippi Valley Type deposits.

The occurrence of emeralds in Colombia is controlled by the tectonic evolution of the northern Andes during the last 65 million years. There are seven mining districts, three of which are located in the Eastern Belt and four in the Western Belt. Both belts have an alignment N–NE concordant with the general trend of the Eastern Cordillera of Colombia. The La Pava mine is located in the Muzo–Quipama District (MQD), one of the most important districts in terms of production and quality of the gems (Fig. 1). Some of the finest emeralds in the world have been found in Muzo, and the trapiche variety of emerald is also occasionally found in this area. The La Pava mine has been exploited for more than 40 years and is currently in the process of being reactivated. La Pava is 100% owned by Vetas Sierra Alta S.A.S.

Giuliani et al. (1993, 1995, 2000) and Ottaway et al. (1994), have described some general features within the MQD. They emphasize the importance of hydrothermal alteration zones known as "Cenicero", which correspond to brecciated hydrothermalized shales transformed by the reaction with evaporitic brines. These zones are spatially related to the occurrence of veins containing carbonates, albite, pyrite, and emeralds. The emerald deposits are stratabound and only occur within calcareous mudstones from a Lower Cretaceous horizon. Although there are numerous works dealing with emerald mineralization in Colombia, most of these have focused on the understanding of regional characteristics and as a result, few works have been done describing a specific mine. The objective of this work is to provide new information about the emerald deposit in La Pava. Relevant observations about the geochemical, structural and stratigraphic setting of the the La Pava emerald mine are presented here.

2 Geological setting

Emeralds in Colombia are found along two NE trending belts in the Eastern Andean Cordillera. The Eastern Belt extends more than 30 km and encompasses three emerald–euclase productive zones; Gachalá, Chivor, and Macanal. On the other hand, the Western Belt is approximately 55 km long and host five mining districts: Peñas Blancas, Coscuez, Maripí, Yacopi–La Palma and Muzo–Quipama. La Pava, Puerto Arturo, Catedral, Tequendama, and Palo Blanco are some of the most relevant mines located in the MQD district. Emeralds are hosted by Lower Cretaceous marine sedimentites, which were deposited in a back–arc basin; the dynamic evolution of the northern Andes led to a tectonic inversion and later exhumation of these rocks during Early Miocene. Based on $^{40}$Ar/$^{39}$Ar data, Cheilletz et al. (1994) suggested an Oligocene (31.6–32.6 Ma) age for the emerald vein formation in the MQD. They stated the hydrothermal mineralizing processes were triggered by a major shortening episode of the Eastern Andes beginning in the late Eocene. Branquet et al. (1999) affirmed the mineralization in La Pava is associated with thrust faults linked to tear faults developed during a compressive tectonic phase. In addition, the deposit was affected by a flower structure located at the intersection of the Rio Itoco Fault with an N30E trending strike–slip fault. More recently, Pignatelli et al. (2015) proposed the formation of the "trapiche" emerald resulted from an abrupt decompression of fluids trapped within anticlines where thrust propagation and failure processes took place.

The La Pava deposit (Fig. 1) is structurally associated with the southern prolongation of the Alto La Chapa–Borbúr anticline, which is a regional fold limited by the Rio Minero Fault (east), Peñas Blancas Fault (west) and the Rio Itoco Fault (south). Mineralization in the MQD is stratigraphically restricted to the Hauterivian–Barremian calcareous mudstones of the Muzo Formation (Reyes et al. 2006).
Figure 1. Generalized geological map of the La Pava emerald Mine.

According to Ottaway et al. (1994), Giuliani et al. (2000) and Banks et al. (2000), the Colombian emerald deposits were originated by the circulation and mixing of hydrothermal brines derived from the dissolution of evaporite layers and their subsequent interaction with organic-rich host rocks. Thermochemical sulfate reduction played a key role as it triggered the releasing of beryllium, chromium, and vanadium from the enclosing black shales, which caused the emerald precipitation. As a result, the mineralized zones display strong hydrothermal alteration patterns; albitization as a consequence of the circulation of brines, carbonatization reflecting the CO$_2$ production by the organic matter oxidation; and pyrite and native sulfur-rich zones derived of the reduction of evaporitic sulfates. As expected, the Colombian emerald deposits are clearly stratabound and share common features with other more traditional sediment-hosted ore deposits. In fact, it is not unusual to find base metal minerals like Cu–Zn–Pb sulfides, barite, and fluorite in the emerald mines.

3 Methods

Two stratigraphic sections at a 1:100 scale were constructed in the surroundings of the La Pava deposit and were compared with underground sections inside the mine. The first section consisted of 465 m of non--altered or poorly altered rocks along the Itoco river; the remaining section was examined along the La Pava Creek. Hand samples were taken every 4 meters in the sections, this yielded a total of 125 rock samples which were analyzed through X-ray diffraction (XRD) and X-ray fluorescence (XRF). The XRD sample preparation consisted of crushing with an agate mortar, sieving and separating of 2 g of > 70 µm powder for scanning. Four sample preparations were performed for XRD routines. In order to estimate the major and trace elements concentrations, homogenized and dried powders were analyzed through a BRUKER Tracer GeoQuant IV XRF equipment. Thirty representative samples were selected to elaborate polished thin sections and were analyzed with an Olympus BX51 petrographic microscope.

4 Results

The Itoco river stratigraphic section (Fig. 2) comprises a series of siltstones interbedded with organic-rich massive mudstones and laminated shales, some levels contain mud concretions and ammonite fossils. A six-metre thick light–grey breccia level occurs in the middle–bottom part. This breccia is concordant with bedding and is made up of albite, calcite–dolomite, pyrite, native sulfur, and minor muscovite. The grain size increases upwards in the section where siltstones predominate
again. Hydrothermal activity is poorly observed with the exception of the light–grey breccia and some restricted gypsum, pyrophyllite, quartz, calcite and chalcopyrite veinlets.

On the other hand, the La Pava Creek section is dominated by organic–rich massive mudstones and black shales, where the number of concretions and the pyrite content increase (Fig. 3). Most of the stratigraphic column reacts with hydrochloric acid showing a significant abundance of carbonates.

Figure 2. a. Panoramic view of the La Pava area indicating the main structural features. b. Simplified cross–section.

Most of the XRD and XRF data are in agreement with the field stratigraphic nomenclature defined for the rocks. The rocks from the Itoco river section are mostly composed of quartz, paragonite, muscovite (2M1 illite) and microcline. Minor phyllosilicates (< 1%) include pyrophyllite, dickite, chlorite, and kaolinite. The pyrite and baryte contents are low but constant along the column, contrary to chalcopyrite which is scarce. In comparison to the Itoco river section, the La Pava Creek shows an increase in the sulfur, calcium and magnesium concentrations which correlates with an increase in the pyrite content and a higher abundance of carbonates (calcite–dolomite). However, the most pronounced difference is the increase and predominance of albite. In the La Pava Creek section, there is a significant decrease in the occurrence of muscovite, microcline, paragonite, and quartz, which correlates with a decrease in the potassium content. This clearly indicates an inversely proportional relationship between the albite and muscovite–paragonite–microcline contents. The appearance of albite and carbonates in the La Pava section is related to metasomatic processes that modified the rock–forming minerals. The overall silica–alumina ratio (SiO₂/Al₂O₃) shows negligible variations between both sections.

It is noteworthy that the La Pava Creek section is closer to the productive zones of the La Pava mine than the Itoco river section. Most of the lithological and mineralogical features observed in the La Pava Creek, look like those present in the underground mine. In contrast, the amount and size of hydrothermal veins increase inside the tunnels.

The structural configuration of the zone is dominated by a compressional style, where the El Águila Fault was locally identified as the major controlling feature. This fault corresponds to a high angle reverse fault which strikes N10E and dips eastwards. The La Pava anticline and syncline are associated with a fault–propagation fold regime in the hanging wall of the El Águila Fault (Fig. 3). The La Pava anticline is an asymmetric NS trending fold, linked with the La Chapa–Burbur fold, which is the most regional structure that controls emerald mineralization in the Peñas Blancas district. The La Pava Creek is located parallel to the eastern limb of the La Pava anticline. The mineralization is generally concentrated in the core and in the steeply dipping limbs of the La Pava anticline. Emeralds are usually found in calcite–dolomite–albite–pyrite–quartz veins and breccia oriented N35E, hosted by highly albitized and carbonatized shales. The veins are close to the light–grey breccia level, but the productive zones are exclusively located in highly deformed areas. Most of the veins are tension cracks formed by the flexural folding; some veins are concordant to the stratification at the fold limbs, whereas veins and breccias are more commonly found along the hinge line.

5 Mineralization

Three mineralization assemblages were recognized according to their textural, temporal and geochemical features. The first stage of hydrothermal activity corresponds to the albitionization of the country rocks. The shales were almost entirely converted into albities as a result of a massive sodium input by the hydrothermal fluids. Albite occurs as disseminated crystals and pseudomorphs in the black shales, and as drusiform crystals in veinlets and breccias. The most notable example of albitionization is the light–grey stratiform breccia. This bleached level is interpreted as the result of the interaction of sulfate–bearing hot brines with organic matter from the shales. The second hydrothermal stage consists of a strong carbonatization that affected the black shales and led to the formation of veins 10–50 cm wide. The main mineral assemblage of the veins includes rhombohedral calcite, dolomite, pyrite, muscovite and minor quartz, albite, apatite, and rutile. Emerald occurs as hexagonal euhedral crystals exhibiting a light–green color and exceptional brightness. Late–stage barite occasionally infills open spaces exhibiting coarse light–yellow crystals. Copper and zinc sulfides may be sporadically found. Finally, supergene oxidation has given rise to the formation of goethite, malachite, chrysocolla, azurite, gypsum and jarosite. The percolation of runoff through carbonate–rich rocks has promoted the formation of widespread aragonite within the main tunnels. The aragonite crystals are often fluorescent due to their trace metal content.
6 Conclusions

An integrated approach consisting of field, petrographic and analytical data shows that emerald mineralization in the La Pava mine is associated spatially with a black shale level that displays a strong Na–Ca metasomatism (albitization and carbonatization). Emeralds are found in veins and breccias compositionally dominated by calcite, dolomite, pyrite, and albite. The formation of the productive veins and breccias is temporally associated with the development of fault–propagation folds. The La Pava Anticline is the main structural feature responsible for focusing and trapping the emerald–bearing hydrothermal fluids.

The unaltered black shales and massive mudstones are composed of paragonite, muscovite, quartz, and microcline. This mineral assemblage suggests the sedimentary strata underwent low–grade metamorphism. Notwithstanding the fact that hydrothermal circulation abruptly modifies this mineralogy; most of the phyllosilicates and potassium–bearing phases are transformed into albite. This study reaffirms the importance of detailed mapping of the local structures and stratigraphy, which in turn, integrated with geochemistry can contribute significantly to the emerald exploration and exploitation of the mining area.

Acknowledgments

This study was financially supported by the National Emerald Federation (FEDESMERALDAS). Vetas Sierra Alta S.A.S is greatly acknowledged for logistical support during field activities.

References


Using weathering and alteration minerals to constrain water table movement and supergene enrichment of porphyry copper deposits in the Central Andes

J.M. Shaw, F.J. Cooper
School of Earth Sciences, University of Bristol, UK

A.J. Boyce
Scottish Universities Environmental Research Centre (SUERC), East Kilbride, UK

K.A. Farley
California Institute of Technology, Pasadena, USA

L. Evenstar
School of Environment and Technology, University of Brighton, UK

Abstract. The Atacama Desert of northern Chile hosts many of the world’s largest porphyry copper deposits (PCDs), many of which have been upgraded through supergene enrichment (Sillitoe and McKee 1996). Enrichment of exhumed PCDs occurs in the near-surface weathering environment, when copper is leached from primary sulphides and reprecipitated beneath the water table to form a concentrated blanket of secondary copper minerals (e.g. chalcocite).

The Atacama is one of the driest regions on Earth, but supergene enrichment requires precipitation to drive the aqueous redistribution of metals. Previous alunite dating studies have suggested enrichment stopped in the middle Miocene, due to an increase in aridity. This conclusion is supported by the youngest supergene alunite ages from several PCDs clustering around 14 Ma (Sillitoe 2005). Hematite also forms in the leached caps of PCDs and hematite (U-Th)/He geochronology provides a tool to track the downward progression of weathering fronts (e.g. Cooper et al. 2016).

This study will combine 40Ar/39Ar dating of supergene alunite (a proxy for the timing of copper enrichment) with hematite geochronology (as an indicator of the progression of weathering fronts) to better understand the link between water table movement and supergene enrichment of Central Andean PCDs.

1 Introduction

Supergene enrichment has been fundamental in producing the economically extractable metal grades of exhumed PCDs in the Central Andes of northern Chile (e.g. Sillitoe and McKee, 1996). Enrichment occurs when exhumed PCDs undergo oxidative weathering in the near-surface environment. Dissolution of sulphides (principally pyrite [FeS2]) by meteoric water produces sulphuric acid, which leaches Cu (e.g. from chalcopyrite [CuFeS2]) and transports it downward in solution (Alpers and Brimhall 1988). Under reducing conditions beneath the water table, Cu is reprecipitated through ion-exchange reactions, forming a supergene blanket enriched in chalcocite [Cu2S] (Sillitoe, 2005). The water table forms the boundary between oxidising and reducing conditions and determines the depth to which leaching and enrichment can occur (Aigue and Brimhall, 1989).

Supergene enrichment is driven by percolation of meteoric water, however northern Chile is currently one of the driest regions on Earth. Previous work suggests supergene enrichment stopped in the middle Miocene, possibly due to an increase in aridity (Alpers and Brimhall, 1988; Sillitoe and McKee, 1996; Cooper et al., 2016), although conditions may have been dry for much longer (e.g. Clarke 2006). Understanding how water table movement and supergene enrichment fit within the framework of Andean aridification and post-mineral cover deposition will be a valuable addition to Cu exploration models targeting enriched PCDs.

2 Study sites – Spence and Cerro Colorado

This project will compare the history of Cu enrichment and water table movement at two PCDs in the Palaeocene-early Eocene metallogenic belt of northern Chile – Spence and Cerro Colorado (Fig. 1). Spence (formed at ~57 Ma) is covered by ~50 to 100 m of Miocene gravels (Cameron and Leybourne 2005), whereas Cerro Colorado (formed at ~52 Ma), a palaeo-high, only has gravel cover (up to ~50 m thick) on its flanks (Bouzari and Clark 2002). The total PCD profile thickness (spanning the gravel/volcaniclastic cover, leached cap, oxide zone, enrichment blanket and hypogene orebody) of both deposits is similar: 450 m at Cerro Colorado and 400 m at Spence. The average thickness (140 m) of the secondary sulphide enrichment blanket is also the same at both deposits (Bouzari and Clark 2002) (Fig. 2). Spence and Cerro Colorado make a good comparison because, despite their similarities, supergene processes have operated within distinct fluvial, sedimentological and tectonic settings at each deposit.
Constraining the timing of supergene enrichment has traditionally involved K-Ar and $^{40}$Ar/$^{39}$Ar dating of supergene alunite \([\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]\) and (less commonly) jarosite \([\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2]\) (Hartley and Rice 2005). Alunite in PCDs may form through direct precipitation from sulphate solutions or through acid weathering of kaolinite, feldspar or muscovite during leaching of granitoid host intrusions (Vasconcelos 1999). Sulphuric acid to cause this alteration is produced through the weathering of sulphides, most importantly pyrite \([\text{FeS}_2]\). Previously published alunite ages suggest Cerro Colorado was undergoing weathering and enrichment from 35.26 ± 0.68 to 14.59 ± 2.46 Ma (Bouzari and Clark 2002). However, alunite may form in both the leached cap and the subjacent enriched zone of a PCD, and therefore alunite ages do not give precise information on the position of the water table.

Hematite, which only forms under oxidising conditions and can be dated using (U-Th)/He geochronology, may be used to track water table movement through time. Cooper et al. (2016) found that ages of hematite sampled from drill core at Cerro Colorado range from ~32 to 2 Ma, defining a period of water table stability from 32 to 16 Ma, followed by a younging-with-depth relationship from 16 to 2 Ma (Fig. 3). The modern water table coincides with the base of an adjacent river canyon, the Quebrada de Parca, and lowering of the water table is attributed to incision of the river from ca. 16 Ma onwards, at a rate of ~10 m/Myr. The onset of water
table decline is approximately coincident with the cessation of enrichment, supporting the case for a middle Miocene increase in aridity.

4 Alunite and hematite in the leached cap at Spence

The history of water table movement at Spence is complicated by the absence of nearby fluvial incision, textural relationships between weathering and alteration minerals and the currently elevated water table, which follows the gravel/bedrock contact, >50 m above its previous low-point which is evidenced by the base of the oxidised zone (Cameron and Leybourne 2007).

Preliminary (U-Th)/He hematite ages from Spence range from ~11 to 2 Ma, considerably younger than the existing alunite ages of ~44 to 20 Ma (Clark 2001). However, cross-cutting relationships in samples collected during the current project show hematite to be texturally older than alunite, meaning our current understanding of water table movement and leaching of the deposit is incomplete (Fig. 4).

Figure 4. SEM (BSE) image of texturally associated hematite (pale grey) and alunite (dark grey rhombs). Alunite appears to post-date hematite formation as the hematite is fragmented (shown by the discontinuity of growth zones) and alunite occurs between hematite fragments. The presence of aluminum-phosphate-sulphate minerals (part of the alunite group) is evidence for multiple stages of mineral precipitation.

4.1 A supergene origin for alunite at Spence

A supergene origin for alunite at Spence is confirmed by its pseudocubic microtexture (e.g. Arribas et al. 1995) and the matching sulphur stable isotope signatures of supergene sulphate and primary hypogene sulphides (Fig. 5). Alunite formed through closed-system sulphide weathering inherits the S isotope signature of the precursor sulphides, whereas sulphate formed after disproportionation of magmatic SO₂ to SO₄²⁻ and H₂S during the lifetime of the magmatic-hydrothermal system has δ³⁴S values 16-28 ‰ higher than sulphides due to isotopic fractionation (Rye et al. 1992; Rye 2005).

Figure 5. BSE SEM image of pseudocubic alunite crystals from the leached cap at Spence (top) and S isotope data for alunite and primary sulphides from Spence (bottom), both suggesting a supergene origin for alunite.

5 Project objectives and programme of work

We will obtain paired (U-Th)/He and ⁴⁰Ar/³⁹Ar ages for texturally associated hematite and alunite to test the following hypotheses:

1. One (or both) dating methods do not accurately record the formation ages of the weathering minerals at Spence (e.g. absolute ages disagree with relative ages).

2. Alunite precipitation (and supergene enrichment) occurred at Spence much more recently than 20 Ma.

The results of this study will provide information on the usefulness of hematite dating in situations where numerous water table drawdown/recharge events may have occurred and improve our understanding of the relationship between deposition of post-mineral cover and the cessation of supergene enrichment. An ash layer situated ~60 m up the gravel sequence at Spence has been dated at ~9.5 Ma (Sun et al. 2018). Any alunite ages younger than this would suggest leaching and supergene enrichment continued to some extent beneath appreciable cover. It has previously been suggested that deposition of more than 50 m of cover would elevate the water table and stop any further progression of weathering and copper enrichment (Sillitoe and McKee 1996).

Acknowledgements

This work is part of an ongoing NERC DTP studentship awarded to J. Shaw. The authors would also like to thank NERC for funding the S isotope dating work at SUERC (East Kilbride). Hematite dating work will be carried out...
by Prof Ken Farley at Caltech, and we are working with Dr Dan Barfod (SUERC) and Prof Brad Singer (University of Wisconsin) to conduct $^{40}$Ar/$^{39}$Ar dating of alunite.

We would also like to thank BHP (CASE partners on the project) for access to mine sites and other support during field campaigns.

References


Multiple fluid infiltration contributed to the supergene Fe deposit at Petronell (Germany) – chronology of events by goethite and todorokite U-Pb dating

István Dunkl, Hilmar von Eynatten, Keno Lünsdorf
University of Göttingen, Germany

Abstract. Goethite and todorokite were deposited alternately in fault-related impregnations in Lower Triassic sandstone along the rift shoulders of the Upper Rhinegraben (URG) in Germany. Laser ablation U-Pb dating of these minerals show two distinct age clusters: around 45 Ma (Mid-Eocene) and 4 to 2 Ma (Pliocene). The older ages suggest that the supergene mineralization occurred coevally with the early rifting phase of the URG, while the young ages are measured in subsequent mineralizations reflecting a late re-activation of the faults and related descendent, meteoric fluid flow.

1 History of mining

The former Petronell mining area is situated in the southern part of Rhineland Palatinate close to Bad Bergzabern. The so called "limonitic" ore was mined intermittently from around 1580 until the second half of the 19th century. From the subsurface mining activity at Petronell the yearly production was around 400 metric tons at the beginning of the 19th century (Walling, 2005). These relatively small deposits characterized by dominantly goethite impregnation of Triassic Bunter sandstone along local and regional faults are widespread in the region. Their former iron production contributed to the regional technological development from the 16th to the 19th century (e.g., Held and Günther 1993).

2 Geology of the region and formation of the deposit

The deposit is located at the western rift shoulder of the Upper Rhinegraben (URG) in the Palatinate Forest (Fig. 1). The URG extends in a NNE–SSW direction for about 300 km between Basel and Frankfurt, is over 30–50 km in width, and forms part of the European Cenozoic rift system (ECRIS; Ziegler and Dèzes 2005). The URG is bordered by more or less symmetrical, up to 1500 m high rift shoulders on its eastern and western sides; the maximum vertical throw between the base of the graben and the uplifted flanks exceeds 4 km. The rift shoulders expose the European basement (mostly Variscan granitoids and metamorphic rocks), Permian volcano-sedimentary sequences, and Mesozoic epicontinental deposits.

Rifting of the Upper Rhinegraben was initiated in mid-Eocene time at around 47 Ma (Illies 1977; Grimmer et al. 2017). The extension occurred in several pulses with contrasting mechanisms. The basin fill records the associated major subsidence phases at around 37–31 Ma, 25–18 Ma and post-5 Ma. Mafic alkaline volcanism has been associated with the development of extensional structures in and around the graben system (for a brief summary on the evolution see Walter et al. 2018).

Figure 1. Geological sketch map of the Upper Rhinegraben (map base: Geological map of Germany, 2 mio, BGR, Hannover, 2004). Star indicates the Petronell deposit situated along the western main boundary fault of the URG.

The goethite impregnations form irregular, partly fault-related bodies in the Lower Triassic Bunter sandstone. The most plausible mechanism for the mobilisation and supergene precipitation of iron assumes a gravity-triggered flow cell that developed following the formation of the fault-controlled relief along the rift shoulder. Potentially Cenozoic lakes and swamps may have developed in the rift valley during the early extensional phase and may have reduced the pH of the infiltrating meteoric water, enhancing the removal of iron from the ferrous cement of the sandstones. The basal strata of the Cenozoic basin fill contains organic-bearing layers (Böcker and Littke 2016), thus assuming their former, wider extent above the current rift shoulders is a reliable
3 Mineralogy and geochemistry

The mineral phases were identified by Raman spectroscopy using 532 nm wavelength laser light, while their chemical composition was determined by laser ablation using an excimer laser and an Element2 ICP mass spectrometer. Laser ablation line analyses were performed in order (i) to characterize the composition of the minerals and zones of the ore, and (ii) to demarcate potential minerals and/or zones where the concentration of U and the Pb/U ratio is appropriate for U-Pb geochronology. The applied spot size was 75 µm (speed: 20 µm/s) and 54 analyses were registered from 46 elements.

The dominant mineral of the Fe-ore is goethite, forming tight impregnations and partly botryoidal crusts in the fissures of the sandstone. The composition of the goethite in the botryoidal crust shows a gradual change from the early layers towards outer layers precipitated later (Fig. 2). The internal zone is richer in trace elements, including increased Al->Fe substitution in goethite. The uranium concentration is typically constant, but in some samples it shows a 3-fold increase towards the younger goethite layers (i.e. towards the rim). In these external zones the Pb/U ratio and the U concentration are appropriate for the application of U-Pb geochronology.

Figure 2. Concentration of some trace elements in a thin goethite crust from the Petronell mine. Laser ablation line analysis along a ca. 4 mm long section (reflected light microscopic image in the upper panel).

Todorokite and pyrolusite are the typical Mn-minerals in the deposit, but they occur in smaller amounts than goethite. The textural context of the Fe- and Mn-minerals is not obvious, sometimes the Mn-oxide phases are older than the main goethite phase, but also younger Mn-oxide generations can be recognised. Oscillating fluid conditions cannot be excluded. The Mn-oxide crusts are rather heterogeneous, exhibiting locally high porosity, and, in some minor cavities, mm-sized euhedral pyrolusite crystals. The goethite content in the Mn-oxide zones is variable. The Al content correlates well with the Fe content, but their ratio varies in different domains. Because Al shows no correlation with Si or K, it is likely that Al is incorporated in the lattice of goethite (Fig. 3).

Figure 3. Correlation of Al and Fe in the zones of the ore with varying goethite content. The Al/Fe ratio varies between the zones.

4 Unconventional U-Pb dating using goethite and todorokite

The laser ablation analyses were performed using spot sizes between 33 and 90 µm. As no matrix matched any Fe-oxyhydroxide and Mn-oxide reference materials available for U-Pb geochronology, we used the most commonly used zircon reference materials (GJ1, Plesovice, 91500 and FC1) for fractionation and drift correction. The ablation behaviour of these reference materials differs from the metal(oxy-)hydroxides, but the bias introduced by this contrast should be less than 10%. The samples contain highly variable amounts of common lead, so the ages were calculated as lower intercepts on the Tera-Wasserburg plot.

We recorded two age groups in the todorokite phases: (i) around 45 Ma (Mid-Eocene) and around 4 to 2 Ma (Pliocene). For the goethite it was possible to date only the outer zone of the crusts, as only in this thin layer was the Pb/U ratio acceptable for geochronology (Fig. 4). These spots yield Pliocene ages, similar to the younger age group detected in the Mn-oxides.

Figure 4. Concentration of some trace elements in a thin goethite crust from the Petronell mine. Laser ablation line analysis along a ca. 4 mm long section (reflected light microscopic image in the upper panel).
Figure 4. Upper panel: Tera-Wasserburg plot of a typical Eocene U-Pb age determined in the early generation of todorokite. Lower panel: Pliocene U-Pb age measured on the external layer of the botryoidal goethite.

5 Conclusions

- The two age groups are well characterised, with very few ages in between these two groups.
- The coherent Pliocene ages detected in different phases indicate that the U-Pb system remained closed after the formation of these minerals. We therefore interpret these data as well-defined temporal constraints on fluid movement (i.e. hydrochronology).
- The older ages match the opening of the Upper Rhinegraben and indicate that the descendent, oxidative meteoric water had reached the currently exposed level of Lower Triassic sandstone by the Mid-Eocene, in the early period of rifting.
- The younger ages coincide well with the youngest, <5 Ma subsidence phase in the Upper Rhinegraben. Probably the associated faulting opened older fissures and generated renewed descendent water circulation leading to the precipitation of the young goethite and todorokite generations.
- So far no ore specimens have yielded Miocene U-Pb ages that are characteristic of fissure-filling carbonates in the Schwarzwald ore district, at the southeastern rift shoulder of the Upper Rhinegraben. This might be due to (i) the small sample numbers (i.e. statistical reason), or (ii) the lack of volcanic activity in the region in contrast to the southern URG.

Acknowledgements

Many thanks to Wolf-Gerd Frey for providing samples from Petronell.

References

The potential use of multi-aliquot goethite (U-Th)/4He geochronology for understanding late Cenozoic climate change across Eurasia

David Currie, Fin Stuart, Luigia di Nicola
Scottish Universities Environmental Research Centre, East Kilbride, UK

John Faithful
Hunterian Museum, University of Glasgow, UK

Serdar Keskin
Trabzon, Turkey

Abstract. Fe-oxide weathering profiles can provide insight into chemical reactions at Earth’s surface in response to tectonic events and climate change (Shuster et al. 2005; Monteiro et al. 2014; Vasconcelos et al. 2015). Here, we characterize goethite using scanning electron microscopy and X-ray diffraction before determining U, Th, and He concentrations of the same sample from a weathering profile in the Attepe Fe-ore deposit, southern Turkey. A He age of 2.32 ± 0.03 Ma was achieved with reproducibility of He, U, and Th at ~1% (4 aliquots for He, 5 for U and Th). This study demonstrates that supergene goethite can provide reproducible chronological information from weathering profiles and may allow for more informed discussion on tectonic and climate events across Eurasia in recent Earth history. However, the extent of He diffusion in this goethite mineralisation is yet to be determined by 3He/4He methodology, ruling out complete robustness of the study. Such weathering events, often linked to aridification, may have influenced dispersal pathways of early Homo into Eurasia from African and the modern Syrian region.

1 Introduction

Chemical weathering and reprecipitation of metalliferous lithologies into economically viable ore bodies is known as supergene enrichment (Vasconcelos 2015 for summary). Chemical weathering is influenced by climate conditions like annual precipitation, cold month mean temperature, and warm month mean temperature and can result in stratified weathering profiles as deep as 1 km below surface (Shuster et al. 2005; Thorne et al. 2012; Vasconcelos et al. 2015). Fe-oxides are ubiquitous near surface weathering products and due to Earth surface temperatures being low enough for Fe-oxides to be He retentive, the (U-Th)/4He age is accepted as the timing of mineral precipitation (Shuster et al. 2005).

Helium retentivity in goethite varies depending on the crystalline and/or presence of intergranular material in samples but can be experimentally determined by 4He/He diffusion experiments (Shuster et al. 2005; Heim et al 2006; Deng et al. 2017; Monteiro et al. 2018). It is common for a study to apply a 5% to 20 % error to He ages to account for diffusive loss of He in goethite. For example, Deng et al. (2017) use goethite (U-Th)/He and 4He/3He geochronology to constrain the timing and rates of chemical weathering utilizing a weathering profile in a porphyry Cu deposit on the eastern fringes of the Tibetan Plateau. By correlating their ages with paleoclimate conditions deduced from nearby supergene Mn-oxides and loess deposits, Deng et al. (2017) were able to infer that monsoonal precipitation controlled chemical weathering and that its intensities varied as a result of surface uplift and drainage reorganization throughout the timespan. Their approach to quantifying diffusive loss of He coupled with detailed petrographic investigation of the sample set is a marker going forward in this field of study.

In this study, we built on progress made by Wu et al. (2019) with multi-aliquot Fe-oxide (U-Th)/He dating and applied the method to a supergene weathering profile in the Attepe mining district, southern Turkey. This is the first attempt to absolutely date a Turkish weathering profile and may help to better understand the timing of tectonic events and climate change in the Cenozoic across Eurasia using Fe-rich weathering profiles.

2 Geological setting and samples

The 100 km² Attepe mining district lies at ~1500m above sea level in the west of the Eastern Taurus Belt, Kayseri-Adana region, southern Turkey (Kupeli 2010). It is one of Turkey’s most important Fe-ore deposits with reserves estimated at >70 mt at grades of 40%-58% Fe₂O₃; ~1 mt of Fe-ore is currently extracted per year (Kupeli 2010). Hosted in Lower-Middle Cambrian shallow-marine and dolomitic carbonates of the Caltepe fm and Mesozoic metaconglomerates of the Karakazolugu fm, Fe-ore occurs as fault controlled hydrothermal vein-type and its more abundant and economically more important supergene enriched weathering product. An uneconomic sedimentary Fe-sulphide mineralisation is reported in the Precambrian bituminous metapelites and metasandstones across the district (Kupeli 2010).

The deposit is concentrated on fault systems with carbonates and underlying metasandstones brecciated by multi-phase deformation imposed by Caledonian, Hersinian and Alpine orogenic events (Kupeli 2010).
Alpine event in the region are reported to have been active during Palaeogene-Lower Eocene times (Kupeli 2010). All mines show evidence of at least 2 generations of faulting with faults providing pathways for hydrothermal mineralizing fluid which are reported to have replaced carbonate host rock (Kupeli 2010). Almost all mining operations are concentrated in the oxidation zones which is composed of supergene enriched veins, lenses, and stocks up to 15m thick. Climate conditions during Alpine orogenic events and related hydrothermal mineralisation were conducive to supergene enrichment in the Balkans and western Turkey (Thorne et al. 2012) and supergene enrichment has been proposed from Eocene to recent times in the Archer mining district (Kupeli 2010).

11 samples from 5 mines have been supplied from the Attepe district for this study. 1 sample, S3, has been characterized using scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) before being analysed for ²³⁸U, ²³²Th, and ⁴He thus far with the ten expected to be analysed over spring/summer 2019. No stratigraphic constrains have been given for each sample making this study a pilot for future work.

3 Methodology

Sample S3 was characterized using SEM and XRD analysis. Several grains of goethite used for ²³⁸U, ²³²Th, and ⁴He determinations were hand-picked and homogenized. Gangue minerals were removed after 500µm, 250µm, and 125µm sieving stages before final gentle crushing to <38µm.

Aliquots of the homogenized crush were weighed into 5 x 2.5 mm Pt-foil tubes which were then crimped at both ends and placed into a degassed Cu pan and pumped to ~10⁻⁸ torr vacuum. Samples were spaced 10mm apart in the Cu pan to avoid cross-contamination during heating. No baking of the loaded pan prior to He analysis was undertaken to avoid partial degassing but the flexible stainless-steel appendage connecting the pan to the He purification line was baked overnight prior to He analysis to remove active gas species trapped on it. He was then extracted by heating each packet to 1000°C ± 30°C (determined by laser pyrometer) for 5 minutes by diode laser with liberated gas purified for 10 minutes by exposure to two liquid nitrogen-cooled charcoal traps. Effective degassing of samples was determined by repeating heating of sample as described. Reheats were <0.8% of first heat and comparable to an empty Pt tube subjected to the same heating procedure. ⁴He concentrations, along with hydrogen and methane, were determined by an electron multiplier in a Hidden HAL3F quadrupole mass spectrometer in static mode with procedures described in Foeken (2006).

U and Th concentrations were determined on separate aliquots from the same homogenized crush used in He determinations following ICP-MS methodology in Wu et al. (2019). Separate analysis of U-Th and He was done to avoid volatilization of U and Th during heating for He extraction.

4 Results

Optical microscopy and SEM analysis revealed a pervasive boxwork texture across S3 (Fig. 1). S3 was identified as goethite with botryoidal, prismatic, needle-like, and platy crystal morphology (Fig. 1). Crystallite were generally <0.1µm but reached up to 25µm in prismatic morphology (Fig. 1). XRD analysis shows homogenized crush used in He dating to be purely goethite (Fig. 2).

A preliminary (U-Th)/⁴He age and trace element concentrations for sample S3 is summarized in table 1. Standard error of the mean on multi-aliquot ⁴He concentration is 1.1% (n=4) and 1% for U atoms/g variability (n=5). Samples have negligible Th content and Th was not considered in final age calculations. (U-Th)/⁴He ages were calculated using average He and U concentrations.
The climate and tectonic evolution of the southern margin of the Central Anatolian plateau (smCAP) is intrinsically linked to the formation of the Attepe Fe-ore deposits. Thorne et al. (2012) suggest that, based on climate studies in current weathering zones, a weathering profile requires >1000 mm/yr precipitation, have cold month mean temperatures between 15 and 27 °C, and warm month mean temperatures between 22 and 31 °C to form. Modern climate records in the town of Kayseri at over 1 km elevation and ~120 km to the north of Attepe mining district shows an average of 385 mm precipitation/yr, cold month mean temperature between 6 and -1°C, and warm month mean between 14 and 21°C, therefore ruling out recent supergene enrichment (C.D 2019). However, climate conditions in western Turkey and the Balkans are suggested to have been in this range during the Middle Eocene (Thorne et al. 2012) and may have continued developing through the Middle Miocene climate optimum. Therefore, a transition from a conducive climate to the current cold-arid climate can be suggested to have occurred from Middle Eocene to recent.

By the Eocene, the same tectonism that led to the closure of the Neotethyan oceanic strip began uplift of what is now the Central Taurides on the smCAP and continued into Miocene times (Jaffey and Robertson 2005). Uplifted Neogene sediments and Quaternary fluvial terraces have been recorded in the Mut Basin, ~250 km SW of the Attepe mining district along the smCAP (Schildgen et al. 2012). Their results suggest multi-phase uplift along the smCAP with active phases between 8 and 5.45 Ma, 1.66 and 1.62 Ma and 1.6 Ma to present based on surface exposure ages of gravels on strath terraces. It could be suggested that these uplift events removed the Attepe mining district from the supergene enrichment zone to the preservation zone by lowering the local water table to allow for precipitation of goethite. However, by conducting a more detailed and stratigraphically constrained study, we may be able to correlate earliest supergene Fe-oxide mineralisation with the onset of uplift and climate change across a substantial area of southern Turkey.

On a more human level, the timing of goethite formation here is close to earliest examples of Homo dispersal from Africa across the Levant (now Syrian region) (Turner 1999). Tchernov (1992) has suggested that global changes in climate and aridification throughout the Pleistocene led to restricted movement in that area. By locating and dating other weathering profiles across Eurasia, the Balkans, and southern Europe, we may be able to build a picture of tectonic events and climate change which in turn may have affected the dispersal of our earliest ancestors across Eurasia.

4 Conclusion

Goethite from a weathering profile in the Attepe mine yielded a (U-Th)/4He age of 2.3 ± 0.03 Ma. Based on mineralogy and boxwork texture, this sample is indicative of supergene enrichment of a carbonate host which is consistent with local geology. We tentatively suggest that aridification across the smCAP is related to regional scale
uplift from at least the Pliocene which has in turn removed the Attepe mining district from a zone of supergene enrichment to a zone of preservation as seen today. This study cannot be conclusive since sample size is limited, stratigraphic information for samples is not given, and potential 4He loss by diffusion has not been determined. However, this may be the beginning of an attempt to develop the multi-aliquot goethite (U-Th)/4He method to provide valuable information regarding the tectonic and climatic history of localities with Fe-rich weathering profiles across Eurasia and beyond. Moreover, locating and dating other weathering profiles across Eurasia, the Balkans, and southern Europe may build a picture of tectonic events and climate change which in turn may have affected the dispersal of our earliest ancestors across Eurasia.

Acknowledgements

Marta and Domokos at SUERC for technical assistance and general helpfulness. Claire at University of Glasgow chemistry department for XRD assistance. Peter and Marli at University of Glasgow for SEM assistance.

References


Mineralogical and geochemical characteristics of alkaline phosphate ore from a supergene zone in the Catalão Region, Brazil

Sebastian Maak, Andreas Kamradt, Gregor Borg
Institute of Geosciences and Geography, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany

Abstract. Advanced tropical weathering of alkaline-carbonatite rock led to the accumulation of increased amounts of economically important minerals and elements - such as apatite, anatase, and rare earth elements within the supergene profile from the Catalão Region, Brazil. Whole rock geochemical analyses reveal a vertical zonation of the phosphate ore, trending from the alkali-rich least altered bed rock at the bottom of the profile to iron and titanium dominated areas in the uppermost parts of the profile. Due to multiphase hydrothermal and supergene processes, the initial mineral paragenesis of the parental rocks is not detectable any longer. The mineral paragenesis is dominated by siliceous matrix and iron hydroxides with different portions of apatite and magnetite. The least altered rock displays the lowest content in rare earth elements (REE) indicating an upward enrichment in REE within the supergene weathering profile.

1 Introduction

Alkaline-carbonatites are intrusive igneous rocks, which commonly contain abundant apatite, magnetite, barite, and fluorite, that may in turn contain elevated concentrations of rare earth elements, phosphorus, niobium, and other elements of economic importance. Alkaline-carbonatite intrusive complexes are structurally controlled by intracontinental zones of crustal weakness (Black et al. 1985). Deep weathering of these complexes occurs all over the world, being particularly intensive in tropical areas of Australia, Africa, and South America. In these regions, supergene decomposition and weathering stage. Thus, all the minerals described here, are strongly altered and only remnants of the original minerals were observed. Magnetite is one of the main gangue minerals occurring in various quantities in all parts of the profile as both euhedral and strongly altered crystals. Due to oxidation processes, martitisation took place, which is documented by fine-crystalline hematite within the magnetites. Commonly, exsolution lamellae of ilmenite, producing striae on lattice planes (111) are formed and are a further indication of intensive oxidation. Overgrowth of titanium rich phases such as ilmenite and anatase and slight dissolution features at the crystal edges also document the alteration processes.

Mica occurs as anhedral and mostly elongated crystals with normal and reverse pleochroism from white to pale yellow indicating the presence of iron. Especially large phenocrysts can be detected easily and were identified as phlogopite (Fig. 1). These phlogopites have a typical layered lattice structure and commonly display folding textures. In some thin sections, phlogopite constitutes the main silicate phase and in others a siliceous cement

2 Sample Materials and Methods

The light microscopic identification of primary minerals and their weathering products was carried out with a Carl Zeiss Axiophot polarisation microscope, combined with a Nikon Digital Sight DS-Fi2/DS-U3 analogue-to-digital converter.

For scanning electron microscopy (SEM), a JEOL JSM 6300 SEM equipped with an EDX-detector XFlash 5010 (Bruker, Billerica; USA) was used for imaging and mineral distribution analyses.

Chemical analyses of whole rock samples were made by a certificated laboratory (ALS, Ireland) using ICP-MS for rare earth and trace elements and ICP-AES for whole rock analyses.

A TerraSpec infrared spectrometer (ASD, USA) equipped with a contact probe was used for reflectance spectroscopy analyses. Infrared-spectroscopy uses energy potentials in the Visible Infrared (VIR, 400–700 nm), Near Infrared (NIR, 700–1300 nm) and Short-Wave Infrared (SWIR, 130–2500 nm) wavelength range of the electromagnetic spectrum to determine mineral compounds.

3 Mineralogy and Mineral Parageneses

The formation of the deposit was influenced by several hypogene hydrothermal processes and an intense supergene decomposition and weathering stage. Thus, all the minerals described here, are strongly altered and only remnants of the original minerals were observed. Magnetite is one of the main gangue minerals occurring in various quantities in all parts of the profile as both euhedral and strongly altered crystals. Due to oxidation processes, martitisation took place, which is documented by fine-crystalline hematite within the magnetites. Commonly, exsolution lamellae of ilmenite, producing striae on lattice planes (111) are formed and are a further indication of intensive oxidation. Overgrowth of titanium rich phases such as ilmenite and anatase and slight dissolution features at the crystal edges also document the alteration processes.

Mica occurs as anhedral and mostly elongated crystals with normal and reverse pleochroism from white to pale yellow indicating the presence of iron. Especially large phenocrysts can be detected easily and were identified as phlogopite (Fig. 1). These phlogopites have a typical layered lattice structure and commonly display folding textures. In some thin sections, phlogopite constitutes the main silicate phase and in others a siliceous cement
constitutes the matrix.

Iron hydroxides occur in all samples and overgrow the siliceous matrix but occur also as interstitial layers in phlogopite and other minerals.

Apatite occurs as sub-millimetre-size, oval-shaped, weathered aggregates with round edges with a greyish coating. Rare earth phosphates occur at the rim of the apatite as microcrystalline zones. Phenocrysts of apatite as well as magnetite display marginal embayments, indicating a magmatic origin, whereas dissolution cavities and fractures illustrate the influence of supergene weathering processes. Apatite is the main carrier of phosphate in the weathering profile and is also the currently mined ore mineral.

Cavities, which probably formed due to dissolution, are lined by secondary silica phases and crandallite group minerals (e.g. gorceixite) growing inwards in concentrically bands.

The main rare earth element carrier minerals are randomly distributed RE-phosphates occurring, among others, as cryptocrystalline agglomerates at the rims of apatite and intercalated in anatase and iron hydroxides. Barite, zircon, and pyrochlore are common accessory minerals in the lower parts of the profile.

4 Geochemistry

4.1 Major Element Geochemistry

The major element geochemistry of the weathering profile is presented and discussed using a ternary $P_2O_5 – (Fe_2O_3 + TiO_2) – (MgO + Na_2O + K_2O + CaO)$ diagram (Fig. 2). In this diagram two samples of the least altered rocks at the bottom of the profile plot closest to the alkali corner. Especially the sample from the bottom of the profile is characterised by high MgO-concentrations and low contents of $Fe_2O_3$, $TiO_2$ and $P_2O_5$. The samples in the hanging wall section show significantly higher CaO and $P_2O_5$ contents. A strong correlation between Ca and $P$ indicates that phosphate in this part of the profile is predominantly contained in apatite. Samples from between 67.70 m to 115.10 m display a trend towards the $(Fe_2O_3 + TiO_2)$ edge and a slight decrease of CaO and $P_2O_5$ compared to the deeper samples. The two uppermost samples from the profile feature the highest $Fe_2O_3$ and $TiO_2$ concentrations and a strong depletion in CaO and $P_2O_5$.

Geochemical data of major elements clearly illustrate a vertical compositional zonation with a trend from alkali-rich, least altered rocks towards iron and titanium dominated, more strongly weathered parts of the profile. The $SiO_2$ concentrations vary strongly from 24 wt-% to 44 wt-%.

4.2 Rare Earth Element Geochemistry

Chondrite-normalized REE distribution patterns (normalisation values from Boynton 1984) for the mean values of the different horizons are displayed in Fig. 3. The chondrite-normalised values range from between 5500 and 9000 for La to Yb values between 10 and 30, documenting the enrichment of light REE compared to heavy rare earth elements (HREE). For each horizon, the distribution pattern of the normalised rare earth elements is very similar as shown by the parallel patterns of the curves. These consistent patterns and the restricted variation of the La/Lu ratios (400-550) indicate only very minor REE differentiation during the supergene processes.

The least altered rock samples (127.40 m–132.00 m) display the lowest normalised REE values, which indicates an upward enrichment of the REE in the weathering profile. The chondrite-normalised values range from between 5500 and 9000 for La to Yb values between 10 and 30, documenting the enrichment of light REE compared to heavy rare earth elements (HREE). For each horizon, the distribution pattern of the normalised rare earth elements is very similar as shown by the parallel patterns of the curves. These consistent patterns and the restricted variation of the La/Lu ratios (400-550) indicate only very minor REE differentiation during the supergene processes.

The least altered rock samples (127.40 m–132.00 m) display the lowest normalised REE values, which indicates an upward enrichment of the REE in the weathering profile. Within the weathering horizons the CaO and $P_2O_5$ rich samples have the highest mean values of REE but the uppermost samples also display an enrichment in rare earth elements. This suggests that the distribution of rare earth elements is not restricted to specific horizons or geochemical environments but...
influenced by other parameters.

Figure 3. Chondrite-normalised rare earth element distribution patterns within the studied supergene profile (chondrite values from Boynton 1984).

5 Reflectance SWIR-Spectroscopy

SWIR-spectroscopy was carried out on 31 crushed and sieved (<1mm) sample splits representative of each profile section. All resulting reflectance spectra in the profile were generally marked by trivalent iron absorption in the NIR-region (910-930 nm), which was caused by the presence of goethite. Lowering absorption depths of the broad Fe$^{3+}$-absorption feature indicate that the content of goethite changes with depth. Thus, the content of goethite decreases with depth, so that the Fe$^{3+}$-absorption in the spectra changed from weak in the deep parts to more strongly developed towards the upper parts and the top of the profile. Goethite is commonly the dominant SWIR-active mineral in the upper intervals of the weathering profile. Vibrational bands in the upper five samples are markedly masked by the dominance of goethite so that the absorption depth of mineral bands increases clearly with depth from the sixth sample in the profile.

Spectra of the entire profile are characterised by vibrational absorption features generally caused by clay minerals and sheet silicates. Major absorption bands were detected at 1415 nm, 1910 nm, 2210 nm, and in between, whereas weakly developed absorption features were observed at 1750 nm, 2235 nm, and 2293-2298 nm.

Generally, the manifestation of the absorption features is subject to changes within the weathering profile, so that single bands seem to fade out in distinct samples. Dominant absorption features are caused by vermiculite, montmorillonite, and locally kaolinite. This mineral association shares the absorption feature at 1415 nm, whereas kaolinite and montmorillonite cause overtone vibrational bands at 2210 nm. Additionally, vermiculite spectra contain weaker absorption features at 1750 nm and 2295 nm. Simultaneous occurrence of minerals, which share wavelength positions are manifested by the general feature shape of the dominant mineral accompanied at least by an inflection or a weak absorption feature on the absorption band shoulders caused by an additional absorption through a further mineral.

Figure 4. Paragenesis of SWIR-active minerals according to their spectral occurrence and absorption intensity within the weathering profile.

Reflectance spectra of the base of the weathering profile shows exclusively vermiculite, whereas the footwall section up to 125.0 m is characterised mainly by the occurrence of montmorillonite and weak absorption of nontronite and/or kaolinite. From the depth of 110.0 m, the reflectance spectra are dominated a clay kaolinite-nontronite association, which is interrupted by a montmorillonite-dominated sample (107.5-105.5m). In the profile section from 105.5 to 97.9 m nontronite occurs in the upper part as the predominant clay mineral, accompanied by montmorillonite and traces of kaolinite, whereas the latter is dominant in the lower part of this profile section where montmorillonite disappears completely. Towards the top, the nontronite absorption intensity decreases up to 85.5 m, but represents - besides montmorillonite - a main clay mineral in this section with subordinate occurrences of kaolinite. Reflectance spectra of the intervals from 85.05 m to 70.0 m are characterised by absorption features caused mainly by montmorillonite, showing kaolinite inflection at the shoulders of the main absorption feature. SWIR-active minerals at the top of the weathering profile (70.0-64.5 m) are mainly goethite, and subordinately kaolinite.

6 Conclusion

The laterisation of an alkaline carbonatite complex from the Catalão Region led to the development of a supergene weathering profile with several well-defined horizons, which were identified by geochemical analyses, optical microscopy and SWIR spectroscopy.

The least altered rocks at the bottom of the profile display higher concentrations of alkali elements.
compared to the upper parts of the profile, indicating a different mineralogy and environment. Due to the inhomogeneity of the fresh bedrock a direct comparison of the least altered rock with the weathered horizons was not possible. Geochemically, the supergene processes are characterised by a general loss of Ca, Mg and K and simultaneous enrichment and accumulation of Fe and Ti. The oxidation Fe$^{2+}$ to Fe$^{3+}$ and the influence of meteoric water constituted the basis for the formation of goethite. Relatively increasing goethite content from the bottom to the top of the profile indicate an evolution from a hypogene alkaline to a supergene acidic environment. The destabilisation of the silicate phases and apatite led to the formation of secondary, hydrated Al-phosphates such as gorceixite. The leaching of Ca from perovskite may also had been important for the formation of titanium-rich phases as a consequence of alteration to anatase. Vermiculite occurs only in the lower parts of the profile and possibly originates from the alteration of primary phlogopite. In the upper portion of the profile vermiculite is not stable and could be an appropriate source of Al for the formation of secondary Al-phosphates. Nontronite has apparently formed in the profile as a pseudomorph replacement of pyroxene or alteration of phlogopite. The distribution of the rare earth elements is not restricted to specific horizons but the REE are more strongly concentrated in the weathered upper part of the profile. The enrichment of the REE has thus taken place in a typical supergene tropical environment.

Acknowledgements

We are grateful to Ceritech AG for providing sample material making this research possible and for approval to publish the data. This study was supported by the German Federal Ministry for Education and Research (FKZ: 033R187C) as part of the CAMONA project within the CLIENT II funding programme.

References

Rare-earth element contents of Kızıldağ and Kemiklitepe bauxite deposits, central Tauride, Turkey: implications for REE potential in bauxites

Bihter Hepvidinli, Nurullah Hanilçi
Istanbul University-Cerrahpaşa, Turkey

Abstract. The Kızıldağ and the Kemiklitepe bauxite deposits are located in the Bolkardağ bauxite province, which is the second most important Turkish province for bauxite production after Seydişehir-Akseki. The bauxite deposits in Bolkardağ province resulted from the lateritization of Lower-Upper Triassic shales. In the Bolkardağ region protolith, saprolite and bauxite transition processes are well observed and permitted to characterized the behaviour of the elements during bauxitization. The bauxite in this region consists of diaspor, hematite, goethite, anatase and magnetite, which developed between the Upper Triassic and Middle Jurassic (Aalenian). While the REE contents from protolith to bauxite decreased from the Kızıldağ bauxite (average 1017, 883 and 750 ppm for protolith, saprolite and bauxite, respectively), it increases in the Kemiklitepe bauxite (average 436, 424 and 1043 ppm) during bauxitization. This can be explained by the fact that the REE-bearing minerals have weathered and REE have leached during bauxitization in Kızıldağ, while in the Kemiklitepe deposit, the REE-bearing resistant minerals in the protolith were transported to bauxite. The Kızıldağ protolith resembles the Chinese clays mined for REE with respect to its mineralogy and REE content, and could be a potential REE source.

1 Geological background of Kızıldağ and Kemiklitepe Bauxite Deposits

The Bolkardağı province consists of three main tectono-stratigraphic units: The Bolkardağı Unit (BU), the Namrun Tectonic Unit (NTU) and the Aladağ Unit (AU). These three tectonic units overlapped with a compressional tectonic regime that began in the Late Cretaceous. All these three tectonic units include bauxite deposits. Kızıldağ and Kemiklitepe deposits are located within the Namrun Tectonic Units (Fig. 1).

The geology of the Kızıldağ bauxite zone is formed by Upper Permian Mizizia-bearing metalimestone (Karlığıntepe Fm.), the Lower-Middle Triassic calcschist (Kocatepe Fm.) and the Middle-Upper Triassic dolomitic limestone (Gökkandı Fm.).

In the Kemiklitepe deposit, the Upper Triassic metalimestone (Karagedik Fm.) and the Upper Triassic metashales are unconformably overlain by Middle Jurassic metalimestone (Tavşancıladağtepe Fm; Fig. 2).

2 Geochemistry

The thickness and lateral continuity of bauxite ore zones in the Kızıldağ and Kemiklitepe deposits is 5 and 15 m, and 100 and 400 m, respectively. Both deposits consist of mainly diaspor, hematite, goethite, magnetite, pyrite and anatase. The protoliths of both deposits are composed of quartz, amesite, chlorite, mica, pyrophyllite, illite, kaolinite, albite and calcite. The bauxites of Kızıldağ result from the transformation of Lower Triassic shales, while those of the Kemiklitepe from Upper Triassic shales. The bauxitization has been developed between the Upper Triassic and Middle Jurassic formations.
The average of Al₂O₃ contents in the Kızıldağ deposit are 27.32% in the protolith, 26.54% in the saprolite, 44.70% in the bauxite; SiO₂ values 46.43% in the protolith, 34.03% in the saprolite, 12.98% in the bauxite; mean Fe₂O₃ contents are 10.58% in the protolith, 24.05% in the saprolite, 26.51% in bauxite; and mean TiO₂ contens are 1.57% in the protolith, 1.77% in the saprolite and 2.76% in the bauxite. The average REE contents of Kızıldağ ore are 1016.7 ppm in the protolith, 883 ppm in the saprolite and 750 ppm in the bauxite.

The average Al₂O₃ contents in the Kemiklitepe deposits are 33.99% in the protolith, 46.38% in the saprolite, 56.28% in the bauxite; mean SiO₂ contents 41.48% in the protolith 28.16% in the saprolite, 2.84% in the bauxite; The average Fe₂O₃ contents are 10% in the protolith, 12.12% in the saprolite, 25% in the bauxite; the mean TiO₂ contens were 1.79% in the protolith, 2.20% in the saprolite and 1.88% in the bauxite. The mean REE value of the Kemiklitepe is 436 ppm in the protolith, 423 ppm in the saprolite, and 1043 ppm in the bauxite (Fig. 3).

During the bauxitization processes the REE were leached due to fluids of pH=6 where REE’s occur as free ions (Turner et al. 1981; Wood 1990). This process probably caused the decrease in REE content from the protolith to the saprolite and bauxite.

In contrast, the Kemiklitepe protolith contains fewer REE than the bauxite. The SEM data evidence the presence of zircons, and the Raman study evidence the presence of REE minerals such as Braitschite, cerianite, allanite and cebeate present in the Kemiklitepe bauxite. The higher ΣREE content of the Kemiklitepe bauxite relative to its protolith probably indicates that REE were present in the zircon, anatase and rutile which were not averted by weathering conditions. It is known that REE are present in the structure of zircon, monazite,apatite, anatase, ilmenite, sphene, and rutile minerals (Braun et al. 1990; some zircons contain up to 20 wt.% REE₂O₅; Nishida et al. 2010).

The average of U content of the Kızıldağ deposit for the protolith, saprolite and bauxite are respectively 12, 14, 19 ppm. At the Kemiklitepe deposit the U content are respectively of 24, 15 and 11 ppm. These values are higher than that of the continental crustal average (1–3 ppm; Cumberland et al. 2016; R. G. M. 1985; Fig. 3).

3 Conclusions

The Kızıldağ and Kemiklitepe bauxites are derived from the weathering of the Lower and Upper Triassic shales. The field relationship between the ore and the wall rock shows that bauxitization process developed between the Upper Triassic and Middle Jurassic. The REE content of the Kızıldağ protolith ranges between 241 and 3089 ppm, and at Kemiklitepe the bauxite contains between 543 and 2745 ppm. REE shows a positive correlation with Na, K, Be, Sr, U and Th in Kızıldağ protolith. At Kemiklitepe it has a positive correlation with Al, P and Ti. This relationship indicates that REE is involved in K, Ca, Mg-bearing minerals (possibly in feldspar, albite and chlorite) in Kızıldağ protolith, while REE are present in minerals resistant to weathering such as anatase, rutile and zircon in the Kemiklitepe protolith. On the other hand, the protolith of Kızıldağ have primary REE minerals, allanite and cerite not leached during the bauxitazion, these minerals also presence in the bauxite. At Kemiklitepe protolith, no evidence for primary REE minerals but in the bauxite the secondary REE minerals have occured during the process of bauxitization.

The ΣREE content of the Kızıldağ protolith and Kemiklitepe bauxite show at least a 1000-fold enrichment according to the NASC and Chondrites value (NASC: ΣREE = 173.2 ppm, Chondrite: ΣREE = 9.9 ppm (Lodders and Fegley 1997; Rudnick and Gao 2003). In terms of their mineralogical composition and REE content, the Kızıldağ protolith could be a REE potential when compared to the Chinese REE-bearing clays produced (average 1200 ppm).

Acknowledgements

This work was supported by Scientific Research Projects
References


Boynton W V. (2013) Cosmochemistry of the Rare Earth Elements: Meteorite Studies


Hydration of volcanic glass and genesis of perlite deposits based on oxygen and hydrogen isotope data

Peter Kodéra, Peter Varga, Peter Uhlík
Department of Economic Geology, Faculty of Natural Sciences, Comenius University, Slovakia

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

Anthony E. Fallick
Scottish Universities Environmental Research Centre, UK

Abstract. Perlite is an important industrial mineral, resulting from secondary hydration of silicic volcanic glass. In the Western Carpathians, there occur three economic deposits and several occurrences, hosted by Neogene volcanics. Chemical and isotopic compositions of perlites were studied for the purpose of understanding the mechanism of hydration of glass in perlites. Strong correlations between water content (expressed as loss on ignition - LOI), Na₂O, δ¹⁸O and δD were determined. Modelled isotopic composition of perlites in equilibrium with present day meteoric liquid and vapour indicates hydration with a significant proportion of vapour. Advanced hydration occurs in porous glass, where the vapour is able to penetrate tiny pores, which speeds-up the process of hydration. Hydration starts at elevated temperatures, but a higher degree of hydration happens by removal of alkali elements accompanied by exchange for diffusing ions of hydrogen at significantly lower temperatures. This probably occurs in geological settings that enable slow cooling so that the decreasing speed of diffusion with decreasing temperature is compensated by a longer time of opening of the system. The proposed model of perlite hydration was tested by modelling of perlite data from very different climatic conditions on New Zealand and in Yellowstone, USA.

1 Introduction

Perlite is the hydrated form of acid volcanic glass, originating by secondary hydration of primary obsidian that results from a quick cooling of degassed acid lava. Typical perlites have a characteristic onion-skin texture that is related to changes in volume during hydration. However, they also occur in the form of porous hydrated glass, which is a typical texture of perlites in the Western Carpathians. For industry, perlite is important for its ability to expand during a quick heating to 900–1200 °C with a 10- to 20-fold increase in volume. The reason for this phenomenon is the transition of hydrated molecular water (2–5 wt.% H₂O) into overpressured vapour accompanied by expansion of partially melted perlite grains. Due to the expansion, perlite obtains an extremely low density with a cellular texture.

This study is focused on determining the conditions of secondary hydration of volcanic glass in the Western Carpathians, especially using the combination of data on chemical and isotopic composition of perlites. The proposed genetic model was applied to similar data from perlites from volcanic systems in New Zealand (Lawless and White 2015) and in Yellowstone (Bindeman and Lowenstein 2016). Perlites from these systems have been hydrated just partially and they come from areas with a different climate and consequently with a different isotopic composition of meteoric water.

2 Methods

Analytical study was performed on perlite samples from the Central and East Slovakia Neogene Volcanic Fields (especially Lehôtka pod Brehmi and Jastrabá deposits) and their continuation in Hungary (Palháza deposit). All localities have a roughly similar age and composition of parental rhyolite magma and meteoric water in terms of their isotopic composition. For comparison, several perlite samples were also studied from New Zealand, as well as obsidian and rhyolite samples from East and Central Slovakia Neogene Volcanites, respectively.

Chemical composition of perlites was determined by silicate analyses in laboratories of Bureau Veritas Commodities Canada, Ltd. Water content was determined by loss on ignition at 950 °C for 4 hours.

For stable isotope analyses only perlites without phenocrysts were used (phenocrysts were removed by handpicking). Prior to analyses, perlites were crushed to a size <160 μm and 1–2 mg of each sample was heated to 150 °C for 12 hours to remove freely adsorbed water. The isotopic composition of hydrogen was analysed at the Earth Science Institute of the Slovak Academy of Sciences. Samples were heated here to 1000 °C by an elemental analyser for thermal decomposition of samples and subsequently hydrogen isotopic composition was measured using a mass spectrometer. Oxygen isotope analyses were performed in SUERC laboratories in Glasgow. Oxygen from perlites was released by reaction with ClF₃ during heating by a laser.

3 Results

3.1 Chemical composition of perlites

For the purpose of understanding the mechanism of hydration of glass in perlites, concentrations of selected
oxides of water-soluble cations (Na+, K+, Ca+) were correlated with water content in perlites (LOI). Binary diagrams show strong negative correlation of LOI with Na2O (Fig. 1), as well as with the Na2O/K2O ratio, but correlation with K2O and CaO contents was not observed or they are just weak, even though at individual localities perlites have different concentrations of these oxides.

**Figure 1.** Comparison of isotopic and chemical composition of perlites, obsidians and rhyolites from the Western Carpathians, New Zealand and Yellowstone. Lines highlight significant correlation trends. Diagrams include data from Lawless and White (2015) and Bindeman and Lowenstern (2016) from New Zealand and Yellowstone, respectively.

### 3.2 Isotopic composition of perlites

Oxygen and hydrogen isotopic compositions of perlites were compared with their chemical composition (Fig. 1). Significant trends of positive correlations were determined between δ18O values and water content (LOI) and between δD values and Na2O content. Contrariwise, strong negative correlations occur between δ18O and Na2O values as well as between δD and LOI values. Data from New Zealand and Yellowstone usually form different trends in the diagrams. Correlations of δ18O and δD with K2O and CaO contents were not observed.

### 3.3 Modelling of perlite hydration

In general, correlation of isotopic composition of hydrated glasses with their chemical composition is described just rarely in regional (e.g. δ18O with K2O; Cerling et al. 1985), or on microscopic scales (δD with H2O in core vs. margin of perlite grains; Bindeman and Lowenstern 2016). These correlations were explained by subsequent mixing of magmatic water in perlite (OH-) with hydrating water of meteoric composition. Our model calculations show that due to a very low content of OH- in perlites compared to hydrated water such mixing would form a hyperbolic rather than a linear trend in terms of δD values.

An alternative interpretation of the observed correlations could be related to changes in isotope fractionation with temperature. However, as hydrogen isotopes fractionate between glass and water in a kinetic way, the fractionation value remains constant despite changes in temperature (~32 ‰; Friedman et al. 1993) and thus the observed correlations cannot be explained just by temperature variation.

However, hydrogen isotope fractionation could be significantly influenced by the conversion of liquid water to vapour, which results in a significant isotope fractionation. In contrast to original water, vapour has significantly decreased values of both δD and δ18O, while the scale of fractionation strongly depends on temperature (at 80 °C: 37 ‰ ΔD and 5.9 ‰ Δ18O, at 40 °C: 62 ‰ ΔD and 8.2 ‰ Δ18O; Horita et al. 1995). Thus, it is possible to assume that an isotopically fractionated vapour could have participated in the hydration of glass. In order to test this possibility, we have modelled isotopic composition of perlites in equilibrium with meteoric liquid and vapour (Fig. 2). The position of analysed perlites in the diagram indicates probable temperatures of final isotopic reequilibration and relative amounts of liquid and vapour, participating in hydration. Their position between the lines of isotopic equilibrium between perlite and meteoric liquid (blue line) and perlite and vapour derived from the liquid (red line) indicates roughly similar participation of liquid and vapour at all studied localities of the Western Carpathians.
Figure 2. A. Isotopic composition of perlites from the Western Carpathians, shown in the diagram with modelled composition of perlites in equilibrium with meteoric liquid and vapour of variable composition at various temperatures, using the rhyolite-water fractionation factors of Zhao and Zheng (2003) and Friedman et al. (1993). Modelled composition of perlites is shown by isotherms, parallel to the meteoric water line (MWL), with highlighted composition of perlites in equilibrium with modern meteoric liquid and vapour (derived from the liquid). O-shift shows the possible change in oxygen isotopic composition of meteoric water due to the reaction with surrounding rocks. B. Detail from the diagram A including information on typical content of water in analysed perlites. Their position in the diagram indicates hydration with a significant proportion of vapour.

Furthermore, the less hydrated perlites (3–4 wt.% H$_2$O; Lehôtka, Palháza) show relatively higher equilibrium temperatures (45–65 °C) compared to more hydrated perlites (4–5.5 wt.% H$_2$O; Jastrabá; 30–45 °C).

However, the above modelling is influenced by various potential sources of error, such as possible change in oxygen isotopic composition due to reaction with surrounding rocks (O-shift), possible influence of oxygen isotopic composition in perlite derived from hydrated water, possible difference in closure temperatures for fractionation of oxygen and hydrogen, and possible influence of adsorbed free water.

4 Genesis of perlites in the Western Carpathians

The interpreted significant participation of vapour in the origin of perlites in the Western Carpathians can be related to their very porous texture that could enable an easy penetration of hot vapour compared to liquid water. This is further supported by an order of magnitude lower viscosity of vapour compared to aqueous liquid and the absence of surface stress. In this way the vapour could have speeded up hydration of glass and to achieve advanced hydration. Perlite porosity studies using computer tomography have shown that pores are mostly interconnected, which lowers the necessary depth for complete hydration of glass to just tens to hundreds of micrometres (Varga et al. 2019). Vapour could have also prevented rapid quenching of glass to a non-hydrated or weakly hydrated obsidian.

In several of the studied localities, hydration with a significant proportion of vapour is indicated by the geological setting, where the contact with liquid groundwaters could be only limited. For instance, at the Jastrabá deposit perlite is developed on the bottom of a rhyolite flow, sitting on permeable volcanoclastic rocks (Zuberec et al. 2005). At the Lehôtka pod Brehmi deposit perlitisisation affected a permeable extrusive breccia pipe that formed a bold morphological elevation (Lexa and Pošteková 2012). Around the world, the majority of perlite deposits have experienced hydration by meteoric water close to the surface of extrusive bodies (Barker and Santini 2006).

As the water saturation in glass increases with decreasing temperature (Duan 2014), the higher amount of water in perlites can be explained by hydration at relatively low temperatures, which is also indicated by our stable isotope modelling of hydration. However, a decrease in temperature also causes a significant decrease in the speed of diffusion of water in glass, therefore it is necessary to assume that perlitisisation occurs just in magmatic bodies with sufficiently long cooling times and with contact with heated meteoric water, especially in the form of vapour.

Based on the observed correlation of Na$_2$O content with the content of hydrated water in perlites it is possible to assume that the removal of sodium occurs by exchange for diffusing ions of hydrogen. Because the isotopic modelling has shown that more hydrated perlites originated at lower temperatures, it is probable that this process needs relatively low temperatures and the system must be open for diffusion of water for a relatively long time. So, the glass hydrated initially by low amount of water at higher temperatures can be further hydrated subsequently. This is also supported by the fact that the diffusivity of molecular water in glass increases exponentially with the total water concentration in the glass (Zhang and Behrens 2000).

5 Modelling and genesis of perlites from areas with different climates

In order to test the proposed model of perlite hydration we processed and modelled perlite data from very different climatic conditions in New Zealand and Yellowstone, which result in different isotopic compositions of local meteoric waters (relatively heavier and lighter compared to the Western Carpathians).

For the New Zealand perlites the analytical points in the model diagram indicate significantly higher temperatures of final reequilibration (~95 °C), but with a similar liquid/vapour ratio compared to Western
Carpathians perlites. Chemical analyses of these perlites showed a lower content of water (2.0–3.4 wt.%), while no decrease in Na2O or K2O was observed, except for the sample with the highest water content (Na2O depletion by 0.5 wt.%). Typical of New Zealand perlites is the presence of non-hydrated cores in perlite grains. The above features are probably the result of a relatively quick cooling with the absence of low-temperature hydration and late-stage isotopic re-equilibration.

For the Yellowstone perlite modelling it was necessary to consider the presence of extremely low 5D water from the surrounding glaciers. Bindeman and Lowenstern (2016) have shown in local perlites the presence of weakly hydrated cores with a significantly heavier isotopic composition compared to local meteoric water. The analytical points in the model diagram indicate a predominantly liquid water source of hydration, but the isotopic equilibrium was probably not achieved. The isotopic composition could have been significantly influenced by the composition of less hydrated cores of perlite grains, especially in samples with a low total amount of water. Rare more hydrated samples (up to 5 wt.% H2O) have the lowest values of δ18O and δD, which again is indicative of hydration by increased participation of vapour with final isotopic reequilibration at ~50–60 °C. Less hydrated samples indicated higher temperatures (up to 80 °C) but without significant contribution of vapour, or the isotopic equilibrium was not reached. The participation of glacial water on hydration appears to be unlikely.

6 Conclusions

The research on stable isotope composition of perlite from Western Carpathians deposits has shown that hydration of glass was probably caused by a mixture of hot meteoric liquid and vapour. Advanced hydration occurs in porous glass, where the vapour is able to penetrate even into the tiniest pores, which speeds-up the process of hydration. Hydration starts at elevated temperatures, but stable isotope data can record just the final isotopic equilibrium (if it was reached). It is likely that to achieve higher degrees of hydration, some removal of alkali elements is necessary accompanied by the exchange for diffusing ions of hydrogen (Na in case of W Carpathians perlites), while the intensity of this process is directly proportional to the decrease of temperature of final hydration. This probably occurs in geological settings that enable slow cooling so that the decreasing speed of diffusion with decreasing temperature is compensated by longer time of the system being open. Furthermore, the increasing amount of water in glass increases the speed of diffusion of water.

This model of hydration of perlites can be applied also to other perlite deposits and occurrences in the world, but in the case of weakly hydrated perlites it is necessary to consider disequilibrium states due to the presence of non-hydrated cores of perlite grains.

Acknowledgements

This work was funded by grants APVV-0339-12, VEGA-138-15 and the company LBK PERLIT, s.r.o.

References


Study of stable isotopes as a proxy for emerald exploration in the Western Emerald Belt, Colombia

Gabriel F. Nino Vasquez and Sheng-Rong Song
National Taiwan University, Taiwan

Abstract. Colombian emerald exploration is difficult, unpredictable and still very empirical. Therefore, complementary methods are necessary to discover new deposits. The study of the fractionation of stable isotopes was tested not only to identify the main source(s) and the evolution of the fluid(s), which caused the formation of emeralds, but also to establish numerical anomalies, inferring a more or less reactive fluid-rock interaction in order to precipitate emerald. Working towards establishing this analytical tool in the Colombian emerald reservoirs, 37 carbonate samples were collected from seven mines for δ¹³C and δ¹⁸O analyses. The study shows ranges of values between 18 and 21.8‰ SMOW δ¹⁸O and -4 to -10.3‰ PDB δ¹³C for hydrothermal fluids, which led the emerald mineralization for the visited mines. 33 shale and pyrite samples were collected from 6 mines for δ³⁴S, the results show that samples ranging between 11.2 to 29.7‰ (VCDT), suggest an evaporitic origin, with a hydrothermal process involved. On the other hand, sedimentary pyrite and shale without hydrothermal signs vary in a range between -12.6 to -5 % δ³⁴S (VCDT), inferring area without emerald mineralization, since this mineral is a by-product of hydrothermal events. Field geology, petrography, Raman and SEM-EDS analyses were complementary in order to characterise mineral associations and their corresponding habits.

1 Introduction

The Colombian emerald deposits located in the Eastern Cordillera are located in two parallel belts which are separated by around 110 km. These deposits are known worldwide due to their high quality and unique geological environment (Giuliani et al. 2019).

The ores hosted in Lower Cretaceous shales and limestones are mostly emplaced in stock-work veins, hydrothermal and hydraulic breccias (Giuliani et al. 2019).

The study of the fractionation of stable isotopes is commonly used in order to identify the main source(s) and evolution of the fluid(s), which caused the formation of different ore deposits (Ohmoto and Goldhaber 1997; Taylor 1979). This geochemical method is an important tool to define the effectiveness and reactivity of the rock-fluid interaction incorporating or leaching elements from the host rock in order to precipitate different hydrothermal minerals at a later stage. In addition, the temperature of a mineral association is possible to calculate using this method.

On the other hand, stable isotope fingerprinting can be used as a complementary exploration method (Engel et al. 1958; White et al. 1990), since numerical anomalies can infer a more or less reactive fluid in the system. Furthermore, previous researchers demonstrated that stable isotope ratios are altered in rocks surrounding orebodies compared to rocks unaffected by hydrothermal alteration, meaning that stable isotope alteration halos can be delineated (Barker et al. 2013). Analyses of δ¹³C and δ¹⁸O, for exploration purposes, have been used mostly in copper, epithermal gold ore and carbonate-hosted mineral deposits (Vasquez et al. 1998).

The analysis of stable isotope fractionation has been applied to Colombian emerald deposits previously, but only with the purpose of determining the composition of the fluid that interacted with the host rocks (Giuliani et al. 1995; 1997). Also, there is an article by Giuliani et al. 1998 where the authors analyse δ¹⁸O in emeralds to determine the geographic origin of the green beryl. However, this tool has not been implemented as an exploration method before the current research. It is important to highlight the necessity to complement it with other geological and geochemical analysis in the potential zone (i.e. mineralogical association, suitable tectonic and hydrothermal zones, Na enrichment and depletion of Li, K, Be, and Mo in the host rocks (Beus 1979), high REE content in the hydrothermal veins (Mantilla et al. 2007), proper spaces originated by structures to lead emerald precipitation, etc).

The aim of this study is to propose a stable isotope range (δ¹³C, δ¹⁸O and δ³⁴S) for exploration purposes in the Western Emerald Belt in Colombia, and establish the nature of the fluid within the deposits.

2 Regional geology settings

The Western Emerald Belt (WEB), located on the western side of the Eastern Cordillera basin, contains a complete lithological record of Cretaceous transgressive sedimentation. Within a facies distribution scheme, the sedimentary subsidence must have played an important role along the distending faults that are currently manifested in reverse or transcurrent regional faults, due to a tectonic inversion. These manifestations are in both NE and NW orientations (Reyes 2006).

In the study area, Lower Cretaceous sedimentary rocks are outcropping. The mudstone and shale-rich composition of the units influences the tectonic deformation of the rocks by their ductile behaviour, and generates intense folds and faults, which are not easy to recognize. The folding is notorious at regional and local scale. The anticlines that separate them are not well defined and they present very sharp closures, tight and generally asymmetric (Reyes 2006).

The geological formations in the area are mostly
sedimentary, which present lateral changes in the lithology. The emeralds in the WEB in Colombia are hosted in the Rosablanca and Paja Formations. However, for the current study, the samples were collected from seven mines located in Paja Formation. The mines were divided in 5 different groups according to their geographic location for a better analysis (Fig. 1). Lithologically speaking there are calcareous and non-calcareous series of mudstones, shales and siltstones from the Hauterivian-Barremian (Reyes 2006). The most important feature in these units, which is crucial when exploring emeralds, is the obvious metasomatism suffered by the rock by highly reactive fluids, which were able to leach and transport major elements and trace elements to finally precipitate emerald, pyrite, carbonates, phosphate, etc.

3 Geological observations for emerald exploration in the Western Emerald Belt

The following are, among others, the most important field geological criteria to be considered in order to delimit areas with emerald potential. These observations were necessary in order to define productive and non-productive carbonates for further isotopic analysis.

3.1 Tectonic and hydrothermal structures

The emerald mineralization in Paja Formation is related to a very strong metasomatism of the black shales caused by the alkaline and saline fluids expelled by compressive tectonics in the Paleogene (Mora et al. 2006; Horton et al. 2010; Branquet et al. 1999). This process is known as the thermal-reduction of the sulphate at 300–330°C due to the organic matter in the black shale (Giuliani et al., 2019; Ottaway et al. 1994; Cheilletz et al., 1996). The fluid was driven by thrust faulting, and due to the pressure: hydraulic breccia (Fig. 2), stockwork veins, geodes and hydrothermal breccias were developed. The shale shows albitization and carbonization which, in a meteoric stage, is altered to kaolin. On the other hand, tight recumbent, asymmetrical and overturned folds are common in the area due to an active tectonic zone. Thus, hydrothermal alteration in the shale and the development of spaces for the further precipitation of emeralds and the set of minerals, which come from it are necessary to be recognized in the field for prospecting purposes.

3.2 Mineralogical assemblage

According to field, microscopic and geochemical observations, the most common minerals associated with emeralds are dolomite, ankerite, calcite, albite, and pyrite. Other less common mineral indicators are siderite, apatite, fuchsite, muscovite, pyrophillite, euclase, barite, etc. However, the presence of those minerals does not necessarily mean the presence of emerald. All the mentioned minerals are emplaced in veins, breccia or within the black shale.

According to Cheilletz et al. (1994) two generations of calcite are distinguished: (i) an early fibrous calcite, and (ii) a later rhombohedral calcite and dolomite associated with emerald. (Fig. 3). However, in the field were recognizable other habits for the carbonates such as rhombohedral elongated and geodes where the spaces are bigger and there is growing of the crystal from outside to the centre of the cavity.

4 Stable isotopic results
4.1 $\delta^{18}$O and $\delta^{13}$C carbonate compositions

37 carbonates from 7 mines along the WEB were analysed in order to determinate $\delta^{18}$O$_{\text{H}_2\text{O}}$ and $\delta^{13}$C$_{\text{CO}_2}$. The assumed temperature for these calculations was 320°C, an intermediate temperature previously measured by Cheilletz et al., 1994 and Mantilla et al., 2007 who studied primary fluid inclusions in calcites and emeralds. The isotopic composition of water ($\delta^{18}$O$_{\text{H}_2\text{O}}$) in equilibrium with carbonates was calculated using Kim, S.-T. & O'Neil, J.R. (1997) and, the isotopic composition of carbon dioxide ($\delta^{13}$C$_{\text{CO}_2}$) in equilibrium with carbonate was calculated using Ohmoto y Rye (1976) formula.

$\delta^{18}$O show values ranging between 17.54 and 25.05‰ in V-SMOW standards. The values are very positive and suggest that magmatic reservoirs were not involved, instead suggesting sedimentary and metamorphic origins (Rollinson, 1993).

On the other hand, the composition of $\delta^{13}$C for the same samples vary in a range between -7.49 to 1.91‰ in V-PDB standards. Both equilibrium and kinetic processes control the fractionation of carbon isotopes. In many cases, the fractionation of $\delta^{13}$C is strongly temperature dependent. However, dissolution and represcipitation processes do not fractionate carbonates (Rollinson, 1993).

The original isotopic composition of the samples for each mine were plotted in a diagram $\delta^{13}$C (PDB) vs. $\delta^{18}$O (SMOW) (Rollinson, 1993) which shows the isotopic composition of a number of different carbonate reservoirs. (Fig. 4). All the samples show a sedimentary/metamorphic origin, discarding any magmatic influence. However, it is possible to identify two different groups according to the collected data; for group 2, which include a group of mines producing more emeralds than the others do, $\delta^{18}$O shows higher values, which means that the fluid is not homogeneous along the belt in composition and/or temperature.

![Figure 4. $\delta^{13}$C (PDB) vs. $\delta^{18}$O (SMOW) composition of the 37 carbonates from WEB mines in different carbonate reservoirs. Modified from Rollinson, 1993.](image)

4.2 $\delta^{34}$S composition of pyrite and shale

The results gathered from our analyses demonstrate that hydrothermal pyrites and shales range from 11.2 to 29.7‰ (VCDT) and suggest an evaporitic origin for the fluid, thus these are interesting areas for exploration. On the other hand, -12.6 to -5 ‰ (VCDT) suggest a sedimentary origin for pyrite and a non-metasomatized shale, which implies no emerald occurrence in these sectors (Fig. 5). The results confirm a non-magmatic influence in the hydrothermal process.

![Figure 5. $\delta^{34}$S isotopic signatures for shale and pyrites in different locations at the WEB. Modified from Rollinson, 1993.](image)

5 Discussion and conclusions

The $\delta^{18}$O and $\delta^{13}$C results in carbonates clearly shows two different clusters for the WEB, where Group 2 is independent from the other ones (Fig. 4). That difference means and heterogeneity in the fluids along the same emerald belt, which can be influenced by changes in temperature or fluid/rock composition. These differences directly affected the hydrothermal system in the area affecting emerald precipitation in different sectors.

For exploration purposes and according to the productivity classification of each sample, to geological observations and emerald occurrences associated to the carbonates analysed in this research, the productive and non-productive samples from all the mines were plotted in a $\delta^{13}$C (PDB) vs. $\delta^{18}$O (SMOW) figure (Fig. 6). For exploration purposes: A range between 18 to 21.8 ‰ for $\delta^{18}$O (SMOW), and -4 to -10.3‰ for $\delta^{15}$C (PDB) represent the isotopic signature of the hydrothermal fluids which led to emerald mineralization for the visited mines. Therefore, any calcite coming from hydrothermal veins from the Paja Formation in the WEB, with an isotopic value close to this...
range of values, and with the appropriate geological setting has the possibility of being associated with emeralds.

At the same time, pyrites and shales in an 11.2 to 29.7‰ (VCDT) isotopic range suggest a hydrothermal source for their formation, which means a complementary proxy for exploration purposes in the WEB.

Acknowledgements

Firstly, Gabriel Nino Vasquez recognizes the effort and support of his tutor, Dr. Song and the National Taiwan University. To the EMEX research group for its commitment and solidarity in the development of our projects around the understanding of the formation of the Colombian emerald. Finally, in the same way to CDTEC team who have been helpful in logistic and professional support for future publications.

References


Photoluminescence analysis to determine the origin of emeralds from the Eastern and Western belts in Colombia


Abstract. Photoluminescence spectra were collected from 84 crystal emeralds (71 from Colombia and 13 from Afghanistan and Zambia) in order to characterize their spectral fingerprint and to determine their origin: (i) either the Eastern or Western emerald belts for Colombian ones, and (ii) from the different worldwide emeralds. The wavelength between 683 and 685 nm is the key to differentiate emeralds through two current peaks called R–lines, which correspond to a metastability doublet of the chromium ion when the sample is excited. The photoluminescence in the emeralds is generated from trace chromium impurities.

The origin–dependent nature of these variations may be helpful to identify geographic origin. The differences between R–line wavelengths and corresponding trace element concentrations, revealed strong correlations between peak position change of the R1 peak, and chromium and iron concentrations.

In the two Colombian emerald belts, differences in the chemical composition of the host rocks i.e., black shales and the mineralization tectonic setting, have an impact on the emerald chemistry. These chemical differences are exploited through several techniques such as LA–ICP–MS to determine the origin of emeralds.

1 Introduction

Emerald is a gem variety of beryl (Be$_2$Al$_2$Si$_6$O$_{18}$). In Colombian emeralds, the colour is due to the presence of trace elements such as chromium, vanadium and iron (Schwarz and Schmetzer, 2002). These elements absorb part of the visible spectrum and this absorbed energy emerges again as a luminescence phenomenon. For the case of chromium, this is known as the spectral band related to chromium. This photoluminescence (PL) spectrum, where the emissions seen, are known as lines R: $R_1 = 683$ nm and $R_2 = 680$ nm, result from the substitution of Al$^{3+}$ by Cr$^{3+}$ in the octahedral site of the beryl structure (Nassau, 1978).

Previous works have correlated the chemistry of the preparations with the photoluminescence spectra. Moroz et al. (2000) suggested that substitution of aluminum by iron and magnesium which is common for emerald in schist–type deposits, changed the position of the peaks in the spectra, and in consequence could be used to differentiate emeralds from different environments. For instance, Thompson et al. (2014; 2017), carried out two different kinds of research in Colombian–type environments. In the first one, he realized that the changes in the R1–peak are generated by the concentration of silicon in the crystal, where substitutions of impurities or crystalline defects can occur in the silicon position. Aurisicchio et al. (1988), through X–ray diffraction, did not find any evidence of such substitutions; and Schmetzer (2015), reported that the change in silicon concentration could arise from some accumulations in the aluminum, which would produce incorporation of another element generating the changes in the R1–peak. In addition, Thompson et al. (2017), concluded that there is a strong correlation between high magnesium and sodium contents with longer wavelengths in the spectrum for the R1–peak in emeralds belonging to schist–type, while the opposite case happens for emeralds with low concentration of these elements, which belong to other types of environments, such as Colombian–type with shorter wavelength values.

Previous research using photoluminescence applied to different emeralds worldwide has not seen a difference between emeralds from the Eastern and Western Colombian emerald belts.

In this paper, we present for the first time using photoluminescence spectra, differences between emeralds from the two Colombian belts and their incidence on the determination of origin.

2 Geological setting

Colombian emerald deposits are geologically remarkable because of their occurrence within sedimentary rocks of the Eastern Cordillera (Fig. 1). The mineralization takes place along two parallel belts located on the external flanks of the cordillera. In the Eastern Belt, the emerald–bearing veins are hosted by a stratiform brecciated level predominantly composed of grey albites. The mineralization occurred at 65–67 Ma, and is controlled by an extensional structural style (Branquet et al. 1999). In the Western Belt, the mineralized veins and breccias are hosted by organic–rich black shales. They formed at 38 Ma during compressional tectonic events (Cheilletz et al. 1994).

The Colombian emeralds are found in hydrothermal breccias and veins hosted by strongly altered (albitized and carbonatized) lower Cretaceous marine rocks and the veins are mostly made up of calcite, dolomite, albite, siderite, and pyrite. In both Colombian emerald belts, there are striking differences in the composition of the host rocks, the geological age and tectonic setting of the mineralization. These differences imprint on the emerald a fingerprint with which is possible to determine its origin.

3 Analysis and samples

84 emerald crystals were selected as follows (Fig. 2): 71 from Colombia (28 samples from Palo Arañado and
Oriente mines, Chivor mining district in the Eastern Belt; 43 from the Amarillal, Palo Blanco, and Catedral mines in the Muzo mining district in the Western belt; and 13 from deposits in Zambia and Afghanistan.

![Figure 1](image1.png)

**Figure 1.** Geological map of the Eastern cordillera in Colombia. The emerald deposits are hosted in Lower Cretaceous series along two belts located on the external flanks of the Eastern cordillera basin, trending NE–SW. In each geological section the locations of the studied emerald mines are shown.

Using a Horiba LabRAM HR Evolution equipment, with an acquisition time of 5 s, accumulations of 10 scans, a wavelength range from 660 to 700 nm, objective plan N 10x / 0.25 ∞ / - / FN22, reflection grid 1800 gr / mm, resolution 0.025 nm, laser 532 nm, laser power 250 mW, power of excitation 0.5 mW and hole 100 μm.

Chemical analysis of each emerald were performed through Laser Ablation Inductively Coupled Plasma Mass Spectrometry LA-ICP-MS at the Center of Excellence in Mineral Resources (CODES) of the University of Tasmania, Australia.

**4 Results**

Examining R–lines extracted from the Photoluminescence spectra of each emerald, we can see that the R1–peak belonging to the Eastern Colombian Emerald Belt samples, sits on the shortest wavelength, while the Western Emerald Belt samples line sits on a longer wavelength, and the Zambian and Afghanistan samples line sits on the longest wavelength.

The Colombian emeralds range between 683,400 and 683,800 nm. Those samples belonging to Afghanistan are between 683,900 and 684,100; while those of Zambia
range between 684,090 and 684,500. Finally, for the two Colombian belts, a clear difference is marked at 683,650 nm, which allows differentiation of the origin between the Eastern Belt and the Western Belt (Fig. 3).

Figure 3. Photoluminescence spectra of emerald samples from both Colombian Emerald Belts. a. Eastern belt, b. Western belt. c. d. Spectra of emerald samples from other countries: Afghanistan and Zambia. The curves from the Colombian emerald samples are shown with a higher intensity (purple and blue lines), while curves from Afghanistan and Zambia appear lower (red and green lines).

Regarding the intensity, Nassau (1978), mentioned that the presence of Fe inhibits or dissipates the chromium photoluminescence emission. Considering the LA–ICP–MS data obtained on Colombian emeralds in the present work, it appears that the Fe contents in emerald from the Western Belt are between 333 and 488 ppm, while for the Eastern Belt they are between 133 and 170 ppm. The Cr contents for the Western Belt are between 702 and 950 ppm, while for the Eastern Belt they are between 930 and 2100 ppm. That is to say, we found more Cr and less Fe in the Eastern Belt, and lower amounts of Cr and greater amounts of Fe in the Western Belt. This feature is related to the change in the intensity of the R1–peak observed in the spectra. For the Colombian emeralds from the Eastern Belt, it is reached up to 18,000 counts per second while those from the Western Belt, it can reach just 3,000 counts per second (Fig. 3).

Additionally, the relationship described for emeralds of the two belts with respect to (i) the concentration of the two elements, (ii) the Cr/Fe ratio, and (iii) the position of the R1–peak that can be compared at the position 683.650 nm (Fig. 4).

Figure 4. A plot of each sample displaying R1 maximum peaks wavelength vs. concentration. a. b. Eastern Emerald Belt samples (circles) with high Cr concentrations and low Fe concentrations, exhibit shorter wavelengths, while Western Emerald Belt samples (diamond) with low Cr concentrations and high Fe concentrations, exhibit longer wavelengths (upper and centre). c. Cr/Fe ratio vs R1 exhibit different fields recognized in the photoluminescence spectrum (bottom).
5 Concluding remarks

From photoluminescence spectra collected perpendicular to the c-axis of several emerald samples (both Colombian Emerald belts), we found that locating the peak wavelength position of the R1-peak can help to determine the origin and also indicate whether a natural emerald belongs to one of the two Colombian Emerald belts. Measurements of Cr and Fe concentrations in emeralds display differences in their origin. As a result, we suggest that crystal substitution of Al sites by Cr and Fe may be responsible for changes of R1-peaks to longer wavelengths between 683 to 684 nm.

Although the location of the wavelength has been taken by other authors to reflect a relation with the concentration of other non-chromophore elements that can be present in the mineralizing system; we wanted to investigate the influence of two of the elements that affect the colour of the Colombian emeralds. We found a correlation between Cr and Fe: the highest concentration of chromium correlates with lower iron contents for emeralds of the Eastern Colombian Belt versus a low concentration of Cr and high of Fe for emeralds of the Western Colombian Belt. The key factor is the influence of the R1-peak position, with a comparison point around 683.650 nm, with different intensity, with which the origin can be determined for the two most important producing areas in Colombia.

Acknowledgments

We gratefully acknowledge the National Emerald Federation (FEDESMERALDAS) for financial support. Additionally, we want to thank the members of the Colombian emerald industry, who supported this research.

References


