The 13th SGA biennial meeting is organized by the CNRS, and a group of French, Belgian and German universities (Nancy, Liège, Aachen and Louvain).

The theme for this 13th edition is “Mineral Resources in a Sustainable World”.

The SGA was founded in 1965 in Heidelberg and the 2015 SGA biennial meeting will celebrate the 50th anniversary of the Society.

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Cover photograph: Artisanal mining in the basement (Dabolava area, Madagascar) (O. Vanderhaeghe)
From **Source, Transport and Metal deposits**…
…to **Mineral Resources in a Sustainable World**

The first biennial meeting of the Society for Geology applied to Mineral Deposits took place in Nancy in 1991, and some of the present day participants were certainly already some of the first actors of the 1st biennial SGA meeting, dealing with the basics of metallogeny: "**Source, Transport and Metal deposits**".

The 13th SGA-meeting is hosted again in Nancy 2015 to celebrate the 50th anniversary of the society. Growing economy results in a global increase in demand for mineral raw materials, which have to be supplied in a reliable but also responsible way to meet all requirements of a sustainable world: this justifies the focus of the 2015 meeting: "**Mineral Resources in a Sustainable World**".

International research on mineral deposits and related topics is presented and discussed within 16 scientific sessions, 5 symposia and 8 plenary sessions. Field trips with various destinations between Poland and Morocco offer excellent opportunity to discover the metallogeny of Europe and northern Africa.

The 13th biennial meeting of the SGA is organized by CNRS (Centre National de la Recherche Scientifique) and a consortium of Universities, including the Université de Lorraine in Nancy, the KU Leuven, the Université de Liege and RWTH Aachen University representing the regions of Lorraine, Flandres, Wallonie and North-Rhine-Westphalia along the borders of France, Belgium and Germany, regions that still express significant historical heritage of both coal and iron mining activities.

The five volumes of these proceedings present 518 extended abstracts over 2134 pages, e.g. the state of the art all along the entire spectrum of scientific topics from economic geology to mine environment and geometallurgy. These abstract volumes give also an expression of the high scientific quality of the 13th SGA-meeting. We would like to express in this foreword our sincere gratitude to the local organizing committee with the scientific, technical and student staff. We also thank warmly all the conveners of sessions, workshops and excursions, and all who made this meeting possible by their tremendous work during the last months.

August 2015

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Session 12

Gems and industrial minerals

Colombian Emeralds and Evaporites: Tectono-Stratigraphic Significance of a Regional Emerald-Bearing Evaporitic Breccia Level .................................................................1291
Yannick Branquet, Gaston Giuliani, Alain Cheilletz, Bernard Laumonier

Crystal Structure of Mineral Yushkinite ......................................................1295
Tatiana L Evstigneeva, Svetlana V Sobol

First Evidence of Green Quartz Related to a Polymetallic Ore Deposit in Argentina ..........1297
Juan Manuel García, Diana Irene Mutti

Chromium Pyropes from Bohemia: Characterization and Identification in Archaeological and Historical Jewellery .................................................................1301
Albert H Gilg, Norbert Gast, Jaroslav Hýrl

A Stable-Isotope Investigation of the Origin of Emeralds from the Ianapera Deposit, Madagascar .................................................................1305
Gaston Giuliani, Stefano Salvi, Didier Bezat, Prosper Andrianjakavah, Anthony Fallick, Amos Fety Michel Rakotondrazafy

Geologic Setting of Complex Pegmatites South-East of Embu, Central Kenya .................1309
Daniel Ichang’i, Gaston Giuliani, Jean-Emmanuel Martelat, Kamau Gachigi

U/Pb Ages of Zircon and Monazite from the Tsavorite-Bearing Neoproterozoic Rocks of Southeastern Kenya, and the Significance of Static Crystallisation of the Tsavorite .................................................................1311
Jean-Emmanuel Martelat, Gaston Giuliani, Daniel Ohnenstetter, Valérie Bosse, Jean-Louis Paquette, Edward Omito, Daniel Ichang’i, Christopher Nyamai, Abigail Wamunyu, Patrick Monié

Comparison between Sapphire Deposits in Kenya, Tanzania and Tanzania: a Case Study of the Dusy, Andranondambo, Umba Valley .................................................................1315
GM Mung’atia, DW Ichang’i

The Boron Isotopic Composition of Tourmaline from Tsavorite Deposits in the Neoproterozoic Mozambique Metamorphic Belt, with a Special Focus on the Mining Districts in Kenya .......1319
Gaston Giuliani, Daniel Ohnenstetter, Claire Rollion, Julien Feneyrol, Jean-Emmanuel Martelat, Edward Omito, Daniel Ichang’i, Christopher Nyamai, Abigail Wamunyu

Indicator-Based Characterisation of Kaolin Deposits .............................................1323
Luke W Palmer, Hylke J Glass

Red Spinels and its Deposits .................................................................1327
Vincent Pardieu

Mineral Survey and Characterization of Talc at Mbiidi, North of Boumnyebel, Cameroon .................................................................1331
Emmanuel Tangko, Charles Nkoumbou

Diffusion of Heavy Metals during Vitrification of Chromium Sludge in a Basaltic Matrix: Model of a Melting Pond in an Alumina Crucible .................................................................1335
Mariona Tarrago, Maite Garcia-Valles, Salvador Martinez, Pura Alfonso

Genesis of Tsavorite Deposits in the Davis Mine, Mwatate South eastern Kenya .............1339
Abigail Wamunyu, Daniel Ichang’i, Gaston Giuliani, Jean-Emmanuel Martelat, Edward Omito

Characterization of Talc Schist’s Weathering Materials in Henguegue (Cameroon) ...........1341
Damaris Laure Woguia, Louise-Marie Ngo Bidjeck
Session 13.1347
Processing of low-grade ore deposits

Compilation of Mining Waste Databases to Prioritize Site Study for Metal Recovery. Perspectives ......................................................... 1349
Guillaume Bertrand, Françoise Bodéan, Anne-Gwenaëlle Guézennecc, Annabelle Fuentes, Gaël Bellenfant, Daniel Cassard, Maurice Save

Re-Processing of Mine Tailings: Discussion on Case Studies ......................................................... 1353
Françoise Bodéan, Anne-Gwenaëlle Guézennecc, Michael Beaulieu, Gaël Bellenfant, Bruno Lemièvre, Catherine Lerouge, Maurice Save

TIMA Bright Phase Search – Tracking Gold Losses using SEM Based Automated Mineralogical System ......................................................... 1357
Marek Dosbaba, Vojtech Wertich

Gravity Processing of a Low Grade Kaolin Residue for the Recovery of Rare Earth Elements (La, Ce, Nd) and Rare Metals (Sn, Nb, W) ......................................................... 1359
Lev Filipov, Quentin Dehaine

Bioprocessing Low Grade Copper Ores - a Promising Alternative ......................................................... 1361
Anne-Gwenaëlle Guezennecc, Patrick D’Hugues

Structural and Physical Properties of Uranium-Ore Agglomerates before Heap Leaching............. 1365
Emereence Houmady, Fabrice Golfier, Michel Cathelineau, Laurent Truche, Nicolas Durupt, Jeremy Neto, Jean-Jacques Blanvillain

Iron Oxides Evolution along the Lateritic Profile of Mabounié Carbonatite (Gabon): a Key Point to Understand Magnetic Separation Processes ......................................................... 1369
Clémence Jouveau du Breuil, Arthur Perroton, Simon B Blancher, Céline Rodriguez, Marie-France Meschi-Daniel, Thomas Wallmach

Comminution as an Economic Efficient Key for the Improvement of Metal Recovery from Low-Grade Kupferschiefer-Type Black Shale-Hosted Copper Ore from the Mansfeld Mining District, Germany ......................................................... 1373
Andreas Kamradt

Surface Chemistry of Ore-Binder Mixture System in Relation to Iron Ore Pelletisation ............. 1377
Akira Otsuki, Yue You, Kazuki Minatogawa

Session 14.1381
Geometallurgy

Geometallurgical Assessment: Beneficiation of Rare Earth Minerals as a Possible By-Product from the Vergenoeg Fluorite Mine, South Africa ......................................................... 1383
Sandra Birtel, Marius Kern, Tobias W Höfög, Joachim Krause, Jens Gutzmer

Clay Mineral Characterization on Ni-Laterite: Qemscan Imaging of Alteration Processes .......... 1387
Simon B Blancher, Odile Laugier, Alain Bouchet

The Value of Ore Body Knowledge for Mining Operations ......................................................... 1391
Dee Bradshaw

A New Approach to Drill Core Scanning by Combination of Mechanical and Optical Tests: Preliminary Results ......................................................... 1395
Xavier Decamp, Godefroid Dislaire, Pierre Barnabé, Eric Pirard, Christophe Germay

From Plant to Mine: a Reverse Approach to Help Resource Estimation and Geometallurgical Modelling ......................................................... 1399
Quentin Dehaine, Lev Filipov

Advances in Mineral Characterisation Techniques: Emerging Tools and Workflows ............. 1403
Shaun D Graham, Al Croppe

The Cover of Mineralium Deposita’s Anniversary Volume Uncovered ........................................ 1407
Astrid Höfling, Hartwig E Frimmel, Virginia Voland, Kilian Dremel, Simon Zabler, Wyatt Ernest Lawrence Minter
Data Collection and Testing for Geometallurgy: Getting More from Drill Core ........................................... 1411  
Julie Hunt, Ron Berry

The Application of Deep Eutectic Solvent Ionic Liquids to Ore Processing – Dissolution Rates for Gold and Other Minerals ................................................................................................................... 1415  
Gawen RT Jenkin, Daniel J Smith, David A Holwell, Robert C Harris, Andrew P Abbott, Christopher J Stanley

How to Build a Process Model in a Geometallurgical Program? ................................................................... 1419  
Pierre-Henri Koch, Pertti Lamberg, Jan Rosenkranz

Pertti Lamberg, Mehdi Parian, Cecilia Lund

Rapid Resource Characterisation of Cu-Chlorides and Sulphates in Porphyry Cu Deposits using Reflectance Spectroscopy ......................................................................................... 1427  
Carsten Laukamp, Angus McFarlane, Victor Montenegro, Leandro Voisin, Gisella Palma

Classification of Geometallurgical Programs Based on Approach and Purpose .......................................... 1431  
Viktor Lischchuk, Pertti Lamberg, Cecilia Lund

Determination of Chromite Composition from Multispectral Reflectance Measurements (400-1000 nm) ................................................................................................................................... 1435  
Alfredo López-Benito, Fernando Gervilla, Juan Carlos Catalina, Ricardo Castroviejo

Mineralogical Controls on the Distribution of Antimony in a Base-Metal Flotation Test at the Rockliden Massive Sulphide Deposit, North-Central Sweden ........................................................................ 1439  
Friederike E Minz, Pertti Lamberg, Christina Wanhainen, Nils-Johan Bolin, Kai Bachmann, Jens Gutzmer

Mineral Identification and Domain Characterisation using Two Automated Hyperspectral Core Logging Systems, Los Bronces Cu-Mo Porphyry Deposit .................................................................... 1443  
Melissa A Quigley, Baris G Yildirim

Ore Fragmentation Modelling for the Evaluation of the Liberation Mesh Size ............................................. 1447  
Olivier Rozenbaum, Julie Machault, Emmanuel Le Trong, Yvan George Ngassa Tankeu, Luc Barbanson

QEMSCAN® Applied to Zn(Pb) Nonsulfide Ores: Advantages and Limitations ............................................... 1451  
Licia Santoro, Maria Boni, Gayyn Rollinson

Geometallurgical Investigation of Ion Adsorption Clays ................................................................................... 1455  
Nicolas B Stoltz, Stefan Ginzel, Patrick T Friedrichs, F Michael Meyer, Daniel JJ Voßenkaul, K Bernhard Friedrich

Session 15  ...................................................................................................................................................... 1459

Phytomining strategic metals and other elements from naturally mineralised soils and mineral wastes

Enhanced Phytoextraction of Nickel from Contaminated Soil by Hyperaccumulator Plant Co-Cropping Asso-ciated with PGPR ........................................................................................................... 1461  
Emile Benírizi, Marie Rue, Alexis Durand, Jean Louis Morel, Guillaume Echevarria, Séverine Piutti

Agromining for Nickel: a Complete Chain that Optimizes Ecosystem Services Rendered by Ultramafic Landscapes .................................................................................................................. 1465  
Guillaume Echevarria, Alan Baker, Emile Benírizi, Jean Louis Morel, Antony Van Der Ent, Vivian Houzelot, Baptiste Laubie, Marie-Noëlle Pons, Marie-Odile Simonnot, Xin Zhang, Petra Kidd, Aida Bani

Cadmium Recovery from Hyperaccumulator Plants ........................................................................................ 1469  
Claire Hazotte, Baptiste Laubie, Marie-Odile Simonnot

Improving the Nickel Phytomining Capacity of Hyper-ac-cumulating Subspecies of Alyssum serpyllifolium ..................................................................................................................................... 1471  
Petra Kidd, Vanessa Álvarez-López, Celestino Quintela-Sabarís, María Isabel Gabello-conejo, Ángeles Prieto-Fernandez, Cristina Becerra-Castro, Carmela Monterroso

Recovering Metals from Sewage Sludge, Waste Incineration Residues and Similar Substances with Metal Accumulating Plants ............................................................................................... 1473  
Johannes Kisser, Heinz Gattringer, Monika Iordanopoulos-Kisser

Heavy Metal Uptake by Species from Metalliferous Sites in Northern Greece ................................................ 1477  
Maria Konstantinou, Ioannis Tsiripidis
Diversity and Evolution of the Molecular Mechanisms Involved in Nickel Hyperaccumulation in Plants .................................................................................................................................1481

The Ability of Wetland Plants to Extract Phytomining of Valuable Metals from Waste Incineration bottom Ash using Hyperaccumulator Plants ........................................................................................................................................1487
Theresa Rosenkranz, Markus Puschenreiter, Johannes Kissèr

Nickel Phytoextraction by Seven Populations of Hyperaccumulating Brassicaceae .................................................................................................................................1489
Marie Rue, Luciana Frota-Madeira, Jean Louis Morel, Marie-Odile Simonnot

Nickel Agromining for ANSH Production .........................................................................................................................................................................................1491
Xin Zhang, Vivian Houzelot, Florent Ferrari, Baptiste Laubie, Edouard Plasari, Marie-Noélle Pons, Marie-Odile Simonnot, Xin Zhang, Guillaume Echevarria, Jean Louis Morel, Aida Bani

Current Developments in Agromining and Phytomining.................................................................................................................................................................1495
Antony van der Ent, Guillaume Echevarria, Jean Louis Morel, Marie-Odile Simonnot, Emile Benizri, Alan Baker, Peter Erskine

Session 16 ..............................................................................................................................................................................................................................................1497
Social and environmental issues in sustainable mining practices

Relations between Arsenic Speciation and Mobility in Mine Drainage Sediments and Microbial Communities .................................................................................................................................................................1499
Pascale Bauda, Simon Devin, Bénédicte Sohm, Christophe Pagnout, Guillaume Morin, Georges Ona N’Guema, Corinne Casiot

A Social Risk Index for Mining Projects: Evaluating Social Acceptability during the Exploration Stage.........................................................................................................................................................................................1503
Kristina Maud Bergeron, Michel Jébrak, Stéphanie Yates, Charles Séguin, Valérie Lehmann, Philippe Angers, Corinne Gedron, Suzanne Durand, Pierre-Yves Le Meur

Predicted Effect of Ore Mineralogy on the Environmental Behaviour of Mine Wastes .................................................................................................................................................................1507
Aurélie Chopard, Mostafa Benzaazoua, Hassan Bouzahzah, Benoît Plante, Philippe Marion

The Behaviour of Cr and Ni in Mine Spoils and Topsoils before and during Restoration Steps.........................................................................................................................................................................................1511
Guillaume Echevarria, Sophie Raous, Marie-Laure Bonis, Sophie Leguédois, Laurent Lhuillier

The Recent Uranium and Current Mining Disputes within the Framework of Environmental Protest Waves in Finland .........................................................................................................................................................................................1515
Toni Ererola

A GIS-Based Exploration Initiative to Help Steer Sustainable Development.........................................................................................................................................................................................1519
Arianne Ford, Steven Micklethwaite, Bernadetta Devi, Phillip McKenna

Environmental Impacts and Management of Ancient Abandoned Mines in the French Alps.........................................................................................................................................................................................1523
Dominique Gasquet, Magali Rossi

Occurrence of Rare Earth Elements in Ecosystems and Assessment of their Ecological Impacts: Research Approaches used in the French Programme Labex Ressource 21 .........................................................................................................................................................................................1527
Veronica Gonzalez, Davide AL Vignati, Corinne Leyval, Laure Giamberini

Fast-Growing Plantations as an Ecoengineering Tool to Improve Revegetation of Mine Waste Rock Slopes .........................................................................................................................................................................................1531
Marie Guittonny-Larchévêque, Arnaud Remaury, Hugo Bouchard, Suzanne Brais, Jane Rickson

Developing Tools for the Integration of Mining with other Land Uses .........................................................................................................................................................................................1535
Mari Kivinen, Pasi Eilu, Katja Kangas, Seija Tuulentie, Heidi Helenius, Jukka Similä
Mining Impacts and Sustainable Development in Guinea ................................................................. 1539
Saa Lolo Koundouno, Lancey Daoudi

Technosols of Mining and Quarrying Areas: Toward Multifunctionality ........................................ 1543
Sophie Leguédois, François Watteau, Apolline Auclerc, Jean Louis Morel, Christophe Schwartz, Geoffroy Séré, Guillaume Guéearria

Lighting Up the Subsurface .................................................................................................................. 1545
John Ludden and Mike Stephenson

Traceability of Base Metals Ores Using Mineralogical and Microtextural Parameters ...................... 1547
Julie Machault, Luc Barbanson, Thierry Augé, Laurent Bailly, Jean-Jacques Orgeval

Science Outreach and Mining Heritage: Drivers to the Rehabilitation of the Mining Village of Lousal, Portugal ........................................................................................................................................... 1551
Jorge MRS Relvas, Álvaro MM Pinto, Andreia Mendonça, Carla Malha, Fernanda Albuquerque, Luca Alegre, Mafalda Abrunhosa, Mârcia Pinheiro, Margarida Oliveira, Marina Alves, Miguel Ferreira, Ricardo Rufino, Rute Rolão, Sérgio Pratas, Tânia Ferreira, Carlos Fernandes, João MX Matos

An Approach in Water Management for Sustainable Mining: Residual Reagents Concentrations Optimisation in Recirculated Process Waters ........................................................................................................ 1555
Stéphanie Somot, Denis Cotnoir*, Éric Proulx, Claude Gagnon, Michel Garant

Symposium A
Metallogeny of North and West Africa ................................................................................................. 1559

Tectonic Evolution of the Gaoua Region, Burkina Faso: Implications for the Mineralization ....... 1561
Lenka Baratoux, Vaclav Metelka, Luc Siebenaller, Mark W. Jessell, Didier Béziat, Stefano Salvi, Sêta Naba, Pascal Ouiya, Athanasy Nare, Guy Franceschi

Cu-Pb-Zn-Au-Ag; Pb-Ag and Mo Mineralizations South of the Imiter Mine (Precambrian Sagro Massif, Eastern Anti-Atlas, Morocco): Geodynamic and Metallogenic Implications ......................................................... 1565
Bouchra Baidada, Abdelkhalak Alansari, Said Ilmen, Moha Ikenne

Seismic Velocities, Anisotropy, and Shear Wave Splitting of Antigorite (Ait Ahmane Serpentinites, Bou Azzer Inlier, Morocco). ............................................................................................................................................... 1567
Mohamed Bhilisse, Amina Wafik, Hassan Admou, Haemyeong Jung, Lhou Maacha

Helium Isotopic Constraints on the Genesis of the Touissit-Bou Beker Mississippi Valley-Type District of Northeastern Morocco ......................................................................................................................... 1571
Mohammed Bouabdellah, Samuel Niedermann, Fransisco Velasco

Copper Mineralization in Adoudounian Cover of the Bou Azzer-EI Graara (Anti Atlas, Morocco): Tectono-Stratigraphic Controls .......................................................................................................................... 1575
Hugo Bourque, Luc Barbanson, Stanislas Sizaret, Yannick Branquet, Claire Ramboz, Aomar Ennaciri, Mustapha El Ghorf, Laklifi Badra

A Cordilleran Zoning Model for the Polymetallic W-Au-Pb-Zn-Ag Tighza-Jbel Aouam District (Central Morocco): Contribution from New He-Ar and U-Th-Pb Data ................................................................................................................ 1579
Alain Chelletz, Magali Rossi, Leïla Tamriri, Dominique Gasquet, Hassan Bounajma, Tristan Mantoy, Lofti Ouazzani, Lahcen Ouchtouba, Etienne Deloule, Pete Burnard, Jean-Louis Paquette

Bijal Chudasama, Alok Porwal, Oliver K Kreuzer

Craton-Scale Lithostratigraphic Correlation as an Insight for the Geodynamic Evolution of the SWAC................................................................................................................................. 1587
James Davis, John Miller, Nicolas Thébaud, T Campbell McCuaig, Mark Jessell, Graham Begg, Kim Hein, Lenka Baratoux

High-K to Shoshonitic Magmatism across the Northern Archean Kéména Man Margin (Guinea): Implications for the Eburneane Orogenic Gold Mineralizations ....................................................................................... 1591
Aurélien Eglinger, Nicolas Thébaud, James Davis, John Miller, Campbell McCuaig, Armin Zeh, Elena Belousova

Mineralogical and Structural Evolution of Vein Mineralization in the Zgounder ore Deposit (Central Anti-Atlas, Morocco). ............................................................................................................................................... 1595
Nouamane El Aouad, Amina Wafik, Hassan Admou
Gold in Co-Ni ore from Bou Azzer El Graara (Central Anti-Atlas, Morocco): Mineralogy and Structural Control .................................................................1599
Mustapha El Ghorfi, Lou Maacha, Mohamed Zouhair and Aomar Ennaciri, Frank Melcher, Thomas Oberthür, Hugo Bourque

Microstructural and Textural Evidence for Protracted Polymetallic Sulphide Mineralization in the Jebilet Massif (Variscan Belt of Morocco) .................................................................1603
Abderrahim Essaïfi, Kathryn M Goodenough, Paul AJ Lusty, Abdelhak Outiugua

Nb-Ta Occurrences Associated to Late Pan-african Leucogranites, Mayo Salah Region, Northern Cameroon .................................................................1607
Periclex Fosso, Rigobert Tchameni, Emmanuel Nomo, Alliance Saha, Anne-Sylvie André, Joseph Penaye

Gold Remobilisation from Arsenopyrite: Crystal-Plasticity and Dissolution-Reprecipitation Reactions .................................................................1611
Denis Fougerousse, Steven Micklethwaite, Angela Halfpenny, Matt Kilburn, Stanislav Ulrich

A New Type of Large Ultramafic Intrusion-Hosted Fe-Ti-V Deposit in the West-African Archean Craton: The N’Guérédonké Complex, Guinea .................................................................1615
Eric Gloaguen, Thierry Augé, Laurent Bailly, Gabriel Courrioux, Thomas Fullgraf, José Perrin

Ag-Bi-Te Sulphosalt Minerals Related to the Amensif Cu-Pb-Zn-Ag-(Au) Carbonate-Replacement Deposit (Guedmiwa District, Western High Atlas, Morocco) .................................................................1619
Said Ilmen, Abdelkhalek Alansari, Lou Maacha, Amine Bajdji

The West African Craton and its Geophysical Signatures .................................................................1623
Mark W Jessell, Graham C Begg, Meghan S Miller

Geochemistry, Mineralogy and Isotope Composition of Pb, Zn and Cu in Gossan from the Perkoa Lead and Zinc Deposit, Burkina Faso .................................................................1627
Bohdan Kříbek, Ilja Kněsl, Jitka Miková, Lucie Erbanová, Jiří Zachariáš, Martin Mihaljevič, Ousman Bamba

Geochronology and Lithostratigraphy of the Siguiri District: Implications for Gold Mineralisation in the Siguiri Basin (Guinea, West Africa) .................................................................1631
Erwann Lebrun, Nicolas Thébaud, John Miller, Julien Bourget, Stanislav Ulrich, Ockert Terblanche

Developing the Lithotectonic Framework and Model for Sulphide Mineralization in the Jebilet Massif, Morocco: Implications for Regional Exploration .................................................................1635
Paul AJ Lusty, Kathryn M Goodenough, Abderrahim Essaïfi, Lou Maacha

The Geology and Mineralogy of the Sadiola-Yatela Gold Camp, Mali, West Africa: Contrasted Mineralisation Styles Derived from a Dynamic Hydrothermal System in the Late-Eburnean and Post-Birimian Karstification-Weathering Processes .................................................................1639
Quentin Masure, Nicolas Thébaud, John Miller, Stanislav Ulrich, Kim AA Hein

Multiple Mineralisation Events, Ashanti Belt, Ghana .................................................................1643
John Miller, Denis Fougerousse, James Davis, Mark Jessell, Campbell McCuaig, Yan Bourassa, Dan Apau, Stéphane Perrouty, Stanislav Ulrich

Lithostructural Study of Mineralization in the Southern Part of the North Orefield of the Polymetallic Hajjar Deposit (Morocco) .................................................................1647
Fortune Tulomba Niemba, Abdelali Khalifa, Lou Maacha, Zouhair Mohammed, Outhounjite Mohammed

Lithostratigraphy of the Bonikro Gold Deposit: Contribution to the Birimian Units in the Southern Fettékro Greenstone Belt, Côte d’Ivoire .................................................................1651
Zié Ouattara, Yacouba Coulibaly, Marie-Christine Boiron

Re-Os Geochronological Evidence for Multiple Paleo-Proterozoic Gold Mineralizing Events at the Scale of the West African Craton .................................................................1655
Laurie Reisberg, Elodie Le Mignot, Anne-Sylvie André-Mayer, John Miller, Yan Bourassa

Multistage Mineralization of the Inata Gold Deposit, Burkina Faso: Insights from Sulphide and Fluid Inclusion Geochemistry .................................................................1659
Luc Siebenaller, Stefano Salvi, Didier Béziat, Sékou Oumar Sangaré, Campbell McCuaig, Philippe Boulvais

Gold Mineralisation during Progressive Deformation along the Ashanti Belt: Wassa Mine, Ghana .................................................................1663
Rebecca C Strachan, David A Holwell, Chris Bonson, Mitchell Wasel, Yan Bourassa
SESSION 12
Gems and industrial minerals

Convenors
Gaston Giuliani, Lee Groat, François Martin, Daniel Ohnenstetter
Keywords: breccias, “beef” veins, evaporite
halokinesis during Lower Cretaceous rifting likely needs to be re-evaluated, at least on the Chivor district scale. Finally, deep (5-6 km) and overpressurized fluids occurred along the eastern border around the K-T boundary. Significant migration of hot, lithostatic hydrothermal fluid pressure prevailing shortly before emerald deposition. Significant migration of hot, lithostatic hydrothermal fluid pressure prevailing shortly before emerald deposition.


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Gems and industrial minerals

Colombian Emeralds and Evaporites: Tectono-Stratigraphic Significance of a Regional Emerald-Bearing Evaporitic Breccia Level

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Abstract. In the eastern front of the Colombian Eastern Cordillera, all the emerald and evaporite deposits and occurrences are hosted within a peculiar stratigraphic level at the Berriasian/Valanginian transition. This level contains evidence of sabkha evaporitic sediment reworking and destabilization on active sedimentary slopes. A main stratiform breccia is interpreted as a residual breccia resulting from salt ablation through dissolution during an emerald-related hydrothermal event and weathering. At 65 Ma, the emerald deposits formed in local extensional structures related to the initiation of a foreland bulge and associated flexure. A kind of bedding-parallel fibrous calcite and pyrite veins (called “beef” by reservoir geologists implied in rock mechanics) attest to a supra-lithostatic hydrothermal fluid pressure prevailing shortly before emerald deposition. Significant migration of hot, deep (5-6 km) and overpressurized fluids occurred along the eastern border around the K-T boundary. Finally, halokinesis during Lower Cretaceous rifting likely needs to be re-evaluated, at least on the Chivor district scale.

Keywords. Colombian emerald, Eastern Cordillera, Chivor mining district, breccias, “beef” veins, evaporite

1 Introduction

It is well established that Colombian emeralds formed from basinal brines which dissolved evaporites hosted within the Lower Cretaceous sedimentary sequence of the Eastern Cordillera (Giuliani et al. 1995). These works demonstrated the genetic relationship between emeralds and evaporites through mineralogy, fluid inclusion and stable isotope studies. No evaporitic rocks were reported and described in the Colombian emerald deposits before Branquet et al. (1999a). However, old field studies dealing with salt core bodies in the central part of the Eastern Cordillera, reported emeralds mined in cap rock residual breccias called “rute” in Colombia (Schelbe 1933). To our knowledge, since Branquet et al. (1999), no works dedicated to the tectono-stratigraphic controls on the Colombian emeralds and their relation with evaporites have been published. In this paper, we present detailed field, petrological and structural evidence highlighting the role of evaporites in the formation of the eastern emerald belt.

2 Geological and emerald deposits settings

The Eastern Cordillera (EC) of Colombia is a back-arc basin inverted during the major Middle Miocene Andean tectonic event. As the result of inversion, thick Lower Cretaceous depocenters are at the core of large anticlinoria flanking the eastern and western foothills of the EC. Localized in both anticlinoria, major Colombian emerald deposits are hosted within Lower Cretaceous black shales, and are clustered into the western (e.g. Coscuez and Muzo deposits) and the eastern (e.g. Chivor and Gachala mining districts) emerald belts (Fig. 1). Here, we only address the eastern emerald belt in the Chivor area. This area corresponds to the EC frontal fold and thrust system onto the easternmost Llanos foothills. The eastern emerald deposits of the Chivor district formed at 65 ± 3 Ma (Cheilletz et al. 1997) and are associated with a strong hydrothermal alteration leading to albization, pyritization and carbonatization, the last two being achieved through thermal sulfate reduction.

3 A regional emerald-bearing evaporitic breccia Level (EEBL)

3.1 Litho-stratigraphy

Field structural and stratigraphic studies undertaken in the Chivor mining district allow us to identify a peculiar stratigraphic level which hosts the emerald deposits and gypsum occurrences (Figs. 1 and 2). This EEBL forms the basal member of the upper part of the Tihonian-Berriasian Guavio formation.

In emerald deposits and occurrences, the EEBL is characterized by: i) a main breccia stratiform level, which overlies the lower black shales and is mainly composed of dismembered and crushed black shales mixed with cm- to meter sized white albite clasts (Fig. 3A, B, D). The lower contact of the main breccia is broadly discordant with overlying bedding in some places (Fig. 3A, B). The upper contact of the breccia is irregular with caving structures and appears to be discordant with overlying bedding in some places (Fig. 3A, B); ii) hecto- to decametric stratoid bodies of white albites lying just above and/or below the main breccia...
3.2 Hydrothermal alteration and weathering

The degree of hydrothermal alteration within the EEBL is highly variable. Only one hydrothermal event is recognized. It is responsible for emerald deposition through carbonatization, albitization and pyritization. In the emerald deposits this alteration is at a maximum and is particularly responsible for the transformation of dolomitic or evaporite bodies into white albitites through Na metasomatism. Emerald-bearing veins are mainly filled with calcite, dolomite, albite and pyrite. This paragenesis also constitutes the hydrothermal cement of a peculiar emerald-bearing polygenetic breccia composed of black shale and white albite clasts (Fig. 3D). This breccia is sparsely found near the top of the main breccia level (Fig. 3E) and also fills polygenetic breccia dykes (Fig. 3A). In the gypsum occurrences, hydrothermal fluid/rock interactions are weaker but isolated albite and pyrite crystals are frequent in thin sections. Noteworthy, non-cemented polygenetic breccias (black shale and white dolomitic or gypsum clasts) occur locally in the Guavió evaporite occurrences. Finally, with the exception of the La Guaria emerald occurrence (Fig. 2), no hydrothermal alteration occurred in the Valanginian Macanal black shales overlying the EEBL.

The EEBL is strongly weathered. Present-day meteoric waters flow through the main breccia level in the emerald deposits, triggering pyrite oxidation and subsequent carbonate dissolution in the polygenetic breccia. In the evaporite occurrences, primary anhydrite nodules replaced by gypsum are karstified, and veinlets and listric cm-scale faults are filled with secondary fibrous gypsum.

3.3 Structures

Sedimentary and soft sediment deformation is widespread in the EEBL. In particular, the basal contact of the EEBL is marked by slumps, groove marks, hydro-plastic Riedel shears and meter-thick layers of intraformational breccias.

During hydrothermal alteration leading to emerald deposition, sub-vertical veins that represent mineralized listric normal faults attest to a small amount of horizontal stretching of the bulk EEBL, the main breccia level acting as a “detachment” plane (Fig. 3A, Branquet et al. 1999). Polygenetic breccia dykes crosscutting the upper albitites are compatible with such horizontal stretching (Fig. 3A). Within the main breccia level in the emerald mines, albitite clasts are dragged and dismembered (Fig. 3B). Such structures associated with scarce drag folds and disharmonic folds demonstrate transport and displacement within and along the main breccia level. Moreover, the albites host numerous bedding-parallel fibrous calcite/pyrite veins i.e. “beef” (Fig. 3E) which are generally barren and pre-date the emerald deposition. The lack of strong hydrothermal alteration affecting the gypsum occurrences makes such deformation difficult to identify at those places.
Finally, the weakness of the EEBL locally enhances its reactivation as thrust and decollement during Middle Miocene Andean compression (Fig. 1, Branquet et al. 2002). This thrusting is attested to by “dry” shear bands and friction slickensides.

Figure 2. Litho-stratigraphic synthesis and correlations between the emerald deposits/occurrences in the Chivor district. Logs are located on Fig. 1. The main breccia level and albitites are hydrothermalized facies hosting most of the emerald deposits at the top of the Guavio Fm.

Figure 3. A. Cross-section through the Chivor emerald deposit. B. Upper contact of the main breccia level with albitites (1), Chivor Klein pit. Drag of albitite clasts within the breccia (2) is marked by tails. C. Evaporites at the Paez Gypsum mine (northeast of Fig. 1B) showing alternation of dolomitic limestone and gypsum beds. D. Polygenic breccia cemented by pyrite, carbonates and albitite. Oriente deposit. E. "Beef" vein composed of fibrous calcite in albitite, Chivor Klein pit.

4 Interpretation

Using our structural works which depict Andean deformation patterns, we established that emerald deposits and evaporites of the Chivor area are hosted in the same stratigraphic level as the top of the Berriasian Guavio Fm. In the emerald deposit, ancient evaporites made of alternating dolomitic/anhydrite or gypsum beds have been massively metasomatized into albitites. This albitite protolith is exposed in gypsum occurrences which appear to be EEBL segments partly “preserved” from the emerald-related hydrothermalism at 65 Ma.

The EEBL is a complex and polyphased breccia. Dolomitic thin layering, nodules, entherolitic and tepee structures are diagnostic of evaporite deposition in a sabkha environment. Soft-sediment deformation, intraformational breccia and discontinuous albitites and evaporite bodies argue for reworking of the sabkha environment through slope instabilities, block break-off and slide down-slope. Overlying the EEBL, black shales with ammonites and olistoliths indicate more open marine conditions coeval with slope instabilities.
Therefore, we propose that the EEBL corresponds to sakhlas reworked and partly dismembered during the Early Cretaceous major transgression, which is coeval with the important rifting event which affected the eastern border of the EC back-arc basin at that time.

In this context, the main stratiform breccia level in the emerald mines and the similar breccias embedding dolomitic gypsum lenses in the evaporite occurrences are likely vanished salt-bearing sediments. Halite was removed through various dissolution events from emergent related hydrothermalism at 65 Ma to present-day meteoric dolomicritic gypsum lenses in the evaporite occurrences. Emerald mining district. On a larger scale, the emerald exploration strategy on the eastern edge of the EC has to focus on lateral stratigraphic equivalents of evaporite and black shale breccia occurrences.

Acknowledgements

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Branquet Y, Chelletz A, Cobbold PR, Baby P, Laumonier B, Giuliani G (2002) An integrated analysis of the “beef” demonstrates that fluid pressures exceeded lithostatic load (Cobbold et al. 2013). At the Cretaceous-Tertiary boundary the overburden of the Guavió Fm. in the Chivor area is about 5-6 km (Branquet et al. 2002). At that time, the area was slightly uplifted in an incipient foreland bulge (Bayona et al. 2008). These authors interpreted deep extensional structures observed in the emerald deposits as resulting from flexural extension. Following this model, we suggest that the emerald-related hydrothermal event recorded an abrupt change in the hydrodynamics of the EC basin which triggered regional-scale hot, deep and over-pressured brine migration around the KT limit.

5 Discussion

As mentioned above, the main breccia level shows transport and drag of clasts. Transport of clasts is also obvious during the formation of polygenic breccia dykes. As the polygenic breccia was cemented by hydrothermal paragenesis below 5-6 km of overburden, near-surface caving processes evidenced by evaporite solution-collapse breccias (Warren 2006) are ruled out. Consequently, a remaining problem is to decipher the nature of the emerald-related hydrothermal event. The latter process has been identified for emplacement of the same fluid-assisted transport. Through fluidization, the latter process has been identified for emplacement of the same process. Following this model, we suggest that the emerald-related hydrothermal event recorded an abrupt change in the hydrodynamics of the EC basin which triggered regional-scale hot, deep and over-pressured brine migration around the KT limit.
First Evidence of Green Quartz Related to a Polymetallic Ore Deposit in Argentina

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Abstract. For the first time in Argentina a variety of green quartz has been discovered in an epithermal system on a Miocene magmatism framework. This mineral is hosted in a vein deposit controlled by shear-zone deformation. Multiple fracturing events took place with filling and replacement of new mineralizing pulses and with more than one breccia episode. There is a transition from grey quartz to the green quartz and both of them are associated with sulphide, sulphosalts, carbonate and manganese oxide minerals. This contribution presents the mode of occurrence of the green quartz and discusses its possible origin. This scenario takes place in the Agua de Dionisio mining district, Catamarca province, Argentina, belonging to the morphostructural province of the Western Sierras Pampeanas.

Keywords. Green quartz, epithermal system, Farallón Negro, breccia

1 Introduction

The aim of this work is to make known the presence of a new variety of quartz in Argentina by describing its macroscopic and microscopic characteristics and analysing the morphostructural features of the mineralized body in order to support hypothesizes about its origin.

The study area is located in the Agua de Dionisio mining district, specifically in the Esperanza Sudeste Vein. The stratigraphic sequence of the region is composed of Paleozoic basement rocks made up of low-grade metamorphic rocks, granites and granodiorites, Tertiary continental clastic sedimentary rocks, the Farallón Negro Volcanic Complex of Miocene age which shows the mineralization, Pliocene sandstones and tuffites and Quaternary fluvial sediments (Salado Paz at al., 2011). The mineral district has disseminated (e.g. Bajo La Alumbre Cu-Au-Mo porphyry) and vein style deposits, such as the Farallón Negro and the Alto de La Blenda gold-silver deposits. The Esperanza Sudeste Vein is located within the latter.

The Farallón Negro District hosts epithermal mineralization with variable grade of sulphidation ranging from high to low types (Sasso 1997).

2 The Esperanza Sudeste Vein geology

The green quartz integrates the mineralization within a breccia of 90 m³ which is located in the NW part of the Esperanza Sudeste Vein. This vein is hosted in the Alto de La Blenda monzonite stock which intruded in the central sector of the Farallón Negro Volcanic Complex. In surface, the stock has an oval geometry and its major axis has a NW-SE orientation. Sasso (1997) obtained an age of emplacement of 7.5 ± 0.3 Ma according to the 40Ar - 39Ar method applied to biotite and hornblende.

The geometry of the Esperanza Sudeste Vein is quite similar to the rest of the veins of the district. It is 200 m long and its thickness ranges between 0.3 m and 6 m. The strike is NW with variable dips from 85º to 48º NE. The wall rock of the vein is the quartz monzonite where different hydrothermal alteration types are observed: argillization, sericitization, pyritization, silicification, propilitization and carbonatization. These alterations are not necessarily superimposed and tend to occur in transitional passages. Silicification and pyritization predominate, giving to the rock a dark green color and high resistance to breakage. Where the country rock is affected by shearing systems, the dominant alterations are argillic > sericite, giving as a result a very friable rock and whitish appearance, which is also recorded where the green quartz is found. The alteration passages are on the metric scale.

According to Salado Paz et al. (2011) the vein is composed principally of different pulses of quartz, rhodochrosite, white carbonate and manganese oxides developing a colloform banded texture parallel to the main strike of the vein, with the presence of hypogenic sulphide minerals: pyrite, galena, sphalerite, chalcopyrite and tetrahedrite-tennantite, and a supergene assemblage characterized by manganese oxides, hematite-goethite and secondary sulphide minerals: chalcocite and covellite.

Rosette, botryoidal and drusy textures are very common due to the circulation of colloidal solutions that filled open spaces. The bands of white quartz with manganese oxides located both at the top and base of the vein develop thicknesses up to a meter and extend along the strike of the vein for tens of meters. Although they are concordant with the vein strike, internally the bands suffer small inflections, varying between 32º and 30º along the gallery.

Moreover, lenticular bands constituted mainly by rhodochrosite and accompanied by white carbonate, manganese oxides and quartz extend for tens of meters along the vein strike and have variable thicknesses ranging from metric to centimetric scale. Some of them dip in the NE direction, as does the rest of the body, but others dip in the opposite direction. Internally, country rock blocks up to 30 cm thick and 2 meters long are observed.
2.1 Green quartz hosting breccia

Towards the NW extremity of the Esperanza Sudeste Vein, level 2517, segment 5, a breccia body, carrier of the green quartz, is detected whose dimensions are 3 m wide by 6 m long and 5 m deep. The orientation of this body is discordant with respect to the direction of the vein and has an attitude of 350°, 50°–60° SW. It is located at the intersection of the main shear that controls the vein and an oblique subordinate one that controls the body.

The breccia is divided into two symmetrical main domains in accordance with the nomenclature of Jébrak (1992). A central domain was identified as an attrition breccia with an internal subdomain of massive breccia, and a peripheral domain was recognized where prevails a crushing breccia with a subdomain of the hydraulic type. The latter subdomain is where the greatest volume of silicate and carbonate is precipitated. The areas between these domains are transitional and are resolved in centimeters.

In the central domain, even though the rock has been intensively ground, polymictic, subrounded and up to 0.5 cm diameter clasts are preserved. Although the fragments are extremely argillized, a monzonite protolith equivalent to the country rock as well as vein material (white quartz ± rhodochrosite) are identified. The matrix has a grey color and is composed of the same material but is highly milled, with a strong clay alteration. Internally, a large amount of sulfides, mainly galena filling and replacing subordinately along foliation planes, constitute the subdomain of massive breccia. Also found are quartz (mostly grey) and white and pink carbonate cementing. From petrographic and chalcopyritic sections and further analysis with a Scanning Electron Microscope (SEM) Carl Zeiss NTS 40 SUPRA in the Centro de Microscopía Avanzada at the Universidad de Buenos Aires, the following sulphur species were detected: galena Pb(0.40-0.42)Fe(0.05)Cu(0-0.04)S(0.40-0.48) with crystals up to 3 cm in size, sphalerite Zn(0.93-1.02)Mn(0-0.04)Fe(0.00)Cu(0-0.02)S(1.04-1.08), pyrite Fe(0.80-0.85)S(1.67-1.72), chalcopyrite Fe(0.53-0.56)Cu(0.52-0.56)Mn(0-0.01)S(1.13-1.17), tetrahedrite-tennantite Cu(0.41-0.74)Ag(0-0.02)S(0.02-0.21)Sb(0.02-0.20)Zn(0-0.19) Mn(0-0.01)S(1.12-1.20), and covellite Cu(0.95-1.01)Ag(0-0.01)S(1.12-1.20).

Towards the peripheral we suggest that the shear stress had less intensity as clasts up to 20 cm in size are observed, hydrothermal alteration effects are weak and there is a lesser proportion of sulphides. In this domain, the silica-carbonate cement is more abundant and the green quartz and its transition to grey crystals are apparent (see Figure 1).

Internally, a subdomain of hydraulic breccia is recognized at both macroscopic and microscopic scale. It is characterized by polymictic, subangular to subrounded clasts composed of white and grey quartz, white and pink carbonates and manganese oxides. The clasts are cemented by pink and white carbonates, white to hyaline grey and green quartz constituting fine to coarse grainy aggregates that exhibit colloform and crustiform banded textures. Also the sulphides mentioned before, but to a lesser proportion.

Figure 1. Peripheral domain hydraulic breccia where the transition from grey to green quartz is observed. Clast boundaries are shown with dotted black lines.

Figure 2. Mineralization events and episodes of rupture interpreted from the textural and mineralogical relationships.
From the textural and mineralogical relationships observed, four episodes of precipitation of minerals and four of rupture are interpreted. Two events of rupture are related to shear mechanisms while the other two to hydraulic fracturing controlled by previous anisotropies (see Figure 2).

In particular, green quartz appears as a transitional variety of grey quartz. Euhedral crystal forms associated with small dilatant spaces that allowed the development of free sides and a bigger grain size are observed. When analyzed with the SEM, the green quartz exhibits low participation of impurities, absence of other trace elements, a marked zonal growth (see Figure 3) and the absence of intracrystalline deformation structures. By contrast grey quartz not only shows dominance of impurities but also anisotropies in mortar texture.

Inspection of fluid inclusions in both varieties of quartz indicates that the green variety contains, according to Roedder’s (1984) classification, primary aqueous fluid inclusions in the crystal’s core, pseudo-secondary within the limits of the growth bands and very subordinately the intercrystalline secondary ones (see Figure 3).

3 Discussion and conclusions

Hebert and Rossman (2008) made a comparative study of green quartz found in the Panorama amethyst deposit located in Ontario, Canada which belongs to an extinct hydrothermal system and green quartz from other localities like Farm Rooisan in Namibia and Bahia in Brazil. They observed that the variety of green quartz is closely related to gray and purple varieties of quartz (amethyst). The authors suggest that exposure to natural radiation could have generated changes in color where the source of the radiation is in the K concentrated in the host granitic rocks of the hydrothermal system. Furthermore, they attribute the coloration of quartz to water incorporation as molecular and hydroxyl species based on analysis of spectroscopic studies. Changes in the salinity of the hydrothermal fluid and the quartz growth rate can lead to color change.

In the Esperanza Sudeste vein, our preliminary data suggest that the deformation in the deposit, along with circulating hydrothermal solutions and the effect of re-precipitated silica due to dissolution pressure mechanisms, led to the generation of the green quartz facies from the deformation of grey quartz.

Preliminary analysis of fluid inclusions would allow us to discriminate different formational environments for the quartz facies, where green quartz is generated once the effective deformation ends. In addition, the effect of zoning on green quartz crystals would suggest changes in the composition of the hydrothermal fluid.

A genesis from a radioactive source is discounted since rocks with high K content are not available in the study area. Green quartz has not been found in areas of the Esperanza Sudeste vein without deformation.

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References

Identification in Archaeological and Historical Jewellery

Chromium Pyropes from Bohemia: Characterization and Provenance

2.1 Introduction

Keywords: Bohemian garnets, chromium pyrope, gemstones, provenance, archaeometry

Bohemia is famous for its fiery red gem-quality garnets. Garnet mining in this area dates back to the 16th century CE (Agricola 1546; Boetius de Boot 1609). Garnet mining in northern Bohemia near Vestředohoří area, about 70 km NNW of Prague, is the last active gem-quality garnet mine in Europe. Garnet has continued to present times with a production maximum in the 19th century. The Podsedice garnet deposit on the southern slopes of the mountainous thuringian zone and covered by more than 120 m of Cretaceous sediments (Fiala and Padra 1971; Rankenburg et al. 2004) and Thailand (Bo Rai, Tha Mai and Phu Fai districts; Lind 2002; Phichaikham in Mongolia (Shavaryn Tsaram; Ulrych and Šever 2005; Kotková et al. 2011; Medaris et al. 2012).

2.2 Vestředohoří area

Alluvial chromium-rich pyrope deposits have about 2.5 wt.% Cr pyrope (Novák 2001). The heavy mineral concentrates contain xenoliths were weathered and the garnets resedimented in up to 6 m thick Pleistocene gravels that cover an area of about 70 km². The volcanic rocks and their alkaline basaltic volcanism. The volcanic rocks and their geological histories. Bohemian garnets can be distinguished from Cr pyropes from the Colorado Plateau.

The original source rocks of the Cr pyropes in the Czech Republic are distinct and related to their specific characteristic inclusion assemblages, and spectroscopic and UV-VIS properties. We use these characteristics to determine the basis of minor element chemistry and spectroscopic characterization allows us to derive criteria to determine spectroscopy, and portable XRF analysis. This include microscopy of inclusions, Raman and UV-VIS using a variety of non-destructive methods. These worldwide as well as red Cr-poor magmatic pyropes, worldwide as well as red Cr-poor magmatic pyropes from Nigeria, Mongolia, and Thailand on the geological histories. Bohemian garnets can be compared more than 90 rough and 25 facetted gem-quality chrome pyropes from various localities in the world.

There are many small alluvial garnet occurrences near Bohemia with those from other significant locations. There are several small occurrences of alluvial Cr pyropes in northern Bohemia including the large Vestředohoří area are serpentinized garnet peridotites that have not been found at surface. Olivine xenoliths were weathered and the garnets resedimented in up to 6 m thick Pleistocene gravels that cover an area of about 70 km². The garnet-bearing peridotites were brought to the surface as xenoliths in diatremes during Tertiary alkaline basaltic volcanism. The volcanic rocks and their geological histories. Bohemian garnets can be distinguished from Cr pyropes from the Colorado Plateau.

2.3 Kolín area

Kutná Hora area of central Bohemia (Hanus 2013). The Cr pyropes are derived from adjacent garnet peridotites of the Kutná Hora Complex in the Saxo-Moldanubian zone (Faryad 2009).

19th century. The Podsedice garnet deposit on the southern slopes of the mountainous thuringian zone and covered by more than 120 m of Cretaceous sediments (Fiala and Padra 1971; Rankenburg et al. 2004) and Thailand (Bo Rai, Tha Mai and Phu Fai districts; Lind 2002; Phichaikham in Mongolia (Shavaryn Tsaram; Ulrych and Šever 2005; Kotková et al. 2011; Medaris et al. 2012).

Red gem-quality Cr-poor pyrope with a pronounced orange tint occur as phenocrysts in alkali basaltic rocks that have recently become an important source of dark red Cr garnet jewellery. The primary source rock of the garnets are not known.
Chromium Pyropes from Bohemia: Characterization and Identification in Archaeological and Historical Jewellery

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Abstract. Alluvial chromium-rich pyrope deposits have been mined in three parts of Bohemia: the České Středohoří, Vestřev, and Kolín areas, with the first being the most prolific region which still hosts an active mine near Podsedice. The chemical compositions, characteristic inclusion assemblages, and spectroscopic properties of Cr pyropes from these three areas in the Czech Republic are distinct and related to their specific geological histories. Bohemian garnets can be distinguished from Cr pyropes from the Colorado Plateau and Tanzania, as well as from red Cr-poor magmatic pyropes from Nigeria, Mongolia, and Thailand on the basis of minor element chemistry and spectroscopic properties. We use these characteristics to determine the provenance of garnets in archaeological and historical jewellery.

Keywords: Bohemia, red gem garnets, Cr pyrope, archaeogemmology

1 Introduction

Bohemia is famous for its fiery red gem-quality garnets that have been mined for centuries (e.g. Schlüter and Weischat 1991). The first historical accounts of garnet mining in this area date back to the 16th century CE (Agricola 1546; Boetius de Boot 1609). Garnet mining has continued to present times with a production maximum in the 19th century. The Podsedice garnet deposit on the southern slopes of the mountainous České Středohoří area, about 70 km NNE of Prague, is the last active gem-quality garnet mine in Europe. Garnet has also been mined sporadically in other areas of Bohemia, e.g. in northern Bohemia near Vestřev, and in the Kolín - Kutná Hora area of central Bohemia (Hanus 2013).

Bohemian garnets are generally very small, mostly less than 6 mm in diameter, while larger stones are exceedingly rare and thus highly prized. In this study we compare more than 90 rough and 25 faceted gem-quality chrome pyropes from various localities in Bohemia with those from other significant locations worldwide as well as red Cr-poor magmatic pyropes, using a variety of non-destructive methods. These include microscopy of inclusions, Raman and UV-VIS spectroscopy, and portable XRF analysis. This characterization allows us to derive criteria to determine the provenance of Cr pyropes in archaeological and historical jewellery.

2 Cr pyrope from Bohemia

2.1 České Středohoří area

The original source rocks of the Cr pyropes in the České Středohoří area are serpentinitized garnet peridotites hosted in ultra-high pressure granulites of the Saxothuringian zone and covered by more than 120 m of Cretaceous sediments (Fiala and Paděra 1977; Seifert and Vrána 2005; Kotková et al. 2011; Medaris et al. 2015). The garnet-bearing peridotites were brought to the surface as xenoliths in diatremes during Tertiary alkaline basaltic volcanism. The volcanic rocks and their xenoliths were weathered and the garnets resedimented in up to 6 m thick Pleistocene gravels that cover an area of about 70 km². The heavy mineral concentrates contain about 2.5 wt.% Cr pyrope (Novák 2001).

2.2 Vestřev area

There are several small occurrences of alluvial Cr pyropes in northern Bohemia including the large Vestřev deposit at Olešnický Creek that was mined between 1994 and 2008 and will possibly reopen in the near future. The garnets are derived from Permian sandstones. The source peridotites have not been found at surface.

2.3 Kolín area

There are many small alluvial garnet occurrences near Kolín and Ktná Hora in central Bohemia about 60 km east of Prague (Vrána 2008; Hanus 2013). They have been mined for a short time at the end of the 18th century CE. The Cr pyropes are derived from adjacent garnet peridotites of the Ktná Hora Complex in the Moldanubian zone (Faryad 2009).

3 Other occurrences of Cr pyrope and magmatic Cr poor pyrope

The largest Cr pyropes come from the Colorado Plateau, U.S.A., in the Four Corners region of NE Arizona, NW New Mexico, and SW Colorado. The garnets are found in the weathering crust of Oligocene ultramafic diatremes of the Navajo Volcanic Field (Eveleth and Lueth 2010). Alluvial deposits in southern Tanzania have recently become an important source of dark red Cr pyropes (Lind 2002) that are presently used in Czech garnet jewellery. The primary source rock of the garnets are not known.

Red gem-quality Cr-poor pyrope with a pronounced orange tint occur as phenocrysts in alkali basaltic rocks in Mongolia (Shavaryn Tsaram; Ulyucz and Ševčik 1986), Nigeria (Jos and Blu Plateau; Frisch and Wright 1971; Rankenburg et al. 2004) and Thailand (Bo Rai, Tha Mai and Phu Fai districts; Lind 2002; Phichaikamjornwut et al. 2012).
4 Inclusions

Pyropes from the České Stredohoří area appear generally inclusion-poor. However, almost 90% of the investigated stones contain numerous subspherical multi-mineral inclusions with sizes of about 10 to 50 µm (Fig. 1, 2), often only occurring at the rim of the crystals. The inclusion always show small tension cracks. They mostly consist of magnesite and pyroxenes with minor amounts of phlogopite, apatite, and graphite identified by Raman mapping. Very rarely, large colourless euhedral olivine crystals and opaque inclusions surrounded by partially healed fractures are observed. Other inclusion minerals are euhedral zircon, Fe-Ni sulphides, Cr diopside, subovodal paraganitic amphibole, and Cr-Al spinel (Bauer 1966; Seifert and Vrána 2003).

Figure 1. Primary crystallized melt inclusions at the rim of Cr pyrope from Mšrunice, České Stredohoří.

Figure 2. Multiphase crystallized melt inclusion in Cr pyrope from Staré, České Stredohoří, consisting of magnesite, pyroxene, phlogopite, apatite, and graphitic carbon.

Chromium pyropes from northern Bohemia generally show the same inclusion assemblages as those from the České Stredohoří area. However, 75% of all investigated stones also display a characteristic three-dimensional network of hollow channels (“trichites”) (Fig. 3). These channels originated by chemical corrosion, probably along dislocations in the crystal lattice, during the long sedimentation cycle.

The pyropes from the Kolín area in contrast are characterized by abundant solid inclusions and are thus easy to distinguish from the other Bohemian Cr pyropes. Almost all of the garnets display a three-dimensional network of acicular rutile needles, mostly along [111], but also equant and platy rutile crystals (Fig. 4). Crystallized melt inclusions containing magnesite, phlogopite, apatite, olivine, rutile, spinel, ilmenite, and Ni sulphide, as well as isolated inclusions of ilmenite, enstatite, paragasite, crichtonite-group minerals, and sulphides are frequent (Vrána 2008).

Figure 3. Etch channels (“trichites”) and a few crystallized melt inclusions in Cr pyrope from Bradlecká Lhota, northern Bohemia.

Figure 4. Oriented rutile needles and a large colorless euhedral olivine crystal in Cr pyrope from Sedlec, Kolín area.

The inclusion characteristics of the Kolín pyropes are very similar to those reported for the Cr pyropes of the Colorado Plateau (e.g. Hunter and Smith 1981; Smith 1987; Griffin et al. 1989; Wang et al. 1999). The Cr-rich pyropes from Tanzania are generally devoid of silicate and oxide inclusions, but contain typical spherical Cu-Fe sulphide inclusions with partially healed tension cracks. No inclusions were observed in the Cr-poor pyropes.

The chemical compositions of Cr pyropes from the three areas. However, 75% of all investigated pyropes from the Colorado Plateau and Tanzania show lower TiO₂/CaO values compared to Bohemian Cr pyropes from the Colorado Plateau and Tanzania.
5 Chemical composition

The chemical compositions of Cr pyropes from the three regions in Bohemia are in general very similar (Schlüter and Weischat 1991; Lind 2002; Seifert and Vrána 2005; Vrána 2008; Soumar 2011; Hanus, 2013; our data). However, pyropes from the České Středoohoří area show a somewhat larger variation in Ti as compared to Vestrev pyropes, whereas Kolín pyropes have on average lower Ti contents and contain some Cr-poor compositions (Table 1; Fig. 5; Vrána 2008). A large variation of Ti content in pyrope has also been recorded in peridotites from T-7 drill core near Staré with higher Ti contents in the Iherzolite pyropes and lower Ti for the harzburgitic or dunitic garnets, which is often accompanied by higher Cr values (Fiala and Pádera 1977; M edaris et al. 2015).

Table 1. Compilation of chemical analyses of Bohemian Cr pyropes with average and 2σ values (for references see text).

<table>
<thead>
<tr>
<th></th>
<th>České Středoohoří</th>
<th>Vestrev</th>
<th>Kolín</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42.34±1.13</td>
<td>42.56±1.31</td>
<td>42.20±1.13</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.48±0.25</td>
<td>0.48±0.11</td>
<td>0.36±0.25</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.98±1.18</td>
<td>21.16±0.79</td>
<td>20.98±1.18</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2.25±0.26</td>
<td>1.97±0.77</td>
<td>2.25±0.26</td>
</tr>
<tr>
<td>FeO</td>
<td>8.74±1.62</td>
<td>8.39±1.77</td>
<td>8.74±1.62</td>
</tr>
<tr>
<td>MnO</td>
<td>0.25±0.14</td>
<td>0.25±0.16</td>
<td>0.29±0.14</td>
</tr>
<tr>
<td>MgO</td>
<td>20.46±0.64</td>
<td>20.49±1.69</td>
<td>20.46±1.64</td>
</tr>
<tr>
<td>CaO</td>
<td>4.56±0.53</td>
<td>4.55±0.30</td>
<td>4.56±0.53</td>
</tr>
</tbody>
</table>

Table 2. Compilation of chemical analyses of Cr and Cr-poor pyropes from various locations with average and 2σ values (for references see text).

<table>
<thead>
<tr>
<th></th>
<th>Arizona</th>
<th>Mongolia</th>
<th>Nigeria</th>
<th>Thailand</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.77±1.31</td>
<td>40.35±0.68</td>
<td>41.45±0.80</td>
<td>41.09±0.81</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.11±0.10</td>
<td>0.56±0.12</td>
<td>0.41±0.10</td>
<td>0.46±0.08</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>22.13±1.93</td>
<td>21.16±0.79</td>
<td>20.98±1.18</td>
<td>20.98±1.18</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2.45±1.61</td>
<td>0.05±0.09</td>
<td>0.03±0.06</td>
<td>0.04±0.08</td>
</tr>
<tr>
<td>FeO(III)</td>
<td>8.57±2.32</td>
<td>15.75±1.55</td>
<td>11.52±1.11</td>
<td>12.64±1.54</td>
</tr>
<tr>
<td>MnO</td>
<td>0.38±0.17</td>
<td>0.40±0.22</td>
<td>0.36±0.07</td>
<td>0.36±0.08</td>
</tr>
<tr>
<td>MgO</td>
<td>19.91±1.84</td>
<td>18.40±0.83</td>
<td>17.81±1.02</td>
<td>17.70±1.48</td>
</tr>
<tr>
<td>CaO</td>
<td>5.13±1.02</td>
<td>5.46±0.33</td>
<td>5.42±0.41</td>
<td>5.44±0.74</td>
</tr>
</tbody>
</table>

Figure 5. TiO₂/CaO versus Cr₂O₃/CaO diagram showing the compositional variation (coloured fields) of Cr pyropes from Bohemia (CS: České Středohoří, VE: Vestrev, KO: Kolín) and the Colorado Plateau, U.S.A. (CP), as well as of Cr-poor pyropes from Nigeria (NG), Thailand (TH), and Mongolia (MO) from electron microprobe data (for references see text). The composition of faceted gemstones of known origin analysed using a portable XRF device are indicated with individual symbols.

7 UV-VIS and Raman spectroscopy

UV-VIS spectroscopic analysis of rough and faceted stones using a GL Gem spectrometer indicates that Bohemian Cr pyropes from the České Středohoří and Vestrev area are characterized by the presence of an absorption peak related to Cr³⁺ at about 685 nm that is lacking in Cr-poor pyropes, and the absence of a distinct absorption peak at about 440 to 450 nm that is clearly developed in the Ti-poor Cr pyropes from Tanzania, U.S.A., and the Kolín area. Similarly, Raman spectra of garnet can also be used to determine the provenance of red pyropes. Cr-poor magmatic pyropes show two very characteristic bands at about 720 and 770 cm⁻¹ (Gilg and Gasta 2012) that are generally absent in Cr pyropes or only very poorly developed in some orange Cr pyropes from Bohemia. A typical band or shoulder at about 830 cm⁻¹ can be related to the variably high Ti content of most Bohemian Cr pyropes and is poorly developed in Cr pyropes from the Colorado Plateau and Tanzania.

8 Geology and gemmology

Gem-quality red Cr pyropes from Bohemia are extracted from Quaternary alluvial sediments; this is important for lost-cost mining and preconcentration of gem-quality stones. However, they are originally derived from largely undepleted, partly metamorphosed garnet-bearing mantle peridotites emplaced into the continental crust during the Variscan orogeny (e.g. M edaris et al. 2015). The undepleted or in part refertilised nature of the host rocks resulted in characteristically high Ti contents for the pyropes which contrasts with most other commercial Cr pyrope deposits, e.g. Colorado Plateau or Tanzania. The gemstones with the best quality come from the České Středohoří area. Here, rapid cooling of the high-T peridotites during crustal emplacement (Kottkova et al. 2011; M edaris et al. 2015) precluded the precipitation of...
oriented acicular rutile in the garnet. In contrast, Cr pyrope from the Kolin area (Faryad 2009) and the Colorado Plateau (Griffin et al. 1989; Roden and Shimizu 2000) experienced a significant low-temperature equilibration event that was responsible for the precipitation of oriented rutile needles. Pyrope phenocrysts from alkaline basaltic magmas (Nigeria, Mongolia, and Thailand) probably compensate their low Cr contents with high Ti values and a rapid cooling during volcanic ascent that prevented rutile crystallization.

9 Bohemian Cr pyrope in archaeological and historical jewellery

Garnet in Meovianian cloisonné jewellery from Bavaria was studied using PIXE, Raman spectroscopy, and optical microscopy. More than 90 Cr pyrope in 16 objects from the 7th and 8th century CE contain Ti-rich Cr pyrope with a composition that is compatible with a Bohemian origin (Gilg et al. 2010). The garnets do not contain any network of hollow channels or acicular rutile and thus very probably derive from the České Stredohorí area. These data indicate that this classical European garnet mining area was already productive about 950 years before the first historical account in 1546 by Georgius Agricola.

A study of small faceted garnets decorating religious objects of the St. Vitus treasure, Prague, by optical microscopy clearly indicated the presence of garnets both from the České Stredohorí and the Kolin areas (Hyrl 2002). We also recently analysed faceted red stones in traditional Bohemian costume jewellery from the 19th century housed in the Sudetendeutsche Museum in Munich using a portable XRF analyser. Only a few red stones were identified as Bohemian Cr pyrope, while many inlays consist of red Pb-rich glass. A single large stone revealed a Ca-rich almandine composition and is most probably derived from the Zillertal area in Austria (Gilg and Hyrl 2014).

Acknowledgements

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A Stable-Isotope Investigation of the Origin of Emeralds from the Ianapera Deposit, Madagascar

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Abstract. Emeralds from Ianapera, Madagascar, have been investigated in terms of their stable isotopic signature. The oxygen isotopic composition of emeralds showed a relatively constant δ18O (V-SMOW) at 11.9 ± 0.7‰ (n = 4) while the beryl core of an emerald crystal gave a δ18O value of 10.9‰. Water in channel and fluid inclusions in emerald has a different range of hydrogen isotopic composition. The channel waters are isotopically heavier (δD = -86 to -61‰ V-SMOW) than the fluid inclusions (δD = -119 to -100‰). On the basis of the isotopic composition of a fluid (δ18O H2O = 12.5‰) calculated at a temperature of 520°C for distal emeralds (in distal phlogopitite veins) and the δD in channels, it is proposed that the Ianapera emeralds formed from 18O-enriched magmatic-hydrothermal fluids derived from a peraluminous granitic magma.

Keywords. Madagascar, emerald, oxygen, hydrogen isotopes, origin of the fluids.

1 Introduction

The geology and genesis of the Ianapera emerald deposit in southwestern Madagascar has been studied by Andrianjakavah (2009) and Andrianjakavah et al. (2009a, b). The deposit belongs to the granitic pegmatite-hydrothermal type as defined by Schwarz and Giuliani (2001). At Ianapera, the granitic pegmatites provided the Be, while Cr and V were extracted by the hydrothermal fluids from mafic-ultramafic rocks. The present contribution investigates the oxygen and hydrogen isotopic compositions of these emeralds in order to trace the source of the fluids responsible for the mineralization.

2 Geological setting and mineralization characteristics

The Ianapera emerald deposit is located in the Neoproterozoic Vohibory domain of southern Madagascar (Jöns and Schenk, 2008; Andrianjakavah et al., 2014). Pegmatite veins intrude migmatic gneisses and conglomerate metasedimentary rocks containing lenses of metamorphosed mafic-ultramafic units (Salvi et al. 2008; Andrianjakavah 2009). Emerald mineralization is hosted by metasomatic phlogopite veins and pegmatites. Andrianjakavah et al. (2009a) and Beziat et al. (2012) distinguished proximal and distal styles of mineralization (Fig. 1): (i) proximal mineralization occurs at the contact of pegmatite veins with Cr-rich mafic-ultramafic rocks. It is characterized by centimetre- to meter-thick phlogopitites formed at the expense of the Cr-bearing rocks. Emerald also occurs within the pegmatites and in quartz (∼tourmaline) veinslets embedded in the phlogopitite; (ii) distal mineralization consists of phlogopitite veins crosscutting mafic-ultramafic rocks.

Figure 1. Proximal (a) and distal (b) mineralization at the Ianapera emerald deposit (Andrianjakavah et al. 2009a).

At Ianapera, emerald has been classified based on field relationships, chemical composition, and physical properties (Andrianjakavah et al. 2009a) as: - Type 1: zoned crystals, with a colourless beryl core and a medium-green emerald overgrowth, found in pegmatite or distal phlogopitite; - Type 2: unzoned emerald crystals, varying from a pale to medium-green colour, within phlogopitite; - Type 3: zoned crystals with a medium-green core and a deep-green rim hosted in quartz veinlets within proximal phlogopitite.

Fluid-inclusion studies have evidenced two types of fluids, a CO2 ±CH4 ±N2 ±H2S-rich fluid, and an H2O-rich fluid containing Na+, K+, Ca2+, Mg2+, Cl−, HCO3−, and SO42− (Andrianjakavah et al. 2009b). Based on this...
evidence, the authors interpreted a pegmatic origin for the aqueous fluid, which gathered Ca and Mg upon interaction with the metacarbonate-rich country rock. The composition of metasomatic minerals suggests that the fluid also carried fluorine and boron, consistent with an orthomagmatic origin for the fluid. The CO₂-rich fluid was interpreted to be of metamorphic origin; locally, it mixed with the aqueous fluid, as suggested by the presence of H₂O-CO₂ inclusions in more distal settings. Using isochores for fluid-inclusion homogenization temperatures and considerations of mineral equilibria, the constrained P-T conditions of emerald formation were estimated to have been between 600-680 °C and 530-650 °C for proximal and distal mineralization styles, respectively, at pressures of 5.0 to 5.6 kbars.

3 Material and methods

The emerald samples used in this study are listed in Table 1. They represent the different types of emerald mentioned above (Fig. 1). These include a proximal zoned emerald from a pegmatite, with a beryl core and emerald rim (sample EB3); an emerald from proximal phlogopite (sample EB1); an emerald from a proximal quartz vein (sample ST1); and emerald from a distal phlogopite (sample EB2). The last two samples are distal emeralds (samples EB2a and EB2b), analysed for their H-isotope composition.

Oxygen isotope ratios (δ¹⁸O/δ¹⁶O) of the emeralds were determined using the Cameca 1270 IMS probe at CRPG/CNRS in Vaucluse, France, with a Cs⁺ primary beam and electron bombardment. Analyses of the δ¹⁶O and ¹⁸O secondary ions were done in multicollection mode, at a mass resolution of 4500. The instrumental mass-fractionation was calibrated with a set of three emeralds of different types. The δ¹⁸O/δ¹⁶O ratios were determined with a precision of 0.2‰ (1σ). The hydrogen isotopic composition of water released from the emeralds was obtained at S.U.E.R.C. in Glasgow. The step-heating method that was used is described in Fallick and Barros (1987). The samples were degassed in vacuo to remove labile absorbed fluid prior to dewatering at 120 °C for 16 hours. The extraction of H₂O from the channels was done in a series of experiments; initially, without stepwise dehydration, directly by melting the powdered material up to 1200 °C (samples EB2, EB3 and ST1), and secondly, by a two-step dehydration: (i) at 800 °C to decrystallize fluid inclusions, and (ii) at 1200 °C to release the water from the channels. Extraction time at each temperature was at least 30 minutes. The analytical precision for δD using the stepwise technique is circa ±2.5‰. D/H and δ¹⁸O/δ¹⁶O are reported relative to V-SMOW using the conventional notation, where δ is the relative difference in isotopic ratio between a sample and a standard, expressed in parts per thousand (‰).

4 Isotopic composition of emerald

The δ¹⁸O measurements and the δD of channel H₂O from the Ianapera samples are reported in Table 1. The oxygen isotopic composition obtained for the types of emerald (types 1p, 2p, 3p and 2d), are within the range of 10.9 to 12.7‰. The δ¹⁸O values for proximal emeralds in the pegmatite are within the same range (sample EB3: 12.7 ± 0.3‰, n = 4) as those in phlogopite (sample EB1: 12.0 ± 0.8‰, n = 5) and quartz veins (sample ST1: 12.25 ± 0.9‰, n = 5). The δ¹⁸O value for beryl forming the core of the Type-1 emerald in the pegmatite (sample EB3 beryl: 10.9 ± 0.3‰, n = 4) is different from the outer rim of the same emerald (δ¹⁸O = 12.7 ± 0.3‰). The δ¹⁸O value for the distal emerald (type 2d) in the phlogopite (sample EB2: 11.7 ± 0.8‰, n = 5) is slightly different but falls within the δ¹⁸O range of the proximal emeralds (12.1 ± 0.8 %‰, n = 20).

The δD values for the Ianapera emeralds are listed in Table 1. The step heating stages used for samples EB1, EB2a, and EB2b show that the δD of inclusion waters released at 800 °C are depleted in deuterium (δD between -119 and -100‰) while that of the channel water released at 1200 °C is between -61 and -74‰ (δDmean = -66 ± 7 ‰, n = 4) as those in phlogopite (sample EB1: 11.7 ± 0.8‰). The ~2‰ variation indicates either a metamorphic origin; locally, it was interpreted to be of metamorphic origin; (ii) channel H₂O with a narrow isotopic range of the proximal emeralds (δDmean = -66 ± 7‰, n = 4) as those in phlogopite (sample EB1: 11.7 ± 0.8‰). Sample EB2 shows that the δDmean is slightly different between -119 and -100‰, and (ii) channel H₂O with a narrow isotopic range of the proximal emeralds (δDmean = -66 ± 7‰, n = 4) as those in phlogopite (sample EB1: 11.7 ± 0.8‰). Sample EB2 shows that the δDmean is within the range of 10.9 to 12.7‰. The δ¹⁸O values for proximal emeralds in the pegmatite are within the same range (sample EB3: 12.7 ± 0.3‰, n = 4) as those in phlogopite (sample EB1: 12.0 ± 0.8‰, n = 5) and quartz veins (sample ST1: 12.25 ± 0.9‰, n = 5). The δ¹⁸O value for beryl forming the core of the Type-1 emerald in the pegmatite (sample EB3 beryl: 10.9 ± 0.3‰, n = 4) is different from the outer rim of the same emerald (δ¹⁸O = 12.7 ± 0.3‰). The δ¹⁸O value for the distal emerald (type 2d) in the phlogopite (sample EB2: 11.7 ± 0.8‰, n = 5) is slightly different but falls within the δ¹⁸O range of the proximal emeralds (12.1 ± 0.8 ‰, n = 20).

The δD values of the inclusion waters released at 800 °C are depleted in deuterium (δD between -119 and -100‰) while that of the channel water released at 1200 °C is between -61 and -74‰ (δDmean = -66 ± 7 ‰, n = 3). The set of data (samples EB3, ST1, and EB2) obtained directly by heating at 1200 °C is between -86 and -61‰ (δDmean = -75 ± 13‰, n = 3). The total H₂O content in the channels is between 1.26 and 1.62 wt%.

5 Discussion

Consistent emerald δ¹⁸O-values are found for the proximal and distal emeralds from Ianapera. The δ¹⁸O values are between 11.7 and 12.7‰ with a mean (1σ deviation) of 12.1 ± 0.8‰ (n = 5). These δ¹⁸O values are in agreement with two isotopic values of 12.7 %‰ reported for two single emeralds from Ianapera by Chellet et al. (2001) and Sabot (2002). On the other hand, these values are very different from those reported for the Mananjary deposits, located in the eastern region of Madagascar, which have δ¹⁸O values between 7.6 and 9.4 %‰ (δ¹⁸O mean = 8.7 ± 0.7‰, n = 6) (Giuliani et al., 2004).
1998; Sabot 2002). Similarly to Ianapera, the latter emeralds are interpreted to be related to pegmatites intruding mafic rocks. The entire data set validates the use of oxygen isotopic compositions for deciphering the geographic origin of emeralds from the two Madagascan deposits.

The zoned beryl-emerald crystal (Type 1, sample EB3) is from proximal pegmatite at the border of a phlogopite zone, and presents a $\delta^{18}O$ variation of 1.8‰ (Table 1). The beryl core has a $\delta^{18}O$ value of 10.9‰, which contrasts with the $\delta^{18}O$ value of 12.7‰ for the emerald rim. However, the $\delta^{18}O$ value of the beryl is comparable with that of beryl in granitic pegmatites, i.e., 9.75, 10.3, and 11.3‰ for, respectively, the beryl of the Adra Renaissance in Algeria, Mangularde in Portugal, and Dryden in Canada (Giuliani et al., 1997; Taylor et al., 1992). The $\delta^{18}O$ value of 12.7‰ for the emerald rim of the beryl is in the same oxygen isotopic range (12 < $\delta^{18}O$ < 12.5‰) obtained for the other proximal emeralds (samples EB1 and EB2) as well as the distal ones ($\delta^{18}O$ = 11.7‰). The ~2‰ variation indicates either a modification of temperature of the fluid or a modification of the oxygen isotopic composition due to the interaction of the metasomatic fluid with the pegmatite and the ultramafic unit, i.e., the Cr-bearing talc-tremolite-dolomite schist (TTDS). Previous studies on emerald deposits have shown that at high temperature the $\delta^{18}O$ of the fluid in equilibrium with emerald is buffered by the $\delta^{18}O$ values of the original protolith (Falllick et al., 1997; Giuliani et al., 1998). The buffering of the $\delta^{18}O$ value of emerald by its host-rock seems a reasonable hypothesis. The TTDS is a Ca-M-g-rich rock (CaO = 13.1 wt%; MgO = 18.75 wt%) and its whole-rock $\delta^{18}O$ composition would plausibly be rich in $^{18}O$. A similar host rock has been described for the Swat emerald deposits in Pakistan, where the $\delta^{18}O$ values for quartz related to the talc-quartz-dolomite-magnesite assemblage are between 15.3 and 17.1‰, with remarkably uniform $\delta^{18}O$ values for the emerald, buffered at 15.6‰ (Arif et al. 1996).

The step heating analyses at, respectively, 800 °C and 1200 °C, show two types of isotopically distinct waters: (i) inclusion water depleted in deuterium (-119 < $\delta^D$ < -100‰), and (ii) channel H$_2$O with a narrow $\delta^D$ range between -61 and -74‰. The contribution of fluid inclusion water represents a few or less than a tenth of 1 wt% of the total water (Falllick and Barros 1987; Taylor et al. 1992; Zimmerman et al. 1997). As a consequence, the $\delta^D$ for total water (experiments without step heating at 800 °C) might have a lower average compared to channel water. The emerald samples EB3 and ST1 have a $\delta^D$ value of, respectively, -61 and -78‰, which are more or less within the range of $\delta^D$ of channel water ($\delta^D_{\text{mean}}$ = -66 ± 7 ‰, n = 3). Such $\delta^D$ values imply that the contribution of inclusion water is negligible for these two samples. Sample EB2 with a $\delta^D$ of -86 ‰ indicates the incorporation of a D-depleted phase. The D-depletion in the fluid inclusions could be related to (i) incorporation of a meteoritic water component in the fluids; (ii) boiling and unmixing of the fluid with a D-depleted residuum; (iii) hydrogen exchange with organic molecules that are rich in hydrogen but poor in deuterium; (iv) reactions of thermal reduction of sulphates, particularly anhydrite, which would release $\delta^D$-depleted H$_2$O and H$_2$S (Taylor 1986); (v) the presence of fluorine which can also contribute to the D/H fractionation via HF (Richter et al. 1977). Meteoric waters and boiling were not evidenced from the fluid inclusion study of the emeralds. A fluorine effect for the D-depleted fluid is one possibility because F is present in metasomatic minerals such as tremolite (up to 0.8 wt%) and phlogopite (between 1 and 2.1 wt%), although there is no evidence for the presence of fluorine in the fluids, whereas common daughter minerals identified in all types of fluid inclusions consist of Mg-Fe carbonates and anhydrite, as well as minor barite (Andrianjakavah et al. 2009b). In addition, the occurrence of H$_2$S in the fluids was detected by Raman spectrometry (~0.05 mol%).

The presence of H$_2$S and sulphates suggest that the $\delta^D$-depleted H$_2$O could result from fractionation of hydrogen between H$_2$O and H$_2$S, at temperatures between 520°C and 685°C.

6 Source of the parental fluids for the emerald

The nature of the mineralizing fluid can be constrained by calculating the $\delta^{18}O$ value of H$_2$O in equilibrium with emerald at the temperature of formation and the $\delta^D$ value of the channel water. The temperature ranges for formation of proximal and distal emeralds at Ianapera are between 600-685°C and 520-685°C, respectively (Andrianjakavah et al. 2009b). However, the fractionation equation between beryl and fluid proposed by Taylor et al. (1992) is valid for the interval 250-500°C, and is only applicable to distal emerald. The calculated $\delta^{18}O$ of H$_2$O at 520°C for sample EB2 ($\delta^{18}O$ = 11.7‰) is 12.5‰ and the $\delta^D$ of H$_2$O in the channel is 86‰. Nevertheless, the $\delta^D$ of H$_2$O in the channel for the distal emeralds varies from -86 to -62‰ ($\delta^D_{\text{mean}}$ = -74‰, n = 3). The hydrogen and oxygen isotope composition of parental waters of the emerald is compatible with a magmatic origin (Fig. 2).

Maggmatic waters with strong $^{18}O$ enrichment are related to S-type granites resulting from the melting of $^{18}O$-rich metasedimentary crustal rocks like the granites from the Cornubian batholith in southwest England (Sheppard 1986) or the tourmaline-bearing leucogranite from Manaslu in the Himalayas ($\delta^{18}O$ whole rock between 11.5 to 13.7‰, France-Lanord et al. 1988).

The calculated $\delta^{18}O_{\text{H}_2\text{O}}$ of 12.5‰ for the distal emerald at Ianapera fits within the O-isotopic range calculated for these peraluminous granites. The $\delta^{18}O_{\text{H}_2\text{O}}$ isotopic range measured in the channel of emerald at Ianapera lies within the range defined for S-type granite magmatism. It is similar to the $\delta^{18}O_{\text{H}_2\text{O}}$ values measured in channels for other emeralds related to granitic intrusions in mafic-ultramafic rocks (Groat et al., 2002) as such as the Australian deposits of Emmaville ($\delta^{18}O_{\text{H}_2\text{O}}$ = -83.4‰) and Torrington ($\delta^{18}O_{\text{H}_2\text{O}}$ = -89‰), Kalhato in Pakistan ($\delta^{18}O_{\text{H}_2\text{O}}$ = -87.7‰), Dyakou in China ($\delta^{18}O_{\text{H}_2\text{O}}$ = -76.4‰; Xu et al., 2010), and Lena in Canada (-87.4 < $\delta^{18}O_{\text{H}_2\text{O}}$ < -62‰; Marshall et al., 2004).
suggests that proximal and distal emeralds are for S-type granitic magmatism.

The isotopic data presented here favour a magmatic-hydrothermal origin for the Ianapera emerald: (i) the isotopic compositional fields are from Sheppard (1986). The O-H isotopic field for distal emerald (dashed blue box) was calculated for 520 °C. The channel δD values are between -62 and -86‰ (δDmean = -74‰, white star).

7 Conclusions

The isotopic data presented here favour a magmatic-hydrothermal origin for the Ianapera emerald: (i) the relatively narrow range of the δ18O values of emerald suggests that proximal and distal emeralds are genetically related; and (ii) the calculated δ18O values of_ignore 12.5% at 525 °C for the distal emerald and the δD values are measured in the channel of emerald fit within the oxygen and hydrogen isotopic range of values defined for S-type granitic magmatism.

References


**Geologic Setting of Complex Pegmatites South-East of Embu, Central Kenya**

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**Abstract.** Complex pegmatites occur south-east of Embu in central Kenya and host the blue to bluish green beryl, aquamarine. Two classes of pegmatites are recognized in the area east of Embu. The first class consists of relatively small, irregular bodies segregated from granitoid metamorphic rocks in the area. The second class consists of intrusive and zoned complex pegmatites, some of considerable dimensions, characterized by the presence of a complex mineralogy. These pegmatites are part and parcel of the world-class East African gemstone province and are closely related with collisional tectonics and metamorphism which produced the Pan-African Mozambique mobile belt during Neoproterozoic times.

**Keywords.** Pegmatites, beryl, aquamarine, tourmaline, topaz, Pan-African, Mozambique Mobile Belt

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**1 Introduction**

Pegmatites south-east of Embu in central Kenya (Fig. 1) have aroused interest in recent times due to the wide, varied and complex nature of their mineralogy. These pegmatites have also been the source of the gemstone aquamarine, the blue to bluish green variety of beryl (Figure 2) (Du Bois and Walsh 1969). Preliminary exploratory and prospection work carried out in the area indicates that these complex and apparently zoned pegmatites contain a variety of potentially economic minerals including beryl, tourmaline, topaz, garnet, scapolite, mica, columbite-tantalite, indications of noticeable rare earth contents in places, and a host of industrial minerals.

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**2 Geologic setting**

Two classes of pegmatites are recognized in the area east of Embu. The first class consist of relatively small, irregular bodies segregated from granitoid metamorphic rocks in the area. These have gradational contacts with the host granitoid rocks and are often surrounded by narrow fine-grained biotite rich aureoles. The second class consists of intrusive and zoned complex pegmatites, some of considerable dimensions, characterized by the presence of a complex mineralogy that consists of feldspars, including amazonite, intergrown with quartz and including potentially economic mineralogy outlined above. Gemological investigations in this area indicate that these pegmatites are part and parcel of the world-class East African gemstone province and are closely related with collisional tectonics and metamorphism which produced the Pan-African Mozambique mobile belt during Neoproterozoic times.

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*Figure 1. An exposure of a complex pegmatite east of Embu, Central Kenya.*

*Figure 2. An exploratory excavation of a complex pegmatite east of Embu, Kenya.*

The geologic setting of the complex pegmatites south-east of Embu involves the emplacement of typical coarse grained complex lithium and beryllium rich granitic pegmatites which produce pegmatite-associated gemstones such as beryl, so far mainly aquamarine, tourmaline and topaz (Keller 1992; Schluter 1997). These
Pegmatites are part and parcel of the world-class East African gemstone province and are closely related with collisional tectonics and metamorphism which produced the Pan-African Mozambique mobile belt during Neoproterozoic times.

3 Economic Potential

The economic potential of pegmatites south-east of Embu was noted earlier during the initial mapping of the area, mainly due to of significant occurrences of mica (Bear, 1952). Further work addressing occurrences of beryllium in Kenya also identified these pegmatites as being of interest (Du Bois and Horne 1962) and also hosting columbite (Du Bois and Walsh 1969). Preliminary exploratory and prospection work carried out in the area indicates that the complex and apparently zoned pegmatites, some of considerable dimensions, contain a complex mineralogy with a variety of potentially economic minerals that includes feldspars, including amazonite, intergrown with quartz, beryl (Figures 3, 4, and 5), tourmaline, topaz, garnet, scapolite, mica, columbite-tantalite, noticeable rare earth contents in places, and a host of industrial minerals. The complex pegmatites are also being investigated in places for effect of desilication by adjacent mafic and ultramafic rock bodies consisting of olivine norites, hornblende gabbros, meta-dolerites, ortho-amphibolites which would provide suitable environment for the formation of gem ruby and sapphire (corundum), spinel, alexandrite and tourmaline. This has generated growing research interest in the geology, geologic setting, mineralogy, geochemistry and age of complex pegmatite east of Embu and surrounding areas with emphasis on the need to reinterpret earlier geological work in light of modern approaches, advances, and understanding (Cerny and Meintzer 1988; Thomas and Spooner 1988; London 2008; Turner and Groat 2014; Simmons 2014).

![Figure 3](image1.png)

**Figure 3.** Two plane surfaces at 120° left in host pegmatite after removal of a large crystal of beryl.

![Figure 4](image2.png)

**Figure 4.** A quartzine from a complex pegmatite south-east of Embu, Kenya.

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U/Pb Ages of Zircon and Monazite from the Tsavorite-Bearing Neoproterozoic Rocks of Southeastern Kenya, and the Significance of Static Crystallisation of the Tsavorite

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Abstract. Tsavorite, the vanadian variety of green grossular, is hosted exclusively in metasedimentary formations in the Neoproterozoic Metamorphic Mozambique Belt. In order to understand the origin of tsavorite in southeastern Kenya we integrated field investigations, geochemical studies, and dating. Two units are seen in outcrop: 1) a metasedimentary sequence, and 2) a quartz-feldspar migmatitic group. This second group of rocks shows classic “Pan-african geometry” with vertical and horizontal foliation planes. The metamorphism attains granulate facies. The metasedimentary sequence is different and recorded lower metamorphism (high-amphibolite facies, 680 °C), and if static recrystallization occurs, few traces of melting were observed. Landslide with sediment deformation structures of the sedimentary depositions are preserved. Systematic LA-ICPMS U/Pb dating was done on monazite and zircon. The migmatitic rocks recorded ages from 615 Ma to 585 Ma. The metasedimentary rocks recorded ages from 600 Ma to 595 Ma. O ffer ages of 850 - 720 Ma seems to be inherited ages from magmatic minerals. The formation of tsavorite is the result of a sedimentary sequence preserved from strain but heated by surrounding granulitic rocks between 600 to 595 Ma. The regional associated tectonic process is unclear but efficient for vertical displacement. We suggest that it is a peculiar event and process, and was unable to completely recrystallize the sedimentary rocks. These last are exceptionally preserved from strain and melt, a case that may be unique in the world.

Keywords. Tsavorite, southeastern Kenya, granulite, LA-ICPMS dating, monazite, zircon, Pan-african

1 Introduction
Tsavorite, the green variety of vanadium grossular, is restricted to a few areas worldwide: southeastern Kenya and northeastern and southeastern Tanzania. Some other very localized occurrences are observed in Madagascar, Pakistan, and east Antarctica. The Tsavo region shows the best tsavorite occurrences from M gama ridge in the north to the Kuranze area in the south, forming a discontinuous ca. 70 km long NW-SE gem belt. Even if outcrops are scarce, many of the mines offer good opportunities to map layers hosting tsavorite. Here, we integrate field investigation with geochemical and mineralogical studies, and undertook systematic dating of thin sections and separated grains in order to emphasize the tsavorite formation story.

2 Tsavorite in southeastern Kenya
2.1 Geological setting
In southeastern Kenya, the different metamorphic rocks can be separated into two main groups: 1) a metasedimentary unit with graphitic gneiss, calc-silicate, meta-arenite, meta-rudite, marble, and garnet amphibolite. These rocks of sedimentary origin are enriched in chromium and vanadium (Fig. 1a) and form three quarters of the Kuranze Group; 2) A quartz-feldspar migmatitic sequence interlayered with metabasite, charnockite, and marble. These rocks define the Kasigau Group but are also found in the eastern part of the Kuranze Group where marbles are dominant.
These rocks show “Pan-african geometry” with vertical and horizontal high-grade foliation planes displaying high strain, like recumbent folds with horizontal axial plane, or folds showing vertical axial planes with north-south horizontal axes sometimes highly transposed. The evolution from vertical to horizontal geometry is controlled by final east-west shortening. This last event could be localized into kilometric-high strained zones (e.g. Galana shear zone, Hauzenberger et al. 2007). The metamorphic conditions are of high amphibolite facies, locally zone, Hauzenberger et al. 2007). The metamorphic conditions are of high amphibolite facies, locally reaching granulitic facies with two-pyroxene metabasites (clinopyroxene - orthopyroxene - plagioclase - quartz) and gneiss showing melting of titanium- and magnesium-rich biotite.

The metamorphic ages of 600 - 595 Ma are recorded in the sedimentary sequence preserved from strain but tsavorite formation results from static metamorphism of tsavorite-hosting metasediments. We suggest that metamorphisms or a 30 Ma continuous process. Very rare younger ages, close to 550 Ma, are compatible with new crystallized rims aged 616 ± 2 Ma (Fig. 3a). In the rim, the Th/U ratio is very low, the cores of measured zircons define an age equal to 885 ± 20 Ma for the zircons. The study was done on four meta-rudites and three graphitic gneisses interlayered with tsavorite-bearing calc-silicate rocks from the metasedimentary sequence. For the quartz-feldspar migmatitic sequence, analyses were done on three granulites showing evidence of biotite melting and four garnet-bearing migmatites which were classified on cross-cutting relations.

2.2 Dating method and samples

We used in situ U-Th-Pb dating by LA-ICPMS on mineral separates and on thin sections at the "Laboratoire Magmas et Volcans" (Clermont-Ferrand, France). Analytical procedures are reported in detail in Paquette and Tiepolo (2007) and Hurai et al. (2010). The spot size was 15 to 9 µm in diameter for the monazites and 20 µm for the zircons. The study was done on four meta-rudites and three graphitic gneisses interlayered with tsavorite-bearing calc-silicate rocks from the metasedimentary sequence. For the quartz-feldspar migmatitic sequence, analyses were done on three granulites showing evidence of biotite melting and four garnet-bearing migmatites which were classified on cross-cutting relations.

2.3 Results

VOI 17a and VOI 17b are samples from the same location: VOI 17a is a migmatite and VOI17b is a leucosome localized in dilatant structures cross-cutting the migmatitic foliation of VOI 17a. In sample VOI 17a the cores of measured zircons define an age equal to 685 ± 2 Ma (Fig. 3a). In the rim, the Th/U ratio is very low, which is compatible with new crystallized rims aged 616 ± 5 Ma (Fig. 3a). In sample VOI 17b, the calculated age is 599 ± 4 Ma (Fig. 3b). Similar ages are found in zircon and monazite in the quartz-feldspar migmatitic sequence. Monazites associated with garnet in granulite defined a single slightly younger age of 581 ± 3 Ma (sample VOI 3b, Fig. 4). Very rare younger ages are close to 550 Ma.
The 850 Ma value seems to be an inherited age of magmatic zircons or monazites. The age spread from 615 to 585 Ma can correspond to different high-grade metamorphisms or a 30 Ma continuous process. Very rare younger ages, close to 550 Ma, are compatible with late strain and fluid circulation related to the Galana shear zone (Hauzenberger et al. 2007; Bosse et al. 2009).

The ages measured for the metasediment are relatively similar (e.g. Fig. 5), but some differences are noticeable. We find younger inherited magmatic ages around 720 Ma. We do not find in the zircon crystals ages corresponding to 615 Ma; instead, the ages are around 600 Ma. Zircons from the meta-rudite are rich in U (6000 ppm) and metamict and the U/Pb data are not interpretable. Ages for the monazites are around 600 to 595 Ma. Thus ages are less scattered in the metasediments.

The metamorphic ages of 600 - 595 Ma are recorded both in the quartz-feldspar migmatitic sequence and the tsavorite-hosting metasediments. We suggest that tsavorite formation results from static metamorphism of the sedimentary sequence preserved from strain but cooked by surrounding granulitic rocks between 600 and 595 Ma.

2.4 Significance of the zircon and monazite ages for tsavorite formation in the Kenyan Neoproterozoic Metamorphic Mozambique Belt

Observations in southeastern Kenya testify to the preservation of evaporitic sediments deposited on a gentle slope produced by extensive tectonism, most probably after 720 Ma (Feneyrol et al. 2013). This is compatible with a period of continental extension and intrusive igneous activity (Tucker et al. 2011). These sediments were metamorphosed between 600 and 595 Ma and recorded at least middle-crust conditions (T ~ 680 °C, P ~ 7 kbar). Considering the geometrical relation of the metasediments and the quartz-feldspar migmatic sequence, it looks like a “sandwich” of a metasediment slice between two slices of quartz-feldspar melted granulites. The meta-sedimentary sequence could form a boudin of high strength, preserved from strain and melting, surrounded by weaker material that was partly melted and highly strained. We suggest that, in this very hot melted crust, vertical motion of material from the suprastructure to depth is efficient.

Note that southeastern Kenya occupies a very peculiar place in the Neoproterozoic Metamorphic Mozambique Belt. It forms a large diachronous continental collision zone with one peak around 640 Ma (East African Orogeny), and a second event between 580 and 550 Ma (Kuunga orogeny, Tenczer et al. 2013). In this belt of stacked slices, the tsavorite-bearing metasediments are very close to one of the biggest shear zones, the Galana shear zone, which is part of a tectonic flower (Fritz et al. 2009). Considering the scarcity of tsavorite, this tectonic context responsible of sedimentary amalgamation inside granulites is very unusual and/or exceptionally preserved.

Figure 3. Results for zircon: $^{206}$Pb/$^{238}$U versus $^{208}$Pb/$^{232}$Th diagrams from sample VOI 17a (a) and VOI 17b (b). VOI 17a is a garnet migmatitic gneiss (biotite - green amphibole - garnet - plagioclase - K-feldspar - quartz). VOI17b is a leucosome localized in dilatant structures cross-cutting the migmatitic foliation of VOI 17a.

Figure 4. Results for monazite: $^{206}$Pb/$^{238}$U versus $^{208}$Pb/$^{232}$Th diagram from sample VOI 3b. Granulite sample showing melting of Ti-rich biotite resulting in peritectic garnet. This rock exhibits classic granulitic strain with viscosity convergence of phases (K-feldspar with exsolved lamellae of albite - quartz - plagioclase) and ribbon structures.
Figure 5. Results for monazite: $^{206}$Pb/$^{238}$U versus $^{208}$Pb/$^{232}$Th diagram from sample VOI 28. VOI 28 is an unstrained metarudite showing sedimentary textures. The sample is from the quarry in Figure 2.

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References


The Boron Isotopic Composition of Tourmaline from Tsavorite Deposits in the Neoproterozoic Mozambique Metamorphic Belt, with a Special Focus on the Mining Districts in Kenya

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Abstract. The dravitic tourmalines associated with different types of rock from the tsavorite-bearing metasedimentary Neoproterozoic sequence in Kenya, Tanzania, and Madagascar show two ranges of boron isotopic compositions: (1) Tourmalines associated with tsavorite nodules have homogenous $\delta^{11}$B values of -19.8 ± 1.2‰ that clearly involve continental evaporitic material; (2) Tourmalines from unmineralized rocks (clastic metasediments, metapegmatite, and marble) have $\delta^{11}$B values between -15.9 and -10.3‰, which reflect a magmatic source for the clastic tourmaline and probably an evaporitic one for tourmaline in marble.

Keywords. Boron isotope, tsavorite, tourmaline, Kenya, Neoproterozoic Mozambique Metamorphic Belt

1 Introduction

Tsavorite, the green variety of vanadian grossular, is a high-value economic gemstone hosted exclusively in metasedimentary formations in the Neoproterozoic Metamorphic Mozambique Belt (NMMB). The green garnet is mined only in southeastern Kenya, northeastern and southeastern Tanzania, and southern Madagascar. It has been sporadically exploited in the Swat Valley in Pakistan and discovered in the Sør Rondane Mountains in East Antarctica. The deposits are located within graphic gneiss and calc-silicate rocks, intercalated with meta-evaporites (Feneyrol et al. 2013). Tsavorite is found as primary deposits either in nodule (type I) or in quartz veins (type II), and in placers (type III).

In the mineralized nodules (Fig. 1), tsavorite is generally located in the core and is sometimes rimmed by V-zoisite, fine-grained V-scapolite, V-diopside, V-titanite, and V-magnetite. It is associated also with calcite, quartz, pyrite, graphite, apatite, anhydrite, gypsum, barite, and tourmaline. The tsavorite nodules were formed during prograde metamorphism, calcium coming from sulphate and ± carbonate minerals, whereas the alumina, silica, vanadium, and chromium probably came from clays and chloride.

Figure 1. A nodule of tsavorite and some rough and cut material from the tsavorite mine (Kenya). Photograph V. Pardieu (GIA)

The present contribution investigates the in situ boron isotope composition of tourmaline associated with different types of rock from the tsavorite-bearing metasedimentary sequence in Kenya in order to trace the source of boron for the fluids responsible for tsavorite mineralization, and also for the unmineralized rocks. The $\delta^{11}$B values of tourmalines associated with tsavorite from Tanzania and Madagascar are reported in order to compare with those from Kenya.
2 Geological setting of tsavorite in Kenya

The first tsavorites were discovered in 1970 in southeastern Kenya at M'indi Range (Bridges 2007) and mining started in the M'gama Ridge in 1973 (Fig. 2). Today, the deposits and occurrences of tsavorite extend from M'wahate to the Tanzania border at Ngomet, defining a NW-SE trend corresponding to the main S1 foliation in the metamorphic formations. Dozens of occurrences of tsavorite are known in the Taita-Taveta district (Fig. 2). These occurrences and small deposits define a tsavorite belt circa 70 km long and 200 m wide with a few more deposits located outside the main gem zone (Feneyrol et al. 2013). The main productive mining districts are those of M'gama Ridge (Minkenco, Gitshure-Baraka, and David Visrum mines), Bocrest, Mindi Range (Consolidated, Tsavo, Bridges Scorpion, Baraka, and David Visrum mines), Mangare-Kisoli (Aqua, Tsavolite, Bocrest, Nadan II and Nyaga Musa mines), and Kuranze-Ngomet (M'biriri, Dickam and Nadan I mines).

3 Material and analytical method

3.1 Material

The $\delta^{11}\text{B}$ values of 121 spot analyses from 15 samples of tourmaline from seven Kenyan tsavorite deposits were analyzed by SIMS (Table 1). The tourmaline from Kenya came from the Lualenyi mines (the Davis mine) and the Gitshure mines (the Ilani mine) in the M'gama Ridge, the David Visrum mine north of the M'indi Range, the Baraka mine in the M'indi Range, the Rockland mine in the Mangare area, the Bocrest mine, and finally in the Ngomet area at the M'biriri mine on the frontier with Tanzania.

The samples from the Davis mine, i.e. TS15-5B, TS15-5A, S2T, S3T, and VOI 26-7 are from metarudites (Fig. 3), while TS15-6 originated from quartz veins crosscutting graphite-bearing gneiss. Samples VOI 132-3 and MWT2 are hosted by graphite-bearing marbles, respectively from Ilani and Baraka. Sample VOI 75B (Fig. 4) is from a metapegmatite at the Visrum mine, north of the Baraka mine.
were studied following their lithology: (1) The detrital tourmalines in clastic nodules or metarudites from the Davie's mine have a δ\(^{11}\)B range between -15.9 and -11‰, with a mean δ\(^{11}\)B value of -13.1 ± 1.8‰ (n = 5); (2) The tourmalines hosted by graphite-bearing marbles have δ\(^{11}\)B values between -15.6 and -10.3‰, respectively for the Ilani and Baraka deposits; (3) The tourmaline-bearing quartz veins from the Davis and M'biriri mines are within a restricted boron isotopic range, between -14.5 and -13.8‰ (n = 3); (4) The tourmalines from placer near the M'biriri mine, Ngomet area, have δ\(^{11}\)B values between -15.1 and -13.8‰ (n = 2); (5) The tourmaline-bearing pegmatite from the David Visrum mine has a δ\(^{11}\)B value of -14.5‰; (6) the tourmaline associated with the ruby-bearing desilicated pegmatite in the Rockland mine has a δ\(^{11}\)B value of -14.8‰; (7) the δ\(^{11}\)B value for tourmaline associated with the tsavorite nodule from the Bocrest mine is -19‰. The Malagasy and Tanzanian tourmaline associated with tsavorite nodules in calc-silicate rocks has δ\(^{11}\)B values between -21.6 and -18.5‰.

Table 1. Boron isotope values (δ\(^{11}\)B, ‰) of tourmaline associated with tsavorite deposits from Kenya, Madagascar, and Tanzania.

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine</th>
<th>Sample</th>
<th>δ(^{11})B</th>
<th>Error 1σ</th>
<th>N of analyses</th>
<th>Rock type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kenya</td>
<td>Davis</td>
<td>TS10-03</td>
<td>-14.2</td>
<td>0.9</td>
<td>9</td>
<td>detritic tourmaline (Pt 1)</td>
</tr>
<tr>
<td></td>
<td>Davis</td>
<td>TS15-5A</td>
<td>-13.3</td>
<td>0.3</td>
<td>3</td>
<td>detritic tourmaline (Pt 1)</td>
</tr>
<tr>
<td></td>
<td>Davis</td>
<td>TS15-4C</td>
<td>-14.0</td>
<td>0.9</td>
<td>9</td>
<td>graphite-hosted tourmaline (Pt 1)</td>
</tr>
<tr>
<td></td>
<td>Davis</td>
<td>V00-33</td>
<td>-15.6</td>
<td>1.6</td>
<td>10</td>
<td>graphite-hosted tourmaline (Pt 1)</td>
</tr>
<tr>
<td>Madagascar</td>
<td>Baraka</td>
<td>MWT2</td>
<td>-13.4</td>
<td>0.4</td>
<td>12</td>
<td>graphite-hosted tourmaline (Pt 1)</td>
</tr>
<tr>
<td>Madagascar</td>
<td>Maddall</td>
<td>M01</td>
<td>-16.4</td>
<td>0.8</td>
<td>8</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Madagascar</td>
<td>Kuranze</td>
<td>VO1-52</td>
<td>-14.3</td>
<td>0.9</td>
<td>9</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Tanzania</td>
<td>Ngomet</td>
<td>VO1-53</td>
<td>-15.6</td>
<td>1.6</td>
<td>10</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Tanzania</td>
<td>Taveta</td>
<td>T1A</td>
<td>-15.1</td>
<td>1.1</td>
<td>13</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Tanzania</td>
<td>Taveta</td>
<td>T1B</td>
<td>-15.6</td>
<td>1.6</td>
<td>10</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Tanzania</td>
<td>Visrum Mine</td>
<td>V00-29</td>
<td>-16.2</td>
<td>0.8</td>
<td>8</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Madagascar</td>
<td>Gogoppy</td>
<td>BF01</td>
<td>-18.6</td>
<td>1.0</td>
<td>13</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Madagascar</td>
<td>OZ</td>
<td>OZ</td>
<td>-12.6</td>
<td>0.8</td>
<td>8</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Tanzania</td>
<td>Llamahu</td>
<td>L1</td>
<td>-18.6</td>
<td>1.0</td>
<td>13</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Tanzania</td>
<td>Mewa</td>
<td>Mewa</td>
<td>-15.1</td>
<td>1.1</td>
<td>13</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Tanzania</td>
<td>V17B</td>
<td>V17B</td>
<td>-13.0</td>
<td>0.8</td>
<td>8</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
<tr>
<td>Tanzania</td>
<td>JF126</td>
<td>JF126</td>
<td>-15.4</td>
<td>1.0</td>
<td>13</td>
<td>tourmaline associated with tsavorite nodule (Mt 1)</td>
</tr>
</tbody>
</table>

5 Discussion

Two consistent ranges of δ\(^{11}\)B values were found for the tourmalines: (1) δ\(^{11}\)B values between -21.6 and -18.5‰ with a mean (1σ deviation) of 19.8 ± 1.2‰ (n = 5). These δ\(^{11}\)B values are for tourmaline associated with tsavorite nodules hosted by calc-silicates from Kenya, Madagascar, and Tanzania. The range of δ\(^{11}\)B values falls in the exclusive range of values for continetal evaporites (Fig. 5) defined by Barth (1993) and van Hinsberg et al. (2011). (2) the second δ\(^{11}\)B range is between -15.9 and -10.3‰. It concerns crystals of tourmaline hosted in different types of lithology from the tsavorite-bearing metasedimentary formation, respectively clastic metasediments, desilicated pegmatite, and quartz veins. The δ\(^{11}\)B range of detrital tourmaline from the Davie's mine, i.e. between -15.9 and -10.3‰, is within the range of δ\(^{11}\)B values defined for continental crust, clastic metasediments, granites, and pegmatites (Fig. 5).

The δ\(^{11}\)B values of tourmaline for the metapegmatite at the David Visrum mine and the desilicated pegmatite at...

Figure 4. Dravite crystals in ruby-bearing desilicated pegmatite from the Rockland mine (Mangare area).

3.2 Analytical method

The boron isotope composition of tourmaline was measured using a CAM ECA ims 1270 secondary ion mass spectrometer at CRPG, Nancy, France during two sessions (09/2014 and 02/2015). Gold-coated samples were sputtered with a primary beam of \(^{16}\)O ions with an intensity of ~20 nA, focused to a spot of about 20 μm. A mass resolution of 3,000 was used for the analyses. Boron isotopes were measured in monocollection mode using a central Faraday cup. Measurements consist of 30 cycles, each cycle constituting 2 s count time on mass 9.5 (Faraday Cup background), and 8 s and 4 s on the \(^{10}\)B+ and \(^{11}\)B+ peaks, respectively. The typical intensities were about 5 × 10⁷ cps on \(^{10}\)B+. The typical internal error was less than ±0.2 ‰. The reference material was a tourmaline (Tourm3116, δ\(^{11}\)B = -9.2 ‰, Chaussidon and Albarède 1992) and the external error based on the repeated measurements of this tourmaline was between 0.3 and 0.7 ‰ (1σ), depending on the analytical session. Lithium concentrations are low (typically less than 100 ppm) such that no matrix effect correction was needed (Smith and Yardley 1996). All the δ\(^{11}\)B values are expressed in delta notation relative to the SRM 951 international standard (\(^{10}\)B/\(^{11}\)B=0.2473±0.0002, NIST certificate, 1999).

4 Boron isotope composition

The mean δ\(^{11}\)B values of the 183 spot analyses from 20 samples of tourmaline from all the deposits are reported in Table 1. The δ\(^{11}\)B values range from -21.6 ‰ to -10.3 ‰. The Kenyan tourmalines, dravitic in composition,
Davis and M’biriri mines (mean magmatic source. The same hypothesis can be used for clastic tourmalines from the Mgama ridge can have a magmatic source. The same hypothesis can be used for the tourmaline from quartz veins from the Davis and M’biriri mines (mean δ11B value ~14.4‰).

Following these considerations the boron source of this range of pegmatite in the tsavorite mining area.

This Bridges CR (2007) Le grenat vert tsavorite : présentation et

Geol. Rundschau 83:640-651

6 Conclusions

SIMS in situ analyses of dravite tourmaline revealed two ranges of boron isotopic composition: (1) Tourmalines associated with nodules of tsavorite from Kenya, Tanzania, and Madagascar showed similar boron isotopic compositions of -19.8 ± 1.2‰. This value clearly involves continental evaporitic material and confirms the genetic model proposed for tourmalite from the metasedimentary series of the NMMB (Feneyrol et al 2013). The metasediments derived from an ancient platform in a widespread and shallow evaporite-bearing epeiric platform with alternation of marine and non-marine seaways, i.e. marine coastal sabkha. (2) The second isotopic δ11B range, between -15.9 and -10.3‰, concerns crystals of tourmaline hosted in different types of lithology, respectively clastic metasediments, desilicated pegmatite, and quartz veins in Kenya. It reflects a magmatic source for the clastic tourmaline and probably an evaporitic one for the tourmaline in marble.

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débat. Revue de Gemmologie AFG 161:4-7


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Figure 5. Boron isotopic compositions of tourmalines from Kenya, Tanzania and Madagascar. The boron isotopic compositions of the different boxes are from Barth (1993) and van Hinsberg et al. (2011).
Indicator-Based Characterisation of Kaolin Deposits

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Abstract. In-situ characterisation of a geological resource is a key step in the mining cycle but spatial grade data of the orebody is often scarce. It is thus necessary to investigate methods of resource estimation that rely on other types of (non-grade) data. This study investigates characterisation of a kaolin deposit with two indicator-based methods, Indicator Kriging and Sequential Indicator Simulation. Risk associated with the kriged estimate of the ore quality is explored using simulation. A combination of these methods makes it possible to produce resource models without the requirement of grade data. This reduces the number of laboratory grade tests and speeds up the planning cycle.

Keywords. Alteration, Kaolin, Indicators, Risk, Kriging, Simulation, Geostatistics

1 Introduction

Efficient extraction of a geological resource is a key part of any mining operation that aims to maximise the Net Present Value (NPV) of a resource. Initial, in-situ characterisation of the resource prior to extraction can assume many forms, e.g. resource/reserve classification, geotechnical classification, or data for short-term grade control. It can involve many different types of data collection such as geological mapping, geophysical reconnaissance and direct sampling of the ore body. This study explores opportunities for rapid development of resource models for kaolin, or china clay.

High-quality kaolin is currently mined from the St Austell granite in Cornwall, south-west England. The mineralisation is highly complex (Bristow 1993), making it suitable for investigating novel geostatistical methodologies. Granite containing kaolin is classified into lithological units or categories based on the observed degree of kaolinisation. Estimates of the spatial distribution of kaolin are generated using indicator methods. To complement estimation by kriging, simulation will be used (e.g. Webster and Oliver 2007).

2 Indicator methods of estimation and simulation

The basis of indicator methods of estimation and simulation is the definition of indicators. These transform a variable (Z) according to a given cut-off (z_c) as follows:

\[ \text{Ind}(Z \geq z_c) = I(Z \geq z_c) = \begin{cases} 1 & \text{if } Z \geq z_c \\ 0 & \text{if } Z < z_c \end{cases} \]

The dataset in this study consists of categories assigned to sampled locations. This implies that cut-offs used by indicator methods necessarily correspond to categories that pre-exist in the data. Each indicator is treated separately until the end of the process, when the separate estimates or simulations are recombined into a single model.

The major drawback of indicator methods that use continuous grade data are order relationship issues (Vann and Guibal 2000). These become apparent when the tonnage observed at a lower cut-off is greater than that at a higher cut-off, which is impossible. Solving order relationship problems can be complex and time consuming. In this study, the use of categorical cut-offs presents a conservative approach, ensuring that any bias leads to underestimation rather than overestimation.

2.1 Indicator Kriging

Indicator kriging (IK) is a non-linear estimation method of estimation based on the kriging algorithm (Vann and Guibal 2000). It is described in detail by Journel (for example 1983 and 1988) and has been used in a wide variety of geoscience applications, with particularly high uptake within the soil science community (Asa et al. 2012).

2.2 Sequential indicator simulation

Sequential Indicator Simulation (SIS) is a simulation method that uses indicators rather than continuous data. Simulations aim to produce a series of equiprobable realisations of data that can then help understand the risk associated with an estimate (see Chiles and Delfiner 2012). SIS is a non-parametric method of simulation that has its origins in the petroleum industry for reservoir modelling (Vann Bertoli and Jackson 2002) and has been applied to a wide variety of applications within geoscience. Some of the limitations of the method are discussed by Emery (2004).

3 Kaolin deposits of the St Austell granite

The St Austell granite in central Cornwall hosts kaolin deposits with kaolinite as the primary clay mineral among a variety of other minerals (Murray and Keller 1993). The granites were intruded during the latest Carboniferous/early Permian periods (Scrivener 2006). Several types of granite were subjected to in situ chemical weathering, producing kaolin through the breakdown of phyllosilicates in the presence of water and weak acids (Psyrillos et al. 1998). Little transportation of the kaolin appears to have occurred, leading to localised variation in the lithology of the kaolinised granite (Manning et al. 1996).

Kaolin has been mined in the St Austell area for over 250 years (Bristow 1993). It has a wide variety of uses including in paper, ceramics, plastics, rubber, paint, ink, and pharmaceuticals. Different end uses require products with different specifications, so many different products are produced (Imerys Minerals 2015).

The study area lies within the Tourmaline granite of...
the western lobe of the St Austell granite (Scrivener 2006). Imerys Minerals provided geological logs of drillhole data collected over a number of years. The dataset comprises of 164 drillholes with 1,246 samples present of between 1.5 meters and 34 meters in length. The dataset thus required regularisation in order to use it for geostatistical estimation and simulation. The location of drillholes is shown in Figure 1.

Imerys Minerals use a set of geological classifications to define the ore based on the degree of kaolinisation present in the ore. These textural and alteration based classification schemes are presented in Table 1. Normally the three upper, most altered grades are considered to constitute ore.

### Table 1. Normally the three upper, most altered grades are considered to constitute ore.

<table>
<thead>
<tr>
<th>Written Description</th>
<th>Study 1</th>
<th>Study 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FKG: Fully Kaolinised Granite</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>NFKG: Nearly Fully Kaolinised Granite</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>PNFKG: Partly Nearly Fully Kaolinised Granite</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>PKG: Partly Kaolinised Granite</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>PWKG: Partly Weakly Kaolinised Granite</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>WKG: Weakly Kaolinised Granite</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>NFG: Nearly Fresh Granite</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>FG: Fresh Granite</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

4 Study 1: Estimation based on categorical data

IK is used to estimate the percentage of any given alteration grade contained in a block. However, the distribution of the alteration grade within a block is not obtained. Estimation was carried out on data which followed the full descriptive grouping of the alteration and textural classification in Table 1, with the exception of the fresh granite and nearly fresh granite categories (which were grouped together).

The process of estimation consisted of the following:

1. Creating experimental variograms of each dataset and modelling a variogram in each case.

2. Indicator kriging of each dataset to estimate the expected proportion of each alteration grade within a given block.

3. Recombining the separate estimates into a single model that can be used for further resource assessment.

Each indicator kriging run was optimised using various kriging outputs. The size of the search neighbourhood was kept the same to allow recombination of the estimations at different cut-offs. Figure 2 displays the proportion of each block that contains granite that is deemed to be ore, i.e. “Grade” 4 or “Grade” 5 (Study 2, Table 1). Figure 3 displays the proportion of each block that contains granite with the highest grade of kaolin, i.e. “Grade” 7 (Study 1, Table 1).

5 Study 2: Simulation for modelling the risk associated with resource estimation

The risk associated with the estimated grades of kaolin is assessed through the creation of combined risk models using SIS. In this study, the full textural classification was grouped into five categories (Study 2). Note that the first category represents a truly fresh granite which, due to the age of the granite intrusion, is never found in practice.

The SIS process consisted of the following steps:

1. Creating experimental variograms of each dataset and modelling a variogram in each case.
2. Performing SIS and generating 100 simulation for each indicator.
3. Generating risk models from each simulation after the method given in Palmer and Glass (2014).
4. Creating best and worst case scenarios using the simulations that maximised or minimised the amount of the two different ore grades; 4 and 5.

Figure 2. Plan view of the distribution of “Grade” 4/“Grade” 5 (Study 2) granite. Red represents a high proportion, while a low proportion.

Figure 3. Plan view of the distribution of “Grade” 7 (Study 1) granite. Red represents a high proportion, while a low proportion.

Figure 4 displays the percentage of blocks, generated from risk models of each grade, of the occurrence of “Grades”. Using individual simulations, scenarios were also produced. The best case scenario is displayed in Figure 5, with a maximum tonnage of ore, i.e. “Grade” 4 and 5 granite, and the highest possible percentage of the highest quality ore (“Grade” 5). Figure 6 displays the worst case scenario, with a minimum tonnage of ore, i.e. “Grade” 4 and 5 granite, and the lowest possible percentage of the highest quality ore (“Grade” 5).

6 Discussion

The estimates produced using IK (Figures 2 and 3) suggest that there is an area of moderately altered granite in the centre of the estimated area. This zone appears to trend north-west south-east. A zone of much more highly altered granite is present within this, appearing to trend

Figure 4. Probability of each grade occurring in a percentage of blocks in the deposit.

Figure 5. Best possible scenario produced from the simulations.

Figure 6. Worst possible scenario produced from the simulations.
north-east south-west. Assuming the best case scenario (Figure 5), there could potentially be a much larger area of moderately altered granite present that again trends NW-SE. Even in worst case scenario (Figure 6), there is still a significant amount of “Grade” 4 granite present. The risk model (Figure 4) further enhances our understanding. If 50% of the blocks are required to be “Grade” 5, there is only a 20% probability of this being the case. If only 10% of the blocks are expected to be of “Grade” 5, the probability increases to 80%. By using estimation, risk models and scenarios in conjunction, significant insight into the resource, its extraction, and downstream processing can be gained.

7 Conclusions

The geostatistical methods of indicator estimation and simulation were used to characterise a kaolin resource based on alteration and textural classification rather than conventional grade data. Geological characteristics of a primary kaolin deposit are very amenable to indicator methods due to the manner they are intrinsically logged. The estimates and associated risk models help to inform decision-making based on probabilistic measures.

Acknowledgements

The authors acknowledge support for this research as part of the Sustainable Technologies for Calcined Industrial Minerals (STOICISM) project funded by the European Union’s 7th Framework Programme (FP7/2007-2013) under grant agreement number 310645. The authors would like to thank the Geology department of the UK Kaolin Platform at Imerys Minerals for their kind help in facilitating this study. Finally, Daniel Roberts and Luke Stockdale are thanked for their contribution made during their Master thesis projects at Camborne School of Mines, University of Exeter.

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Diffusion of Heavy Metals during Vitrification of Chromium Sludge in a Basaltic Matrix: Model of a Melting Pond in an Alumina Crucible

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Abstract. The process of inertization of chromium sludge in a basaltic matrix is modelled in laboratory conditions using an aluminous crucible to account for the refractory material of a melting pond. The deformation and the viscosity-temperature curve of the glass have been measured by Hot-Stage microscopy. The maximum treatment temperature is 1450°C. The reactions at the crucible – melt interface and inside the melt itself have been characterised by optical and scanning electron microscopy. Although there is some cation transference between the melt and the crucible, only the innermost part of the crucible reacts with the melt, thus accounting for the safety of the process. The crystallisation of spinel-like phases has been both observed in microscopic analysis and has been further supported by X-Ray diffraction analysis.

Keywords. Chromium sludge, Glass, Basaltic matrix, Inertization, Vitrification

1 Introduction

Vitrification of toxic wastes such as sewage sludge, contaminated soils or nuclear wastes is a widespread inertization technique which has been endorsed by several studies (Colombo et al. 2003, Bingham and Hard 2006, Garcia-Valles et al. 2007, Prahesh 2012, Mymrin et al. 2014). Although it is already an established technique, it still lacks insights on the physical behaviour (viscosity-temperature) of the melts from which glasses are obtained. A nother issue which must be addressed is the creation of an inertization environment that enables a correct stabilization and solidification process must be secured for the vitrification treatment (Aydin and Aydin 2014).

This study deals with those problems: the dependence of viscosity on temperature for a glass made of a mixture of basalt and chromium sludge, the crystallisation of spinel-like phases during glass production and if any reactions take place between the melt and the crucible.

The composition of sludges from wastewater treatment plants is appropriate to make glass because its composition is similar to that of basic rocks. A main problem of vitrification using a basaltic matrix is that viscosity measurements are not accurately predicted by current viscosity models of silicate liquids due to the differences in chemical composition (such melts are greatly enriched in heavy metals such as chromium, zinc, copper, nickel... or sometimes other major components such as phosphorous or calcium). Sludge composition has an intrinsically high variability, hence making it harder to establish comprehensive models of vitrification.

The study reproduces at the laboratory scale the conditions inside a melting pond to describe the formation of spinel-like phases during the production of the glass and the reactions at the interface between the crucible and the melt.

2 Material and methods

Basalt from Lanzarote (Canary Islands) has been used as a vitrification matrix for galvanic sludge. The chemical composition of the calcinated raw sludge were obtained by X-ray fluorescence (XRF), using a sequential X-ray spectrophotometer Philips PW2400. Trace elements were analysed in a Unicam 939 atomic absorption spectrometer and induction couple plasma Perkin Elmer Optima 3200 RL.

The studied glass is made using a ratio basalt/sludge of 90/10. The mixture is placed in an aluminous crucible (70% alumina, 30% mullite; previously fired to 1500°C to close any remaining porosity) and undergoes the following thermal treatment:

- Heating from 50°C to 950°C at 3°C/min and a 2h isothermal step to burn any remaining organic matter.
- Heating from 950°C to 1450°C at 1°C/min and a 2h isothermal step to melt the mixture.
- Cooling from 1450°C to 1350°C at 1°C/min and a 12h isothermal step to enable the nucleation and growth of spinel-like.
- Quenching to room temperature (Fig. 1a).
- Heating to 675°C to relax any tensions of the quenched glass (Fig. 1b).

Figure 1. Glass production process and thermal treatment: quenching (a) and annealing (b).

Hot-Stage M Microscopy (HSM ) has been used to study the evolution of viscosity of the glass during heating (at
5ºC/min up to 1450ºC). The glass is ground to a grain size lower than 45µm according to DIN 51730. Analysis was performed with Hot-Stage software (Garcia-Valles et al. 2013). The output points are used to plot the viscosity-temperature curve (Vogel 1921). These experimental results have been compared to published theoretical models intended for industrial glasses (Fluegel 2007) and for all silicate melts (Giordano et al. 2008).

Thin sections including a portion of glass and the underlying crucible have been cut in order to observe the textural evolution and to measure the cation diffusion at the interface. These thin sections have been analysed at a petrographic microscope Nikon Eclipse LV 100 POL and at a LEICA 360 scanning electron microscope (SEM) equipped with an energy dispersed spectroscopy (EDS) detector for microanalysis.

The mineral phases formed during the thermal treatment were characterized by X-Ray Diffraction in a Siemens D-500 X-ray diffractometer (Cu Kα radiation, 40 kV, 30 mA, graphite monochromator, 2θ from 4º to 70º).

3 Results and discussion

3.1 Chemical composition

The chemical compositions of the raw materials (basalt and chromium sludge) and of the obtained glass are shown in Table 1. The main components of the chromium sludge are CaO and Cr₂O₃. The glass contains 5.09 wt% of chromium oxide.

Table 1. Chemical compositions of the basalt, the sludge and the obtained glass.* (Queralt 1988).

<table>
<thead>
<tr>
<th></th>
<th>Basalt*</th>
<th>Chromium sludge</th>
<th>Glass</th>
</tr>
</thead>
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Table 2. Chemical analysis of elements (wt%) using SEM-EDAX through a Leica 360.

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3.2 Viscosity – temperature evolution

The morphological evolution of the glass during heating is used to determine the dependence of viscosity on temperature according to the fixed viscosity points (Scholze 1962) as shown in Fig. 2.

The glass starts shrinking at 1205º (η = 9 Pa·s) due to the start of sintering. Viscous deformation starts at 1218ºC, the temperature of the softening point (η = 5.1 Pa·s). Further plastic behaviour happens at 1350ºC, at the half ball point (η = 3.6 Pa·s). The flow point marks the melting of the glass at 1448ºC (η = 3.1 Pa·s).

It is clear from the increasing slope of the deformation curve which shows the relationship between height decrease and temperature (Fig. 2) that the deformation rate generally increases with temperature.

3.3 Textural analysis and chemical diffusion

The viscosity-temperature curve of the studied glass (Fig. 3a) shows the evolution of the viscosity of the glass during a heating treatment. The measured viscosity points have been plotted together with curves obtained using theoretical models for silicate melts. The analysis shows that current models for silicate melts are not accurate for melts containing a significant amount of chromium. In this case, the models underestimate viscosity around 2 log units (Fig. 3b).

![Figure 2. Deformation curve of the studied glass.](image)

![Figure 3. Viscosity-temperature curve of the studied glass.](image)
3.3 Textural analysis and chemical diffusion

The interface between the crucible and the melt is a main area of interest of the melting pond because it must be assessed whether the crucible reacts with the melt, how diffusion of cations affects the crucible and how the melt does behave along the contact.

The crystallisation of several crystals of spinel-like phases (Fig. 4 and 5) linked to the thermal treatment has been detected alongside the crucible-melt interface. The reaction region at the crucible, which is more coloured than the unaltered one, has a regular thickness of around 200-300 µm. In the vitrification process, the Cr is incorporated in the structure of the newly formed spinel-like phases.

![Figure 4. Thin section, crucible (left) - glass (right) interface in transmission optical microscope, plane polarized light. Spinel-like phases are included in the glass matrix.](image)

The largest crystals grow far from the crucible limits, being located in the central part of the glassy matrix (Fig. 6). The crystals have a euhedral habit corresponding to unconstrained growth inside the melt.

![Figure 5. Spinel-like phases inside the glass in reflected plane polarized light.](image)

XRD analysis showed the presence of spinel-like phases consistent with the microscopic observations. These phases could not be univocally identified in the standard XRD analysis both because they are mixed with a very high amount of amorphous material (> 90%) and because their grain size is around 10 µm.

Analysis with SEM-EDAX (Table 2) through a vertical profile (steps every 0.5 mm, 10 points at the crucible and 28 at the melt) provides the average composition at every spot. Mg, Ca, Ti, Fe and Ni have a certain degree of diffusion from the melt to the crucible. This diffusion is not homogeneous as, for example, Ca diffusion rate in the melt is lower than Ca diffusion rate inside the crucible, so that a Ca-impoverished zone in the melt is located just at the vicinity of the crucible.

At this scale, it is also proved that Cr is the element which defines the limit between the crucible and the melt.

Table 2. Chemical analysis of elements (wt%) using SEM-EDAX through the vertical profile.

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The limit between the melt and the crucible is evident from the evolution of Cr and Ni through the profile: the crucible completely lacks Cr and Ni, whereas they are present in the melt (although there is slight Ni diffusion in the crucible Fig. 7). Al (in spite of the aluminous composition of the crucible) and K are not good markers of the limits of the crucible because they diffuse to the melt (Fig. 8).
Spinel-like phases grew in the melt during the thermal treatment to obtain more information of the reaction and diffusion rates using electromelted aluminium crucibles which would have lower reactivity. Quantitative XRD analysis and Rietveld refinement would offer a more precise identification of spinel-like phases.

4 Conclusions

This study offers insights on the production process of a glass containing toxic sludges. Temperatures around 1450°C are enough to melt the mixture in order to make a glass containing 5 wt% of Cr₂O₃ by quenching.

The safety of the process is ensured by the fact that the reaction between the aluminous crucible and the melt is slow because the crucible is only minimally degraded at the interface with the melt during the experiment. Spinel-like phases grew in the melt during the thermal treatment.

Further studies should consider a longer thermal treatment to obtain more information of the reaction and diffusion rates using electromelted aluminium crucibles which would have lower reactivity. Quantitative XRD analysis and Rietveld refinement would offer a more precise identification of spinel-like phases.

Acknowledgements

The authors would like to thank the staff of the Scientific-Technical Service Unit of the University of Barcelona (CCiTUB) for their technical support. This work was carried out in the framework of the Consolidated Group 2014 SGR-1661 (Recursos Minerals: jaciments, aplicacions, sostenibilitat). Financial support was provided by the Fundació Bosch i Gimpera Project 307466. M. Terragó is supported by a grant from the Ministerio de Educación, Cultura y Deporte.

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DIN 51730 (1976) Determination of ash fusion behaviour, German Standard
Genesis of Tsavorite Deposits in the Davis Mine, Mwatate South eastern Kenya

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Edward Omito
Mines and Geology Department, Taita Taveta, P.O. Box 1043-80304, Wundanyi, Kenya

Abstract. The Davis Tsavorite Mine is geologically located within the Neoproterozoic Metamorphic Mozambique Belt (NMMB) in Mwatate area of the Taita Taveta, South East Kenya. The Lualenyi Member in the Mgama-Kuranze area hosts open pit Lualenyi Tsavorite Mines, including the Davis Tsavorite Mine itself located on Kide Hill in the Mgama Ridge. Tsavorite occurs as nodules in boudins within the host horizons. The Davis Tsavorite Mine is interpreted to be in an active continental crust environment of sedimentary origin where the tsavorite formed in metasedimentary rocks in the amphibolite facies.

1 Introduction

The Davis Tsavorite Mine is located along the Mgama Ridge with two active mining pits (Pits 2 and 3). The active mining pits are exclusively restricted within the Mgama ridge where the sample localizations are indicated (Fig. 1). The formation history of metamorphism and the resultant altitudes provide critical insights of the lithostratigraphic order in the mine. This order reflects the distinct lithologies that comprise the complex formation environment for tsavorite. Pit 3 has five tsavorite mineralization horizons consisting of graphitic gneiss and graphitic schist with intercalations of calc-silicate bands (Fig. 2). The tsavorites within the Davis Tsavorite Mine are primary deposits hosted as nodules within graphitic gneiss and calc-silicates. This suggests a lithostratigraphic control of the mineralization (Bridges 1974; Feneyrol et al. 2010).

2 Tsavorite in the Davis Tsavorite Mine

2.1 Geological setting

The Davis Tsavorite Mine nodules are contained in graphitic gneiss, calc-silicates, graphitic schist, and feldspar gneiss. Tsavorite is found as 15-20cm long nodules forming horizons parallel to the foliation within calc-silicate bands hosted by graphitic gneisses and few areas within the mine, in graphitic schists. Their concentrations are more important at the crest of isoclinal folds.

On a regional scale covering the major rocks in the Mwatate area, the belt of metasedimentary rock strikes to 340° NW to N 0° and dips 0° N to NE 70° respectively. These structural trends have influenced the orientation of the isoclinal folding and stretching that has dominated the lithology of the area. Tsavorite deposits are strongly and directly associated to the North plunging lineation, boudinage, and the development of small-scale N-S shear zones (Feneyrol 2012). Tsavorite nodules (pockets) are located essentially in green calc-silicate bands which are the lithological environments for tsavorite formation (Fig. 3). Structural conditions are important in the formation of tsavorites within the Davis Tsavorite Mine. Large scale structures such as faults and shear zones are often the place of heat and fluid transfers that are favourable for gemstone formation.

From the recorded structural features in the Davis Tsavorite Mine, it is evident that metamorphism acting on the original graphic strata resulted in metasedimentary lithology. The resultant metamorphic units of gneisses and schists were previously sedimentary rocks that underwent strain, stretching, folding, and faulting. The main direction of strain is E - W and dipping of rocks has produced isoclinal tight folds, and a complex regional structural history. Boudins and anti-boudins are the only localities of the tsavorites and their formation has been due to both regional and local tectonic forces such as strain, foliation, and folding. On a regional scale, diastrophism within the NMMB during metamorphism influenced the local structural setting of the Davis Tsavorite Mine.

2.2 Petrography

The host rock for tsavorite nodule mineralization is calc-silicate bands of graphitic gneiss. It has been highly altered in lithohorizons from the Davis Tsavorite Mine.Opaque mineralization from iron oxide (Fig. 4) of thin section microphotograph AW/KP/20, a thin section sample derived from the mine. Sample AW/KP/20 is highly altered due to the presence of dark oxides in thin section in the low grade green schist facies as evidenced by the presence of chloritization. This may have occurred within the retrograde phase of tsavorite...
formation during low-grade metamorphism. The source rock is possibly silica rich due to the presence of Quartz. Both Quartz and plagioclase feldspar have low birefringence and this is displayed by the white to grey first-order interference colours in XPL.

Evidence of shearing in the area that produced favourable condition to isoclinals folds is seen in AW/KS/20 in which mineralisation is crushed. AW/KS/20 (Fig. 5) represents highly altered fine-grained graphitic gneiss with lenses of quartz. Its cataclastic fabric (sheared or crushed-rock fabric) is due to regional deformation that developed folding episodes which produced gneissic rock.

Figure 1. Topographical map of the study area with sample localization and altitude of the Davis Mine pits.

2.3 V/Cr ratio of tsavorite from the Davis Mine within worldwide mines

Davis Mine tsavorites are hosted in calc-silicate bands of graphite-rich gneisses which are coloured by chromophoric elements like V and Cr. Chromophoric elements originate from graphite-rich meta-sediments which were originally organic matter. The trace element contents of tsavorite show that V and Cr are the two main chromophorous elements that give the green colour to the vanadian grossular. The V/Cr ratios of tsavorites worldwide are highly variable and range from 0.05 to 15.9 (Feneyrol, 2012). Based on EMPA analyses carried out on twenty crystals, the average V/Cr ratio of the Davis Tsavorite Mine samples is 4.0. This value 4.0 falls within the approximate range of Kenyan Tsavorite deposits in South East Kenya along the thick green V/Cr line (Fig. 6). The blue squares are the V/Cr ratios of tsavorites within South East Kenya. The Kenyan tsavorite have a V/Cr ratio between 0.2 and 4.3. The V/Cr ratios are < 1 for tsavorite from Baraka, M watate and Kuranze deposits, but those of Equador, Tsavolite and Aqua mines lie between 4 and 4.3.

Figure 2. Calc-silicate bands within Graphitic schist. Tsavorite nodule mineralization is formed at the crest of tight folds.
Gems and industrial minerals

1341

formation during low-grade metamorphism. The source rock is possibly silica rich due to the presence of Quartz. Both Quartz and plagioclase feldspar have low birefringence and this is displayed by the white to grey first-order interference colours in XPL. Evidence of shearing in the area that produced favourable condition to isoclinals folds is seen in AW/KS/20 in which mineralisation is crushed. AW/KS/20 (Fig. 5) represents highly altered fine-grained graphitic gneiss with lenses of quartz. Its cataclastic fabric (sheared or crushed-rock fabric) is due to regional deformation that developed folding episodes which produced gneissic rock.

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2.4 Contribution of fieldwork carried out in the Davis Tsavorite Mine

The present contribution from the Davis Tsavorite Mine gives detailed mapping, field relationships, lithostratigraphy and structural data for the Davis tsavorite deposit, as well as setting out the main features of the mineralization. It is important to understand the relationship between the NMMB and gemstone deposits to gain a better understanding of gemstone formation processes and to efficiently direct exploration.

The importance of the lithostratigraphic and tectonic control is based on field evidences. Formation of tsavorite requires considerations of lithology and structures (boudinages, folding, and shearing). Tsavorite occurs in strata-bound calc-silicate bands of graphitic gneiss horizons. Many tsavorite deposits are strongly and directly associated to the N plunging lineation, boudinage and development of small scale N-S shear zones. The mineralization within meta-sedimentary lithologies is stratabound due to the stratigraphy and the regional shearing and folding events that produced suitable nodule structures for tsavorite formation in the area. Furthermore, there is no vein formation for tsavorites and their host rock. Veins would indicate a rich history in fracturing and metasomatism due to fluid-rock interaction. The metasedimentary lithologies are metarudites, graphitic gneisses, and calc-silicate bands within graphitic gneisses. They are indicators of tsavorite nodule formation. The sedimentary origin of the metasedimentary formations is identifiable from detritic mineralization found in meta-arenite and graphitic gneisses. The metamorphosed zones within the mine are observed in tsavorite pockets, folding, and directional calc-silicate bands within graphitic gneisses. The metasedimentary mineralization and structural environment marked the beginning of surface rock research in the mine.

Figure 3. Tsavorite nodule mineralization within graphitic gneiss.

Figure 4. Photomicrograph of thin section AW/KP/20 in XPL showing chloritization, garnet, Fe-Ti oxide, Quartz and plagioclase feldspar.

Figure 5. Photomicrograph of thin section AW/KS/20. Fine grained graphitic gneiss in XPL showing a crushed mineral fabric of quartz lens, chlorite and rhombohedral hematite.

Figure 6. The V vs. Cr diagram of the tsavorite from the Davis Mine shown in the green line labelled V/Cr=4.05. Although the chemical composition of tsavorite is variable, the V/Cr ratio of tsavorite for a same deposit remains constant. They are in the range 0.2 to 9.3. (Modified from Feneyrol 2013).
Acknowledgements

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References

Characterization of Talc Schist’s Weathering Materials in Henguegue (Cameroon)

Damaris Laure Woguia*, Louise-Marie Ngo Bidjeck
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*Institute of Geological and Mining Research Cameroon

Abstract. Field work in the area of Henguegue (Cameroon) shows that within the weathering profile, talc schist is found in the upper parts as scree, the bedrock is mica schist. A macroscopic study of the profile allows to differentiate from the base to the top; an alteritic level, a globular level and a clay level. Mineralogical analyses indicated that the weathering materials consists mainly of talc, goethite, kaolinite, chlorite, quartz and secondary muscovite, and anatase. Geochemically, high contents of silica, calcium and sodium, associated with those of alumina would be related to the presence of mica. However, magnesium contents associated with silica in high proportions are linked to the presence of talc, on the one hand, and to the ultrabasic nature of the rock on the other hand. The high contents of chromium and nickel also mark the ultrabasic sign of these materials and allow one to delineate areas of influence of different source rocks encountered in the profile. These results and contents are not sufficient to constitute a metallogenic index.

Keywords: Characterization, Talc schist, Weathering, Materials, Mica schist, Talc, Henguegue, Cameroon.

1 Introduction

The general architecture of Cameroon shows two different geological areas. The cratonic area, representing the northern edge of the Congo craton consisting of Archean and Paleoproterozoic formations (study area), and the Pan-African chain of Central Africa (Cameroon, Chad, Central African Republic) in the north of the Congo Craton. The first ever investigations on talc in Cameroon were reported (Laplaine 1969), and more recently other indices were found in the localities of Lamal-Poughe, Bibodi, Pouth-Kélé (Nkoumbou and al 2006a, 2006b, 2008a, 2008b).

This study highlights the spatial distribution of different mineral species found in the weathering profile of talc schist in the Henguegue area. It is based on the petrographic, mineralogical and geochemical characterization of these weathering materials.

The study area (Fig.1) is located in the north of Boumnyebel, and it’s between latitudes 3° 59'N and 4° 00'N and longitudes 10° 58'E and 11° 00'E. It is at about 5km from the town of Bot-makak in the Center Region.

Eleven samples were collected for analysis, 8 weathered materials (WD1 to WD8) and three fresh rock samples (WD9= Mica schist, WD10=Marble, WD11= Talc schist). X-ray diffraction (XRD) were performed at the center of promoting local materials in Cameroon, estimation of major elements was done by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry), while those of trace elements and rare earth elements were carried out by ICP-MS (Inductively Coupled Plasma- Mass Spectrometry), at ALS Chemex Laboratory in Canada.

2 Assay results

The Bedrock in the study area consists of mica schist. Occurrences of dolomite marbles and talc schist were found, and they may be fragments of a Pan-African ophiolite. The well from which the observations were made was dug on the East side of the hill of Henguegue, with coordinates 03° 59'33" N and 10° 59'17" E (Fig.2). The well has a depth of 6.70m. Samples were collected at different levels of the profile and were subjected to macroscopic, mineralogical and geochemical analyses and the results thereof, are presented below.
2.1 Macroscopic and porosimetric characterization of the weathered materials

**Macroscopic characterization**

Three levels have been distinguished above the bedrock. These are, respectively; an alteritic level, a globular level and a clay level with a humus level on top (Fig.2). Mineralogical analysis by XRD reveals that: the alteritic level (670-380 cm thickness) is composed of quartz, kaolinite, goethite and muscovite; the globular level (380-290 cm) is composed of talc, quartz, goethite, kaolinite, chlorite and anatase. In the clay level (290 cm) we found talc, chlorite, goethite, kaolinite and quartz.

**Porosimetric characterization**

Total porosity of the different weathered materials was determined by densitometry:

Total porosity \( P_t = \left(1 - \frac{D_b}{D_p}\right) \times 100 \);

\( D_b \) and \( D_p \) represent respectively, the bulk density and solid particle density. \( D_b \) is given by: \( D_b = \frac{P_s}{V_s} \), and it’s determined by the paraffin method.

\( V_s \) is the volume of the paraffin layer.

\[ V_s = \left( P_2 - P_1 \right) \times 0.99/\text{cm}^3 \]

\( D_p \) is calculated by the gas pycnometer method:

\[ D_p = c - a / (b + c) - (a + d) \]

Bulk and solid particle density data were used to determine the total porosity by the \( P_t \):

\[ P_t(\%) = D_p - D_b / D_p \]

The results are shown in the Table 1. They show that the values of the bulk density decrease from parent rock to weathering phases. Solid particle density values are constants. The clay level is the densest material. Data relating to the total porosity shows that it is highly variable and generally very high within the weathered zone.

2.2 Distribution of mineral species within the weathered zone

The figures below highlight the distribution of the major and trace elements, and standardization of rare earth elements along the weathered profile.

### Table 1. Total density and porosity of weathered material

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bulk Density ((D_b))</th>
<th>Solid particle density ((D_p))</th>
<th>Depth ((cm))</th>
<th>Total porosity ((P_t)(%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay level</td>
<td>WD1</td>
<td>1.30</td>
<td>2.66</td>
<td>50</td>
</tr>
<tr>
<td>Globular level</td>
<td>WD2</td>
<td>1.21</td>
<td>2.39</td>
<td>320</td>
</tr>
<tr>
<td>Alteritic level</td>
<td>WD3</td>
<td>1.45</td>
<td>2.49</td>
<td>370</td>
</tr>
<tr>
<td>WD4</td>
<td>1.93</td>
<td>2.40</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>WD5</td>
<td>1.39</td>
<td>2.46</td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>WD6</td>
<td>1.79</td>
<td>2.62</td>
<td>520</td>
<td></td>
</tr>
<tr>
<td>WD7</td>
<td>1.54</td>
<td>2.61</td>
<td>570</td>
<td></td>
</tr>
<tr>
<td>WD8</td>
<td>2.32</td>
<td>2.41</td>
<td>620</td>
<td></td>
</tr>
</tbody>
</table>

### Distribution of the major elements along the profile

Major elements were grouped into two categories; high contents (\( \text{Si}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{and M} \text{gO} \)) and those with low contents (\( \text{CaO}, \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{MnO}, \text{P}_2\text{O}_5 \text{ and TiO}_2 \)). In the first group, it is clear that silica, whose content is higher in the bedrock, remains high throughout the profile. Aluminium increases very slightly in the weathered levels and gradually decreases towards the whole clay level. Iron increases up to 17.2 % all over alteritic level, and then decrease in the clay level. Magnesium has a very low content in the regolith; it slightly increases in the superficial levels.

Oxides with low concentrations show that the sodium and calcium are highly evacuated at the base of the profile. Potassium is slightly higher at the base of weathered profile, but then, decreases gradually to the top of the profile. Phosphorus, Manganese and Titanium have low variable contents along the profile.
**Evolution of trace elements (Ni, Co, Cr) along the profile**

We note from Fig 4 below, that the contents low in the bedrock remain constant for the Co, and increase for Ni and Cr within the profile.

**Figure 4. Distribution of Ni, Co and Cr in the weathered profile.**

**Normalisation of rare earth elements along the profile**

The study of the behavior of chemical elements along the studied profile reflects the complexity of the weathering material observed and allows one to define two areas of influence; the regolith on the one hand, the globular and clay levels on the other hand. Rare earth elements have been normalized (McDonough and Sun 1995) according to two types of lithologic facies encountered in the profile, namely the mica schist for depth level and talc schist for superficial levels. Thus we have:

- at the base of the profile, mica schist is very rich in rare earth elements and high enrichment are found in La, Ce and Nd. LREE shows enrichment than HREE in Fig.5A;
- at the top of the profile, we have a flat profile with inflections at Eu and Tm. Basically, there is an enrichment in most of the rare earth elements (Fig.5B).

**2.3 Evaluation of the intensity of weathering along the profile**

The evaluation (Nesbitt and Young 1982) of the intensity of weathering is based on the calculation of the Chemical index alteration (CIA), and give percentages of oxides by the following relationship:

\[ \text{CIA} = \left( \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + 2\text{K}_2\text{O}} \right) \times 100 \]

Based on this calculation, when the values of the index is between 30 and 60%, it corresponds to rock with very low weathering intensity. When CIA is between 62 and 85%, it corresponds to moderately weathered materials and when it falls between 85 and 100%, it's corresponds to completely weathered materials.

**Figure 5. REE normalized to the lithological unit’s spectrum. A: Depth level samples (WD5 to WD8) normalized to mica schist (WD9); B: Superficial level samples (WD1 to WD3) normalized to talc schist (WD11).**

**Table 2. Evaluation of Alteration Intensity.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depth (cm)</th>
<th>Levels</th>
<th>CIA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WD1</td>
<td>50</td>
<td>clay</td>
<td>96</td>
</tr>
<tr>
<td>WD11</td>
<td>120</td>
<td>Weathered</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Talc schist</td>
<td></td>
</tr>
<tr>
<td>WD2</td>
<td>320</td>
<td>globular</td>
<td>94</td>
</tr>
<tr>
<td>WD3</td>
<td>370</td>
<td>alteritic</td>
<td>94</td>
</tr>
<tr>
<td>WD4</td>
<td>420</td>
<td></td>
<td>93</td>
</tr>
<tr>
<td>WD5</td>
<td>470</td>
<td></td>
<td>92</td>
</tr>
<tr>
<td>WD6</td>
<td>520</td>
<td></td>
<td>89</td>
</tr>
<tr>
<td>WD7</td>
<td>570</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>WD8</td>
<td>620</td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>WD9</td>
<td>670</td>
<td>Mica schist</td>
<td>69</td>
</tr>
</tbody>
</table>

It can be observe that, talc schist which is found in superficial levels is completely altered and mica schist is slightly altered.

**3 Discussions and conclusion**

In tropical areas of South Cameroon, several studies have shown that the weathering profiles generally have the following sequence: an alteritic level, a globular level, more or less indurated and a clay level (Yongue F 1986, Kamgang B 1987, Bitom D 1988). The presence
of residual primary minerals such as mica or clays 2/1 or 2/1/1 as chlorite shows the influence of local conditions such as the nature of the rock and the poor drainage that would result in a moderate alteration on the base of the profile. Neoformation of kaolinite is strong in the study area, because of the availability of the silica so that all the aluminia is recombined to give clays (Duchaufour 1983). The absence of gibbsite may be related to moderate drainage conditions. The presence of the chlorite in the superficial levels may indicate an alteration of talc in chlorite or intercalations. Geochemical analysis shows that talc schist and mica schist have high contents in silica. In addition to this, mica schist is slightly rich in alumina, while talc schist is rich in magnesium.

Positive anomalies in Ce are known in the lateritic profile, below the area of accumulation of iron oxyhydroxide (Braun and al 1990). They are associated with areas of non-ferruginous clay as Cerianite (CeO2). Cerium occurs as Ce3+ in solution and as Ce4+ in the oxidation conditions (Carpenter and Grant 1967), where it precipitates as insoluble CeO2 (Braun and al 1990). It's then absorbed on clay exchange sites (Aagaard 1974), (Roaldset 1974), (Braun and al 1990). The high contents of chromium and nickel also mark the ultrabasic sign of these materials and allow one to delineate areas of influence of different source rocks encountered in the profile. The concentrations of Ni, Cr and Co at the top of the profile in the upper levels and seen the exploitability limit at grades of 0.8% Ni and 0.2 % for Co (Ngo Bidjeck 2004). We can’t talk about metallogenic index.

Acknowledgment

Thanks to the Director of IRGM (Institute of Geological and Mining Research) for his material and financial support as well as the Director of MIPROMALO for running the XRD analysis.

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SESSION 13
Processing of low-grade ore deposits

Convenors
Lev Filippov, Beate Orberger
Site Study for Metal Recovery. Perspectives.

Compilation of Mining Waste Databases to Prioritize

BRGM, 3 Av. C. Guillemin, BP 36009, 45060 Orléans, France

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This work, at both national and European levels.

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Compilation of Mining Waste Databases to Prioritize Site Study for Metal Recovery. Perspectives.

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Abstract. In a global context of growing raw materials scarcity, the Valodem project, conducted by the French Geological Survey (BRGM) aimed identifying national mining wastes that could possibly be reprocessed to recover metallic commodities (base- but also strategic or critical metals). To achieve this goal, French data on mining wastes have been compiled from various databases, and analyzed to identify most interesting mining wastes and evaluate their potential for reprocessing. Twelve waste deposits were selected for further capitalisation of data and one for sampling, analyses and pilot operation. The present paper briefly presents the methodology, results and perspectives of this work, at both national and European levels.

Keywords. mining waste, metal recovery, critical metals, methodology, database

1 Introduction

Until recent times, mineral resources were considered abundant and easily extractable, and their supply was not seen as a major issue. However, the strong economic growth, in a large part driven by the BRIC countries, combined to the continuous increase of the world population, has raised growing concerns on their availability. In addition, many metals and metalloids that had no or little application in the past are now critical elements to produce added value devices in many domains (ICT, energy saving technologies, etc.) Thus they could be of strategic importance for the economy of developed countries (EC, etc.).

A recent project (Valodem 2012-2014) handled by the French Geological Survey (BRGM), aimed namely at identifying interesting ancient mining wastes at the national level as possible secondary resources deposits and assessing their potential for metal recovery. The final objective was to select case studies for further sampling, laboratory experiments and pilot operation, to test modern recycling processes for metal recovery.

This paper summarizes the methodology developed in this project to gather pertinent data from databases (Guézennec et al. 2013; Bellenfant et al. 2013) and presents the main results and perspectives at the French and European levels.

2 Methodology and databases

The methodology undertaken was essentially based on databases querying and cross analyses. This was done through three main steps: (1) selection of pertinent criteria to select wastes deposits for re-processing; (2) combination of data from several databases; (3) selection of a limited number of pertinent sites through expert knowledge and gathering additional data from BRGM archives.

The data that was used for the cross-analyses was extracted from three main databases (1) the EU-FP7 ProMine project Anthropogenic Concentrations (AC) database (Cassard et al. 2012, in Press) (2) the BDSTM database (French Database of Sites and Mining Titles) (Bouroullec et al. 2001) and (3) the Dechmine database (Thomassin et al. 2001).

The ProMine AC database focuses on major anthropogenic concentrations in Europe and on the most interesting in terms of volume/tonnage and content (i.e., possible presence of critical metals). It is thus the most exhaustive inventory of concentrations which could be processed for the recovery of strategic/high-tech/critical commodities. Each site is described through about 35 fields distributed into four groups detailed in Cassard et al. (2012, in Press). The total number of records in the database is 3,412, among which 644 are located in France. This database, along with other datasets produced by the ProMine project, was included in a homogeneous multi-layer information system covering the whole European territory and available through the Internet (http://ptrarc.gtk.fi/ProMine/default.aspx).

The BDSTM Database of Sites and Mining Titles in France is used by the BRGM to identify mining sites that require environmental monitoring. This database includes environmental data, as well as data from mineral deposits, location of tailings and - when available - their tonnages and grades.

The Dechmine database (Thomassin 2001) identified and described 756 mining wastes sites over 9 European countries (Bulgaria, Finland, France, Germany, Greece, Ireland, Portugal, Spain and Sweden) with their location, the period of activity, the type of process and the type of waste generated.

A selection of 41 raw materials -minerals and metals- was defined as strategic at the European level (European Raw Materials Initiative, 2008). Among this list, 14 were defined as critical raw materials with significant concern for future supply in the European Union: Antimony – Sb, Beryllium – Be, Cobalt – Co, Gallium -Ga, Germanium – Ge, Indium – In, Magnesium -Mg, Niobium – Nb, Platinum Group Metals - PGMs, Rare Earths Elements - REE, Tantalum- Ta, Tungsten –W (note however that a recent EU communication (2014) updated the list to 20 CRM; concerning metals Ta was removed and Cr added). Silver-Ag and Titanium-Ti have been added on the French side, taking into account the specificities of the French industrial context. These critical metals can be hosted in polymetallic deposits and are usually minor commodities considered as by-products of the main paragenesis.
3 Results

The querying and cross-analysis of the databases led to the selection of 86 documented former mining sites; data fields are namely key parameters for metal recovery discussion (Table 1). These sites amount for a total of approximately 70 M t of mining waste, possibly rich in critical metals (Table 2). Unfortunately, data on the real content for these commodities – or by-products – was most of the time missing in the databases.

![Diagram of mining data flow](image)

**Figure 1.** French mining sites with tailings more or less rich in critical metals (EU list + silver).

<table>
<thead>
<tr>
<th>Exploited substance</th>
<th>Number of sites</th>
<th>Total tonnage (kt)</th>
<th>Treatment waste</th>
<th>Exploitation waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>1</td>
<td>3,000</td>
<td>1,800</td>
<td>1,200</td>
</tr>
<tr>
<td>As</td>
<td>2</td>
<td>0,400</td>
<td>0,380</td>
<td>0,021</td>
</tr>
<tr>
<td>Au</td>
<td>8</td>
<td>3,177</td>
<td>2,412</td>
<td>0,765</td>
</tr>
<tr>
<td>Bi</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>0,134</td>
<td>0,125</td>
<td>0,009</td>
</tr>
<tr>
<td>Ge</td>
<td>3</td>
<td>2,660</td>
<td>2,500</td>
<td>0,160</td>
</tr>
<tr>
<td>Pb</td>
<td>22</td>
<td>11,916</td>
<td>20,115</td>
<td>1,774</td>
</tr>
<tr>
<td>Pyrite</td>
<td>3</td>
<td>20,714</td>
<td>14,006</td>
<td>5,208</td>
</tr>
<tr>
<td>Sb</td>
<td>22</td>
<td>0,327</td>
<td>1,002</td>
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<tr>
<td>Sn</td>
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<td>5,789</td>
<td>4,780</td>
<td>1,009</td>
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<tr>
<td>Sr</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ta</td>
<td>2</td>
<td>1,837</td>
<td>1,500</td>
<td>0,370</td>
</tr>
<tr>
<td>Ti</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>15</td>
<td>18,670</td>
<td>17,396</td>
<td>1,274</td>
</tr>
</tbody>
</table>

**Table 2.** List of potentially recoverable commodities in the 95 mining sites in the Valodem database, and associated tonnages of waste (kt)

4 Perspectives

The work undertaken to access the potential for re-processing of mining waste shows that the existing data are rare and not fully appropriate to estimate the type of processes that have been applied. The selection of sites through key parameters and additional information from mining archives is thus crucial to sort out the most interesting sites. In addition, the work presented herein allowed some feedback and the updating of data in the ProMine pan-European Mineral Deposit database to a certain extend.

Also the recently started H2020 ProSUM project is an opportunity to further build-up our knowledge on this topics, on the French side but also at the European level through the work of other involved European Geological Surveys.
At last the inventory made on closed waste facilities by each Member State (following The European Directive 2006/21/EC of 15 March 2006 on the management of waste from extractive industries) is an opportunity to gather new data. In France, the final inventory (2012) listed 2,100 metallic sites. This inventory also yielded several hundreds of samples that will allow further analyses for presence and grades of critical metals that have not been analysed previously. A study undertaken for the French Ministry of Ecology, Sustainable Grow and Energy will handle part of this task in 2015 and further, with the analyse of samples selected by typology of ores. Finally, the content of critical metals in tailings will possibly help – when their source deposits are known – to produce new mineral predictivity maps, in order to help identifying favourable areas for mineral exploration, including re-evaluation of former abandoned deposits.

Acknowledgements

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References


Re-Processing of Mine Tailings: Discussion on Case Studies

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Abstract. Mining waste are regularly cited as potential secondary resources that could give access to residual concentrations of the exploited metals and also unrecovered metals, nowadays of economic importance for new high-tech applications. This article describes the investigation of three distinct mine tailings, and discusses the opportunity of re-processing such secondary mining resources, as part of the overall mining site management.

Keywords. critical metals, sampling, portable X-ray fluorescence spectroscopy, separation techniques, process development

1 Introduction
In France, a large number of mining sites operated in the past, generated large amounts of wastes, either tailings discarded at the end of the comminution/concentration stages, waste produced by hydrometallurgical treatments, or slag recovered at the end of pyrometallurgy processes. In some cases, these wastes contain rare metals, including strategic or critical metals necessary for high-value applications (EU list 2014). These rare metals were not extracted in the past or were exploited by technologies which performance has greatly evolved since then. In addition, these sites often require rehabilitation works, mainly because of their impact on the environment (particle release, metal/pollutant leaching, acid mine drainage, etc.).

In this context, BRGM has investigated in more detail three different mining wastes dumps in connection with rehabilitation projects in progress. Three case studies are presented and discussed, after selection of the site using criteria of volume, date of exploitation, process techniques, etc. (see Bertrand et al. this congress)

2 Tailings of a former lead and silver mine
2.1 Site description
The investigated former Pb-Ag mining site (Auvergne, France) consists in four stockpiles accounting for 87,000 m³ of physical treatment tailings. The rehabilitation project and the first sampling results in order to evaluate metal potential were described respectively in Bellenfant et al. (2013) and Guezennec et al. (2013).

The mine was operated till 1905 for Pb and Ag production: 50,000 t and 100 t were produced respectively. The polymetallic mineralization consists of quartz veins containing silver-bearing galena [PbS], sphalerite [ZnS], pyrite [FeS₂], arsenopyrite [FeAsS], bournonite [PbCuSbS₃], and chalcopyrite [CuFeS₂]. It is hosted by hydrothermalized granite and gneiss gangue.

The historic beneficiation schemes comprised successive steps of grinding and physical separation at millimetric scale. Flotation was performed only during the late stages of the mine life; the treatment mainly consisted in gravimetric separation and manual sorting. Gravimetric separation at that time did not enable to treat particles lower than 100 µm. This usually led to significant losses of silver.

2.2 Methodology
The methodology is summarised in figure 1.

Figure 1. Methodology performed on the Pb-Ag mining residues

A representative sampling was performed for each dump, in order to evaluate more accurately the remaining metal content. On-site pXRF (portable X-ray fluorescence spectroscopy) chemical screening analyses were performed on the dump surface and on samples taken at regular intervals down to 5 m depth using a shovel; the bottom being estimated at 67 m. In the laboratory, bulk samples of approximately 5 kg were dried at 40°C, homogenised and re-analysed on a selection of samples. ICP-AES after total alkaline digestion, X-ray diffraction and microscopic observations were also performed to investigate metal speciation and liberation size. This was intended to determine namely how far tailings should be ground further for metal recovery.

Some samples were then sieved to produce particle size fractions (+2 mm, 800 µm, 400 µm, 200 µm and 80 µm) which were weighed and analysed by pXRF and ICP. Lab scale experiments were then performed to concentrate the most promising size fractions and evaluate the interest of performing a pilot operation.
Re-Processing of Mine Tailings: Discussion on Case Studies

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Abstract. Mining waste are regularly cited as potential secondary resources that could give access to residual concentrations of the exploited metals and also unrecovered metals, nowadays of economic importance for new high-tech applications. This article describes the investigation of three distinct mine tailings, and discusses the opportunity of re-processing such secondary mining resources, as part of the overall mining site management.

Keywords. critical metals, sampling, portable X-ray fluorescence spectroscopy, separation techniques, process development

1 Introduction

In France, a large number of mining sites operated in the past, generated large amounts of wastes, either tailings discarded at the end of the comminution/concentration stages, waste produced by hydrometallurgical treatments, or slag recovered at the end of pyrometallurgy processes. In some cases, these wastes contain rare metals, including strategic or critical metals necessary for high-value applications (EU list 2014). These rare metals were not extracted in the past or were exploited by technologies which performance has greatly evolved since then. In addition, these sites often require rehabilitation works, mainly because of their impact on the environment (particle release, metal/pollutant leaching, acid mine drainage, etc.).

In this context, BRGM has investigated in more detail three different mining wastes dumps in connection with rehabilitation projects in progress. Three case studies are presented and discussed, after selection of the site using criteria of volume, date of exploitation, process techniques, etc. (see Bertrand et al. this congress)

2 Tailings of a former lead and silver mine

2.1 Site description

The investigated former Pb-Ag mining site (Auvergne, France) consists in four stockpiles accounting for 87,000 m³ of physical treatment tailings. The rehabilitation project and the first sampling results in order to evaluate metal potential were described respectively in Bellenfant et al. (2013) and Guézennec et al. (2013).

The mine was operated till 1905 for Pb and Ag production: 50,000 t and 100 t were produced respectively. The polymetallic mineralization consists of quartz veins containing silver-bearing galena [PbS], sphalerite [ZnS], pyrite [FeS₂], arsenopyrite [FeAsS], bournonite [PbCuSbS₃], tetrahedrite [(Cu,Fe,Ag,Zn)₁₂Sb₄S₁₃], and chalcopyrite [CuFeS₂]. It is hosted by hydrothermally altered granite and gneiss gangue.

The historic beneficiation schemes comprised successive steps of grinding and physical separation at millimetric scale. Flotation was performed only during the late stages of the mine life; the treatment mainly consisted in gravimetric separation and manual sorting. Gravimetric separation at that time did not enable to treat particles lower than 100 µm. This usually led to significant losses of silver.

2.2 Methodology

The methodology is summarised in figure 1.

A representative sampling was performed for each dump, in order to evaluate more accurately the remaining metal content. On-site pXRF (portable X-ray fluorescence spectroscopy) chemical screening analyses were performed on the dump surface and on samples taken at regular intervals down to 5 m depth using a shovel; the bottom being estimated at 67 m. In the laboratory, bulk samples of approximately 5 kg were dried at 40°C, homogenised and re-analysed on a selection of samples. ICP-AES after total alkaline digestion, X-ray diffraction and microscopic observations were also performed to investigate metal speciation and liberation size. This was intended to determine namely how far tailings should be ground further for metal recovery.

Some samples were then sieved to produce particle size fractions (+2 mm, 800 µm, 400 µm, 200 µm and 80 µm) which were weighed and analysed by pXRF and ICP. Lab scale experiments were then performed to concentrate the most promising size fractions and evaluate the interest of performing a pilot operation.
2.3 Results

Field investigations using pXRF demonstrated the homogeneity of waste piles from similar beneficiation schemes, while piles produced by different schemes yielded slightly different results. The mass balance of particle size fractions and associated Pb content are summarised on Figure 2. Results show that the major part of Pb, Ag and As is confined in the fine fraction <100 μm, which represents only 7% of the total mass.

![Figure 2](image)

**Figure 2.** Distribution of Pb with particle grain size in the tailings.

In view of specific interest for further separation experiments, a mineral characterisation of this concentrated fraction (<100 μm) revealed that most of primary galena, which is the major ore mineral, is destabilised in favour of secondary anglesite (PbSO₄) with minor beudantite and Pb-bearing jarosite. This result was verified all along the profile of the four spoil heaps, in agreement with the quite homogeneous yellow colour of all samples. Ag occurs as micron-sized grains included in residual primary galena and in secondary sulfates. It is difficult to define its distribution due to its small size and its dissemination. Small grains of Ag:AgS were suspected in several phases.

Due to these mineralogical characteristics, concentration tests were carried out on the fine fraction (<100 μm) using gravimetric methods: Mozley laboratory table and Falcon gravimetric centrifugal concentrator. The best results were obtained with the Mozley table: as can be seen in Figure 3, 17% of the total Pb is concentrated in 1% of the total mass of tailings (including the fractions over 100 μm). Pb content reaches 34% in the concentrate.

As the mineralogical analyses revealed that a significant amount of lead remained in the finest particles of the light fraction produced by the Mozley table (tailings), micro-hydrocyclone tests were performed on this fraction to separate the particles under 10 μm. Finally, by combining the concentrate produced with the Mozley table and the fine particles of the light fraction, 40% of total Pb is recovered in 4.6% of the initial mass of tailings with a Pb content of 18%. In addition Ag recovery reaches 11% with a content of 152 ppm.

It must be noticed that elements with potential environmental impacts (such as As or Sb) behave similarly to lead and can be concentrated at a high level (not shown here). This, on one hand could be penalizing for metallurgical processes, but on the other hand, contribute to reduce site pollution.

![Figure 3](image)

**Figure 3.** Gravimetric concentration tests using Mozley table. Pb distribution in the different fractions.

2.4 Conclusion

The study of this former mining site has been very important to check each step of the methodology we propose, to evaluate properly the concept of metal recovery from sampling and analyses to laboratory tests and finally a pilot operation. These latter results will be the subject of a full paper. Briefly, from the results obtained at laboratory scale, a continuous piloting operation was designed including separation, classification and concentration steps. Four tons of tailings were treated, which enable to determine the recovery of Pb and associated metals. The secondary recovery scheme can be integrated into a global site management and rehabilitation strategy, reducing a large part of metals and pollution. On the other side further reuse of the concentrate will be a new issue considering the sulphate carriers and also the arsenic content. Further re-use of the mineral residues, now metal-poor, could be evaluated in connexion with the local industrial needs.

The results are very encouraging and allow developing a methodology to investigate a larger Pb/Ag site identified elsewhere. In a more general way the methodology could be applied to investigate bigger former mining sites in Europe and include re-processing in their whole rehabilitation management.

3 Tailings of a former lead and zinc mine

3.1 Context

In with the framework of the French Ing-ECOST-DMA project (see references), the chemical composition of the tailings from the former mine of Carnoulès, Gard, France has been determined in respect to its content in potentially recoverable rare metals. Namely, indices of germanium associated to sphalerite in primary ores, sampled at the same location was the starting point.

On the other hand several environmental studies have been conducted over the past 15 years on this site (not exhaustive list: Leblanc et al. 1996; Koffi et al. 2004; Casiot et al. 2003; Casiot et al. 2009) in relation with acid mine drainage related to the oxidation of arsenic-bearing pyrite by underground waters. This drainage which contains significant concentrations of As is still a great matter of concern.
3.2 Site description

The lead-zinc mineralization from the SE Cevennes Mountains Region (detritic layers) was mined mainly over the period 1833-1962 for the production of Pb (2 Mt at 5-2.5 %), 3500 t Zn and Ag (estimated at 50-60 g/t), Alkaady (1986). The sulphide ore mineralization is dominantly composed of marcasite, pyrite, galena, sphalerite, Ag-sulpharsenides and As-Ag-Fe-Cu sulpho-antimonides. Quartz and barite are the main gangue minerals. The historical process consisted mainly in gravimetric separation, but it was not optimal because of the small size of metal-bearing grains. Flotation was undertaken at the very end of the operating life.

The current tailings pile, mainly composed of the so-called Fe-Pb-Zn-As sulphide sand (Leblanc et al., 1996) was estimated at 1.2 Mt (Koffi, 2004). The sequence consists of a surface clay layer (30-70 cm) which limits meteoric infiltration, fine sulphide sand (2 – 9 mm) of <30 µm to 1 mm particle size, sand with gangue rocks, gangue rocks and quartzite (substratum). Hydrology, modelling of the heap allowed describing a bilayer aquifer with three hydrological zones exhibiting different physico-chemical characteristics (Koffi et al., 2004).

3.3 Materials and methods

Sixty-three samples of powdery materials from four vertical profiles (T1-T4) were prepared and analysed in this study. The four profiles were drilled by HydroSciences Montpellier in 2002; samples were taken every one meter from surface downwards to 13 to 21 m depth. They were partly analysed for Fe, As and S in a previous study (Casiot et al. 2003). The samples have been preserved since at -20°C (T1, T2) or at ambient temperature (T3, T4). Decaking, splitting and drying at 40°C were performed to prepare composite samples for analyses.

Portable X-ray fluorescence spectroscopy (pXRF) analyses were performed on all samples. Laboratory ICP-AES analyses were performed on selected samples containing various amounts of Pb, Zn and As, after total alkaline digestion with sodium peroxide at 450°C. Correlation curves were established between pXRF and laboratory analyses. They are linear for Pb (up to 10000 ppm), Zn (2000 ppm) As (6000 ppm) and also Ba (12000 ppm) and Sr (1000 ppm). The correlation curves were therefore used as a simplified calibration for pXRF measurements. Ga, Ge, In content could not be measured by pXRF and were analysed by ICP-MS after total digestion on the samples with the highest Zn concentrations.

3.4 Results

Pb, Zn, As contents in the four vertical profiles (figure 4) show a large variability, apparently independent of the three different hydrological zones described previously.

The decreasing trend towards the bottom of the deposit, seems to be linked to sulphide oxidation zoning, which itself resulted in metal leaching over time thus metal depletion at depth, especially for T1; this result was already described for Fe, As and S in Casiot et al. (2003). Median values for 63 samples are 6,665 ppm Pb and 560 ppm Zn. These values are very low and do not justify further metallurgical tests. Median As content is 2,141 ppm.

Figure 4. Pb, Zn, As contents along the four vertical profiles.

Considering the very low Zn content of the tailings for re-processing objectives -tailings from other mines are known to contain up to several % of Zn- three analyses of Ga, Ge, In, Ta, Tl were performed to document further the site (Table 1); they confirm the conclusion that element values are too low to justify further work.

Table 1. Rare element content in the most concentrated Zn samples (mg/kg DM)

<table>
<thead>
<tr>
<th>Element</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>7.1</td>
<td>3.3</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>1.8</td>
<td>1.6</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>0.54</td>
<td>0.41</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>24</td>
<td>24</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

3.5 Conclusion

Zn (Pb) analyses on 63 core samples (0-20 m depth) on four distinct locations revealed very low base metal content of the tailings and logically, of associated rare elements (Ga, Ge, In). These results do not justify further sampling and lab treatment tests to evaluate the benefit of re-processing the tailings to recover valuable (rare/critical) metals.

4 Tailings of tungsten old mine

4.1 Site description and methodology

The last case study consists of two waste dumps accounted for 700,000 m3 of tailings from a former tungsten mine. The mine was produced 12.4 kt of WO3 (1963-86). The dump content is estimated to 1,500 t WO3 and primary reserve around 3, 400t. The skarn-type mineralisation consists of dominant scheelite [CaWO4] and pyrrhotite, with minor galena, (arseno)pyrite, chalcopyrite, bismuthinite and traces of gold.

4.2 Preliminary results

On this site, only preliminary investigations were carried out: on-site pXRF analyses and sampling. The field campaign allowed identifying two facies along a redox profile: red oxidized powdery sample on the top (around
heterogeneity of the resource. Sampling efficiency is potential total metal contents and to assess the available samples are essential then to estimate the mineralogical data. The site survey or further analyses of period of exploitation and, in addition, to geological and implemented and its efficiency in relation with the analysing relevant data, namely on the process flotation tests will be performed to evaluate the metal types of tailings to recover W and Cu, and Au. Namely this article presents three distinct case studies where the first results on metal contents are very encouraging Figure 5. Metal content in a vertical profile of each dump. 4.3 Perspectives The first results on metal contents are very encouraging to perform laboratory concentration tests on the two types of tailings to recover W and Cu, and Au. Namely flotation tests will be performed to evaluate the metal recovery potential of the two types of resources. 5 Conclusion - Discussion This article presents three distinct case studies where metal recovery potential of former mine tailings were evaluated. These examples highlight the importance of analysing relevant data, namely on the process implemented and its efficiency in relation with the period of exploitation and, in addition, to geological and mineralogical data. The site survey or further analyses of available samples are essential then to estimate the potential total metal contents and to assess the heterogeneity of the resource. Sampling efficiency is greatly enhanced by on-site analyses in order to guide the investigations and optimise sampling (Robbat 1997). Selected samples should be submitted to laboratory analysis program, including a mineralogical study. The latter should focus on the secondary host minerals, which can differ from the mineral phases contained in the primary ores depending on oxidation and weathering over time (i.e., sulphides into sulphates, etc). Metal distribution should be evaluated on particle grain size fractions. If metal concentration is effective, physical separation tests could be performed, at lab scale then at pilot scale. Further processing reuse of the concentrate is still an issue to be evaluated, depending on the new metal mineral carriers and associated elements such as arsenic. Further re-use of the metal-poor mineral fractions could be evaluated in relation with local industrial needs. Acknowledgements The authors thank BRGM Mine Safety and Risk Prevention Department for access to sites 1 and 3 and P. Gentil and F. Cottard; A nabelle Fuentes for her help in sampling campaign at site 1 and lab analyses, during her training and BRGM laboratories; Pascal Auger for pXRF analyses on the logs of site 2. The studies on site 1 and 3 have been funded by BRGM under Valodem project. The work on site 2 has been co-funded by the French Research Agency (ANR) under the Ing-ECOST-DMA project (Carnoulès site) coordinated by Dr C Casiot. References A lkady A (1986) Le système fluviatile en tresse de Carnoulès (Gard). Thesis Univ. of Montpellier. Bellemf ant G, Guézenne c AG, Bodéna n F, D’Hugues P, Cassard D (2013) Re-processing of mining waste: Combining environmental management and metal recovery? Mine Closure Proceedings, Eden, UK Bertrand G, Bodénan F, Guézenne c AG (2015) Compilation of mining waste databases to prioritize site study for metal recovery. Perspectives. This congress Casiot C, Lebl anc M., Elbaz-Poul ichet F (2003) Geochemical processes controlling the formation of As-rich waters within a tailings impoundment. A q Geochem 9:273-290 Casiot C, Egal M, Elbaz-Poul ichet F (2009) Hydrological and geochemical controls on metals and arsenic in a Mediterranean river contaminated by acid mine drainage; preliminary assessment of impacts on fish. A ppl Geochem 24:787-799 Guézenne c AG, Bodéna n F, Bertrand G, Fuentes A, Bellemf ant G, Lemière B, D’Hugues P, Cassard D, Save M (2013) Re-processing of mining waste: an alternative way to secure metal supplies of European Union, REWAS 2013: Enabling Materials Resource Sustainability, TM S (The M inerals, M etals & M aterials Society), 231-237 Ing-ECOST-DMA project (2014-2017) Eco-engineering applied to integrated management of As-rich tailings and acid mine drainage, co-funded by The French Research Agency (ANR) Koffi K, Leblanc M, Elbaz-Poul ichet F (2004) Reverse oxidation zoning at a mine tailings stock generating arsenic-rich acid waters. M ine Water and the Environment 22:7-14 Leblanc M, A chard B, Ben Othman D, Lucky JM (1996) A cumulation of arsenic from acidic mine waters by ferruginous bacterial accretions (stromatolites). A ppl Geochem 11:541-554 Robbat Jr A (1997) Dynamic Workplans and Field Analytics: The keys to cost-effective site investigations, Tufts Univ.
TIMA Bright Phase Search – Tracking Gold Losses using SEM Based Automated Mineralogical System

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Abstract. The assessment of processing efficiency becomes increasingly important in the light of current stagnation in the commodity market. Specifically the drop of gold prices pushes many operations to its limits. This study focuses on capabilities of automated mineralogical analysis when searching for gold losses during the ore beneficiation process. The TIMA Bright Phase Search allowed for finding scarcely occurring gold grains in tailings in a fast and efficient way. The device was able to characterize gold grain size, locking and liberation degree in addition providing all necessary data to identify the exact cause gold loss.

Keywords. Automated mineralogy, processing, metallurgy, optimization.

1 Introduction

Gold ores are usually considered as low grade when compared to common base metal ores. The gold content commonly ranges from 2 ppm to 10 ppm. It can only exceptionally reach values as high as hundreds and thousands ppm. Recovering of such small quantities from often very variable ores is a matter of complex beneficiation process implying many steps of possible metal loss. Quality control is thus extremely important in order to maintain the profitability of a particular mining site. Automated SEM based mineralogical analysis is virtually the only tool which is able to assess not only the gold quantity in the tailings but also its relationship to other minerals allowing to identify possible causes of gold losses. A general example will be described in following text.

2 Methods

The TESCAN Integrated Mineral Analyser (TIMA) was used for acquiring the data. It is a SEM based automated mineralogical solution capable of automated identification and quantification of minerals present in the sample. The system also provides further texture related information like a grain size, mineral association, liberation degree and others in addition. Mineral classification relies on X-ray spectra (EDS) and backscattered electron (BSE) signal primarily, although other signals like secondary electron (SE) and cathodoluminescence (CL) can be also used to provide further information about the sample. The data were acquired at 25 kV acceleration voltage and 5nA beam current in a high vacuum mode. The working distance was set to 20 mm. The applied pixel spacing was 2 μm.

The processing waste was obtained from a minor gold producer in Europe in a form of a loose powder.

The sample represents a week average tail from the processing plant. The mass of sample was subsequently reduced using laboratory splitter from initial 0.5 kg to about 10 g sufficient to create three epoxy mounts. More blocks would however be necessary to achieve reliable statistics. The epoxy mounting was performed under vacuum conditions in order to remove any gaseous bubbles from the curing epoxy. The block surface was ground and polished and finally coated with 10 nm of carbon. This conductive layer allowed the actual SEM imaging and EDS mapping.

3 Bright phase search

TIMA software provides three software modules for data acquisition and processing – Modal Analysis, Liberation Analysis and Bright Phase Search (BPS) module. Each of them is designed to be used for a specific task. The first two modules can be applied in a general way virtually on any sort of geological samples in order to get information about mineral abundance and related textural data. BPS module is more suitable for cases in which the mineral of interest constitutes only a small part of the sample and it is formed by heavier elements providing BSE contrast against gangue minerals.

Figure 1. a. BSE image of the sample. b. Particles containing phases with BSE signal above relative value 80. c. BSE image of gold hosting quartz particle. d. Particle phase map obtained by TIMA.
Typical uses involve characterization of PGM, gold and REE ores. The BPS module provides association information on the mineral of interest and so it does not acquire data only from the mineral of interest but it scans the whole particle containing it. Mineral locking can be easily studied as a result.

TIMA is capable of distinguishing the mineral particles from the epoxy based on the different BSE signal (so called BSE thresholding). As for the BPS - which was specifically used for the gold tailings sample under study- the threshold is set to a higher value than in the case of Modal and Liberation analysis. In this way TIMA avoids not only to epoxy but also to minerals with lower than specified value of BSE signal shortening the acquisition time from hours to minutes provided the mineral of interest is only scarcely present.

Unlike other similar devices on the market TIMA can be equipped with up to four EDS detectors allowing speed up of the analysis and reduction of the sample topography influence. The system can be optionally supplied with an automated sample loading device - AutoLoader which can become advantageous especially in case of low grade ores or tailings, where the bright phase search acquisition time is very short.

4 Results

The processed gold ore was generally rich in sulphides (galena, sphalerite, pyrite, chalcopyrite etc.) which consequently occur even in tailings. Application of high BSE threshold was necessary in order to only focus on gold and minimize the time of acquisition. The level was set to 90, which should be sufficient to distinguish gold from galena. Subsequent analysis revealed that the gold was relatively rich in silver (up to 20 %) which lead to a drop of BSE signal below the limit. The BSE threshold was decreased to 80 and a phase filter which uses X-ray spectra in addition to BSE level was applied (see fig. 1 a, b). The system thus acquired data only from particles containing gold and did not take the galena into the account.

The study revealed that gold is present only in very small amounts which comply well with the fire assay results (<1 ppm). Only five gold hosting particles were found among 1.5 million of gangue particles. The gold passing processing plant to the tailings is relatively fine grained. It was found that the gold size varies from 1 to 5 microns. Gold occurs as inclusions in quartz (Fig. 1 c, d). The processing plant relies on collection of sulphides which typically enclose gold in the primary ore. The gold found in tail has low surface liberation degree (typically less than 5 %). The gold is thus not collectable by the flotation as a result.

5 Conclusion

Traditional approaches relying entirely on fire assays of different size fractions would not allow the identification of the exact cause of gold occurring in tail. Even more, attempts to find the gold grains using common SEM would have only a limited chance of success because of the widespread galena with similar BSE signal. Using the TIMA BPS module with phase filtering can provide a direct answer within several dozens of minutes. Similar approach is not restricted to tailings. It can be applied characterization of any low grade ore.
Gravity Processing of a Low Grade Kaolin Residue for the Recovery of Rare Earth Elements (La, Ce, Nd) and Rare Metals (Sn, Nb, W)

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Abstract. This paper follows a previous study which has shown that rare-metals (Nb, Sn, W) and LREE (La, Ce, Nd) are pre-concentrated in the micaceous residue of a kaolin plant. However the low grade and fine size range of the metal-bearing minerals make difficult their recovery by gravity concentration. We experiment an enhanced gravity concentration flowsheet which starts by screening the residue into 3 size fractions +150 µm, 150-53 µm and ≤53 micron. Then each fraction is treated separately, using a combination of spiral and shaking table for the coarsest fraction and Falcon concentrator for the finer fraction. The preliminary results show that LREE and Sn can be easily pre-concentrated suggesting that this residue stream (and the associated tailings dams) could be considered as a potential resource for these metals.

Keywords. Low grade, Rare earth, rare metals, gravity concentration

1 Introduction

Rare-metal granites because of their low-grades have always been considered of poor economic value but when altered they are often exploited for their industrial minerals. The potentiality of these metals as by-product of industrial mineral production is therefore most considerable and illustrated by many deposits worldwide. This study focuses on a china clay deposit of SW England which lay on the St Austell rare-metal granite (Manning et al. 1996). As a consequence of the kaolinisation process, the accessory minerals of the host granite have been partially liberated in the clay matrix which enables their pre-concentration in the hydrocyclone underflow of the kaolin plant. This leads in a pre-concentration of rare-metals (Sn, Nb, W) and light Rare-Earth (LREE) in a micaceous residue which is thus considered as a potential source for these metals as by product of kaolin production (Dehaine and Filippov 2014).

Gravity concentration is the most common technique used for pre-concentration of high specific gravity REE-bearing minerals and is usually followed by additional gravity, magnetic, electrostatic and occasionally flotation separation steps (Jordens et al. 2013). The contrast between the high specific gravities of the accessory minerals (4.25-7.3 g cm⁻³) and the low specific gravity of the silicate gangue minerals is suitable for gravity concentration (Table 1).

In this study we investigate the use of several gravity concentration techniques including spiral concentrator, shaking table and Falcon concentrator, following the procedure described in Figure 1, to recover a heavy minerals pre-concentrate from the micaceous residue.

Table 1. Mineralogical composition of the micaceous residue and specific gravity of the corresponding minerals (Dehaine and Filippov 2014).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weight %</th>
<th>Mean SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>10.15</td>
<td>2.60</td>
</tr>
<tr>
<td>Feldspar</td>
<td>15.16</td>
<td>2.60</td>
</tr>
<tr>
<td>Quartz</td>
<td>29.79</td>
<td>2.62</td>
</tr>
<tr>
<td>Muscovite</td>
<td>14.81</td>
<td>2.82</td>
</tr>
<tr>
<td>Chlorite</td>
<td>1.13</td>
<td>2.95</td>
</tr>
<tr>
<td>Biotite</td>
<td>14.58</td>
<td>3.09</td>
</tr>
<tr>
<td>Tourmaline</td>
<td>9.90</td>
<td>3.12</td>
</tr>
<tr>
<td>Apatite</td>
<td>0.86</td>
<td>3.19</td>
</tr>
<tr>
<td>Topaz</td>
<td>1.50</td>
<td>3.55</td>
</tr>
<tr>
<td>Rutile (Nb)</td>
<td>0.82</td>
<td>4.25</td>
</tr>
<tr>
<td>Zircon</td>
<td>0.64</td>
<td>4.65</td>
</tr>
<tr>
<td>Monazite (La, Ce, Nd)</td>
<td>0.07</td>
<td>5.15</td>
</tr>
<tr>
<td>Fe oxides</td>
<td>0.52</td>
<td>5.20</td>
</tr>
<tr>
<td>Cassiterite (Sn)</td>
<td>0.08</td>
<td>6.90</td>
</tr>
<tr>
<td>Wolframite (W)</td>
<td>&lt;0.01</td>
<td>7.30</td>
</tr>
</tbody>
</table>

Figure 1. General flowsheet of the gravity concentration process tested in this study.

2 Gravity processing

2.1 Material characterisation

All the samples used in this work were supplied by Imerys Ltd., U.K. An approximately 4 tons samples have...
been collected and aggregated from the secondary hydrocyclones underflow during the processing of master grade (highly kaolinitised ore) extracted from Melbur and Virginia pits. This stream corresponds to a micaceous residue described in Dehaine and Filippov (2015).

In order to improve the efficiency of the gravity separation process, this material needs to be screened into several size fractions. The size fractions have been selected on the basis of the washability of the material. The washability of the material is obtained by dense medium separation combined with centrifugation using pure and diluted bromoform (SG = 2.89 and 2.79 respectively) on the different size fractions. The Fig. 1 presents a typical washability of a micaceous residue sample. At least two populations can be distinguished, a population of light particles centred around the 180-125 µm size fraction and a population of light particles centred around the 90-63 µm size fraction.

![Figure 2](image)

Figure 2. Typical washability of a micaceous residue sample showing two distinct populations.

Based on these observations it has been decided to work separately with 3 size fractions. Thus the samples have been screened successively with a Rotosieve device, using sieves of 150 µm and 53 µm respectively. These sieves opening are slightly larger than what suggest the two distinct populations observed because the real cut size is significantly lower than the sieve opening (around 130 µm and 45 µm respectively).

### 2.2 Spiral concentration results

Preliminary concentration tests have been realized on a 5 turn KILA Reichert spiral (Mineral Deposit Limited, Australia). The purpose of this primary test was to study the effect of wash water using an experimental closed-circuit setup similar to the one presented in (Sadeghi et al. 2014). In order to qualify the efficiency of the separation it has been decided to work with the heavy mineral grades. Thus each product has been treated by dense medium separation (with bromoform SG = 2.89) to assess the heavy mineral grade. Figure 3 show the results obtained in terms of heavy minerals grade in the concentrate and heavy minerals recovery. These results seem to be very sensitive to the wash water, in particular the concentrate grade which increases when the wash water flowrate exceeds 5 L/min. On the contrary wash water seems to have a negative effect on heavy mineral recovery.

![Figure 3](image)

Figure 3. Effect of wash water on spiral concentrate heavy minerals grade and heavy minerals recovery.

This opposite effect on grade/recovery is classic and since spiral operate the first concentration steps, recovery must be favoured over the grade. Thus the future concentration test will be operated with a wash water flowrate as low as possible.

### Acknowledgements

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### References


Bioprocessing Low Grade Copper Ores - a Promising Alternative

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Abstract. This paper presents an overview of the work performed by the BRGM team in the last 10 years on the development of bio-hydrometallurgy dedicated to the processing of low-grade copper ores from the Kupferschiefer deposits. It covers selection and adaptation of microbial consortia, optimization of process operating parameters such as solid contents, the relationship between bioleaching performance and mineralogy, testing operating parameters to overcome chalcopyrite recalcitrance, design of process options and economical assessment. The selected bacterial inoculum (autotrophic, working at 42°C) enables to achieve high Cu recovery (up to 95%). In continuous piloting tests the increase of the solid load in the pulp from 15% to 25% doesn’t affect the bioleaching efficiency despite the high and unusual Cu concentration reached in the liquor (40 g L⁻¹). Operating at 25% solid load reduces by 2.3 the size of the leaching tanks compared to 15% solid load, which leads to a significant decreasing of the CAPEX.

Keywords. Bioleaching, copper, black shales, Kupferschiefer

1 Introduction

In Europe, most of the primary resources with high or moderate metal grade, reasonable accessibility and easy to process are exhausted. In today's context of resource scarcity, two types of “deposits” get more attention:

• Complex low grade ores which have not been considered as profitable deposits till now: European primary resources still available for exploitation have more complex mineralizations (e.g. polymetallic and polymineral, carbon rich), or low metal contents; they also have higher levels of toxic impurities such as arsenic, antimony and mercury, penalizing current pyrometallurgical technologies (Byrne et al. 1995).

• “old waste deposits” related to past mining and metallurgical activities: they contain residual quantities of base and precious metals (Cu, Ni, Zn, Co, Au, Ag) as well as potential reserves of valuable metals (associated metals) which were not exploited in the past.

As existing processes and technologies are often not profitable for these types of unconventional resources, new process options still need to be developed in order to overwhelming the complexity of the ore composition while remaining cost effective. In this context, bioleaching is more and more considered as a promising technology. Even though heap and dump bacterial leaching of sulphidic minerals are well established and the bacterial treatment of refractory gold concentrate using Stirred Tank Reactors (STR) is an industrial reality, the European mineral industry is still sceptical and reluctant to adopt biohydrometallurgical techniques. Heap leaching is often considered as un-adapted due to space constraints, slow leaching kinetics and low recovery rate. The possibility of using STR for the treatment of other metals than refractory gold, such as copper sulphides, has already been demonstrated but improvements are still needed to meet economic viability.

The Kupferschiefer deposits host the largest known copper reserve in Europe (Borg et al. 2012). These black shale type ores are currently exploited in Poland through pyrometallurgical smelting. In Germany exploration campaigns were recently leaded in order to assess and prepare future exploitation of this ore deposit type. The main copper-bearing minerals are: chalcocite, bornite, chalcopyrite and covellite. This type of ore is also characterized by high amounts of carbonate and organic carbon as well as potentially rich with arsenic (volatile in pyrometallurgical processes). In the last years the ores are characterized by increased As and C contents, and lower Cu contents. It leads to a lower quality concentrate as well as operating and environmental issues during smelting.

In this context, several European research projects were dedicated to the development of new bioleaching approaches as alternative and complementary routes to the conventional smelting methods for the processing of Kupferschiefer ores (BioShale in EC-FP6, Promine in EC-FP7). This paper presents an overview of the work performed by BRGM teams in the last 10 years. It covers selection and adaptation of microbial consortia, optimization of process operating parameters such as solid contents, testing operating parameters to overcome chalcopyrite recalcitrance, relationship between bioleaching performance and mineralogy, design of process options and economic assessment.

The new insights and future development for the integration of bioprocess options in the metallurgical treatment of black-shale type ores will be discussed. The R&D challenges necessary to tackle in order to improve the process economy will be analysed and compared.

2 Main experimental work

2.1 Selection and adaptation of microbial consortia

In BioShale research project (2004-2008) different types of microbial consortia were tested: acidophilic autotrophic bacteria, acidophilic and neutrophilic heterotrophic bacteria (d'Hugues et al. 2008). As no evidence of efficient biodegradation was found with heterotrophic bacteria, the process development was mainly focused on the use of the classical autotrophic bacteria with regards to the solubilisation of metals.
present in the sulphide minerals.

The microbial culture finally selected comes from a combination of two BRGM bacterial consortia originally cultured on a coaliferous pyrite for the first one and on a copper concentrate for the second one (d’Hugues et al. 2003; Morin and d’Hugues 2007). The adaptation of the consortia was performed by subculturing several times in batch mode on the Polish copper concentrate before being used as an inoculum. Fig. 1 presents the copper dissolution kinetics obtained from the bioleaching of the Cu concentrate in a 2L batch test at 42°C and 10% (w/w) solid concentration after adaptation. Final Cu recovery reached 95% and the maximal Cu dissolution rate was evaluated at 137 mg L⁻¹ h⁻¹. At the end of the experiments, the Bioshale-BRGM consortium was co-dominated by Acidithiobacillus (At.) caldus (40±2%) and Leptospirillum (L.) ferrirhophilum (34± 2%). The species Sulfabacillus (Sb.) benefaciens BRGM2 and Sb. thermosulfidooxidans were detected at lower ratios (13±3% and 12±3%, respectively).

![Figure 1](Image)

**Figure 1.** Batch bioleaching in stirred reactors with the Bioshale-BRGM consortium. Copper concentration versus time for 3 identical tests (at 42°C and 10% solid concentration)

### 2.2 Bioleaching demonstration in Stirred Tank Reactor

Following successful cultures in batch tests, bioleaching in continuous conditions is necessary to determine the process specifications for the application of the stirred tank technology to the sulphide concentrate produced from black shale ores. Several adaptation bioleaching operations were carried out (Spolaore et al. 2009; Guezenne et al. 2014a) in a laboratory-scale unit equipped with three stirred reactors, one of 50 L (R1) followed by two of 20 L of operating capacity (R2, R3). The reactors are arranged in cascade so that the pulp flows from one tank to the next one by overflowing. CO₂-enriched air (1%) is injected beneath the turbine at the bottom of the tank. The mixing system (BROGIM® - BRGM/MRM) is mounted in all tanks on a rotating shaft.

The tests were performed using the consortium presented in the preceding section. In the reactors temperature was maintained constant at 42 °C and pH was regulated around 1.5. The main operating parameters that were studied were the solid load (15% to 25%), the agitation speed (250 to 450 rpm) and the aeration flow (100 to 2000 L h⁻¹).

In bioleaching operation the limitation of copper recovery is often linked to incomplete dissolution of chalcopyrite. To improve chalcopyrite dissolution, it is recommended to work at reduced redox potential (< 420 mV) to limit passivation of the mineral surface (Amjadi et al. 2010; Gericke et al. 2010). The reduction of redox potential can be achieved by controlling the oxygen transfer rate (Córdoba et al. 2008; Pinches et al. 2000; Third et al. 2002; Tshilombo et al. 2002). In this study the agitation speed and the aeration flow were thus slowed down in order to decrease redox potential and improve chalcopyrite dissolution. Finally the control of oxygen transfer was not sufficient and the redox potential remains closed to 600 mV. However Cu dissolution was positively impacted by these changes of operating parameters: when decreasing the agitation and aeration rates Cu dissolution increased from 60% to 73% (Fig. 2).

![Figure 2](Image)

**Figure 2.** Influence of oxygen transfer on copper dissolution versus residence time during continuous bioleaching

As can be seen in Fig. 3, Cu recovery is not affected by the increase of the solid load from 15% (w/w) to 25% (w/w). This solid content is quite high compared to those encountered in most of the commercial applications of bioleaching in CSTR (between 15 and 20%). In the literature, there is a controversy on the feasibility of working at such high solid contents. Some authors think that bioleaching operations are limited to 20% (w/w) solid load in the pulp because beyond this limit, physical mixing and microbial problems may occur (for complete references, see the review of Rawlings 2005). On the other hand Van Aswegen et al. 2007 link the maximum solid concentration to the maximum oxygen mass transfer capacity. As a consequence, depending on the resource sulphide content, it is conceivable to work with solid contents above 20% (w/w). A further challenge related to bioleaching at very high solid contents deals with bacterial metal tolerance. It is generally considered that mesophiles are less tolerant to copper than thermophiles: 25 g L⁻¹ vs. 35 g L⁻¹ (Batty and Rorke 2006; Clark et al. 2006). In this study no mixing or microbial issues were encountered. The Bioshale-BRGM consortium (which is mesophile to moderately thermophile) has shown a rare copper tolerance since copper content increased up to more than 40 g L⁻¹ without any negative effect on the bacterial community.
presented in the preceding section. In the reactors thermosulfidooxidans species and reached 95% and the maximal Cu dissolution rate was being used as an inoculum. Fig. 1 presents the copper content increased up to more than 40 g L\(^{-1}\) without any negative effect on the bacterial community. As can be seen in Fig. 3, Cu recovery is not affected by residence time during continuous bioleaching.

### 2.3 Mineralogical analysis

Mineralogical analyses were performed to evaluate the modal composition of the concentrate and of the residues obtained in the primary and secondary reactors during the continuous bioleaching operations (analytical technics, procedures and parameters are detailed in Gouin 2008). Copper sulphides in the concentrate mainly consist of bornite (Cu\(_2\)FeS\(_4\), 36%), chalcocite (Cu\(_2\)S, 23%), chalcopyrite (CuFeS\(_2\), 20%), other undetermined copper sulphides (19%) and covellite in smaller proportions (1%). During the bioleaching process, chalcocite and bornite were almost completely dissolved in the first tank. These minerals have the lowest rest potential of the sulphides that compose the concentrate; as a consequence, their dissolution is enhanced by the other sulphides (covellite and chalcopyrite). Some covellites were produced in the first reactor; this mineral is known to be an intermediate product of the dissolution of both chalcocite and chalcopyrite (Dixon 2000; Leahy et al. 2007; Tshilombo et al. 2002). Covellite was then almost completely dissolved in the secondary reactors (R2, R3) in contrast to chalcopyrite which represented the major part of the final residue. The decrease of agitation and aeration rate operated during the bioleaching continuous demonstration did not significantly overcome the recalcitrance of chalcopyrite to leaching. This result is in good accordance with the redox potential measured in the reactors which remains high (around 600 mV).

From these results a schematic view of mineral dissolution mechanisms was proposed by Gouin (2008) and Guezennecc et al. (2012)

![Figure 4. Schematic view of the sulphide dissolution mechanism during bioleaching of Cu shale concentrate.](image)

### 3 Economic assessment and future developments

A preliminary techno-economic evaluation of the concentrate processing, including bioleaching as well as copper and silver recovery, was established based on both experimental data collected during the experimental campaigns and the literature. OPEX was estimated to 0.31 €/lb Cu (i.e. around US$ 0.38/lb Cu) (Spolaore et al. 2009). This is higher than the operating costs for in-place and dump leaching (US$ 0.18–0.22/lb Cu) but in the range of the operating costs for heap leaching (US$ 0.34–0.60/lb Cu (du Plessis et al. 2007; Pradhan et al. 2008). It seems to be even cheaper than certain concentrate leaching (US$ 0.49–0.77/lb Cu) or smelting (US$ 0.45–0.65/lb Cu) (du Plessis et al. 2007). The CAPEX could be considered as relatively high. However it must be noted that the CAPEX is considerably decreased with a process design at higher solid load in the feeding pulp. This is mainly due to the reduction of global bioleaching tank volume: operating at 25% solid load requires 2.3 less tank volume than operating at 15% solid load for the same Cu recovery and the same residence time.

Following these calculations, elements on process economy were reviewed in order to point out the most pertinent ways to improve it. Information coming from several pre-feasibility studies of bioleaching installations (confidential BRGM data) was analysed and combined to literature data. It appeared that the most important investments costs generally come from bioleaching and electrowinning unit operations. When focusing on bioleaching itself, capital costs largely depend on global tank volume and agitators. The higher operating costs are power (mainly related to oxygen supply) and chemical compounds (Rossi 2001; Morin and d’Hugues 2007; van Aswegen et al. 2007). The latter are of particular importance in this study as sulphuric acid injection is required to neutralise carbonates from the concentrate.

From these data as well as the results of the experimental work, several ways of improving process economy has been identified (Guezennecc et al. 2012):
- increasing revenues by improving chalcopyrite dissolution and thus bioleaching operation efficiency. As can be seen from the experimental work presented in the previous sections, the limitation of copper recovery is linked to incomplete dissolution of chalcopyrite. This should be achieved through a better control of redox potential (< 420 mV) to limit passivation of the mineral surface.
- reducing capital costs by reducing global bioleaching tank volume, which means decreasing residence time in the bioleaching unit and increasing the feed solids content. The feasibility of the copper concentrate bioleaching at a pulp concentration of 25% was demonstrated at laboratory scale in continuous mode without any mixing or microbial issues. These encouraging results open new perspectives in the design of an alternative process to smelting, but still remain to be confirmed at industrial scale. Higher solid concentrations are needed to be tested.
- reducing operating costs by working with reduced agitation and aeration rates will decrease power.
consumption.

Another way of decreasing CAPEX and improving bioreaching process economy might be also to develop new types of bioreactors as an alternative to classical heap leaching or CSTR. This new concept has already been proposed for other types of resources (Guezennec et al. 2014b) and offers new possibilities for future applications of bioreaching technology.

4 Conclusion and Perspectives

In the Frame of the Two European projects (Bioshale and Promine), it was demonstrated that the treatment of copper black shale concentrate using biohydrometallurgy was technically feasible and efficient. Several options were identified to improve the profitability of the continuous bioreaching of the copper concentrate in stirred tank reactors such as: (i) the improvement of the chalcopyrite dissolution efficiency, (ii) an increased solids throughput, (iii) a new type of bioreaching reactor. These specific and important challenges will be addressed in a recently started project Ecometals (Kutschke et al. 2014).

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Structural and Physical Properties of Uranium-Ore Agglomerates before Heap Leaching

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Abstract. This study presents an attempt to characterise the structure of agglomerates coming from low grade uranium ore. Microscopy analysis and X-ray tomography allowed highlighting small pellet structures at the edge of agglomerates. These structures could be related to the low connected porosity measured on these agglomerates with mercury intrusion porosimetry (MIP).

Keywords. Agglomerates, Heap leaching, porosity, X-ray tomography

1 Introduction

Heap leaching allows processing low grade ores. Basically, this industrial mining process consists in percolating a leaching solution slowly down through an ore heap to extract the metals of interest (uranium, copper or nickel). Physical and chemical factors (as temperature, reagent flow rates, particle size distribution and pores distribution) and the ore mineralogy influence this process. Fine particles and clays are indeed often the cause of clogging within heaps. This causes also permeability variability that may compromise the efficiency and homogeneity of the leaching process (Ghorbani et al. 2011). To solve this problem, copper, nickel and uranium industry uses agglomeration of the ore particles. This process allows adjusting the particle size distribution by gathering fine particles, using mostly capillary forces, cohesion forces between particles and adhesion forces (e.g. hydrogen bonds, electrostatic and Van der Waals forces). This process is a way to improve the heap permeability and to reduce fine particle migration during leaching (Dhawan et al. 2013; Janwong 2012; Bouffard 2005).

Agglomerates for heap leaching are formed by the adhesion of ore particles mixed at least with water within a rotation drum. In some cases, a binder can be added to the water, to make the agglomerates stronger (Pietsch 2002). Then agglomerates are stored for maturation in a time span from 14 to more than 300 hours. The storing time depends on the nature of the ore and the nature of the binder. During this time, the bonds between the particles of the agglomerates are hardened (Dhawan et al. 2013; Pietsch 2002).

According to Bouffard (2005), four consecutive steps can be identified during the agglomeration process: (i) wetting of particles; (ii) growth of the agglomerate by three phases (nucleation, coalescence of the nuclei in an agglomerate and organisation of fines around the agglomerates); (iii) consolidation and compaction of the agglomerate; and (iv) fragmentation and abrasion.

Two kinds of agglomerates may be distinguished (Bouffard 2005, Dhawan et al. 2013, Janwong 2012): (i) pellets which are formed by the packing of fines together and (ii) agglomerates which contains a rock nucleus. Fine particles are usually agglomerated around that nucleus.

The agglomerates characteristics (e.g. structure, size distribution, strength, cohesion etc...) are controlled by five main parameters:

(1) Retention time in the drum. This parameter influences the shape of the agglomerates and their size distribution. According to Bouffard (2008), a low retention time makes small agglomerates.
(2) Drum speed. A high speed favours more collision between particles, i.e. the formation of bigger agglomerates (Pietsch 2002). This parameter also influences the maximal size of agglomerates. Agglomerates over this size are breaking (Iveson et al 2001).
(3) Ore characteristics (clay content, particle size distribution etc...). The nature of the agglomerated ore influences the choice of the binder but also the size and the structure of the agglomerates (Janwong 2012).
(4) Binder. The binder allows fine particles to agglomerate and to produce stronger agglomerates, without reduce leaching performances (Kodali 2010).
(5) Moisture content. This variable comes from the initial ratio liquid/solid (L/S ratio) during agglomeration and from the maturation time. High moisture content favours the formation of bigger agglomerates. However, high L/S ratio makes agglomerates with poor quality (Velarde 2005; Janwong 2012).

As agglomerates quality influences heap leaching efficiency, numerous tests (as soaking, column permeability, particle size distribution analysis etc...) to control agglomerate quality have already been performed (Dhawan et al. 2013; Velarde 2005; Janwong 2012; Lewandowski and Kawatra 2009; Liu et al. 2012; McClelland 1988). However, these tests mostly focus on a column or a batch of agglomerates. By this way the impact of the agglomerates structure on heap leaching remains poorly understood.

In this study we characterise the structural and petrophysical properties of agglomerates from analytical techniques (e.g. X-ray tomography, thin section analysis, mercury intrusion porosimetry (MIP)) and we relate these properties to the ore recovery efficiency.
2 Characterisation of agglomerates before leaching

2.1 Ore

A low grade uranium ore from Niger has been used for the agglomeration process. The ore contains about 800 ppm of uranium and more than 10 % of clays. Three kilograms of crushed ore have been agglomerated during 90 seconds with a L/S ratio of 0.08. In addition, sulphuric acid at a ratio of 25 kg/t has been used as binder.

A particle size distribution (PSD) analysis (Figure 1) has been conducted to separate particles in the range between about 1 mm to 40 mm and determine characteristic diameters of the agglomerates. Dry sieving was performed with caution to avoid damaging the agglomerates. Particles having a diameter of 5, 10 and 20 mm have been used in this study.

![Figure 1. Cumulated particle size distribution of the agglomerates](image)

2.2 Agglomerate structure

The external aspect of five agglomerates (two with a diameter of 5 mm, two with a diameter of 10 mm and one with a diameter of 20 mm) has been studied by microscope. Small ovoid structures have been noticed at the surface of all type of agglomerates as it is shown in Figure 2. Those structures were mostly composed of fine particles.

![Figure 2. Ovoid structures at the surface of a nucleus agglomerate type (diameter of 5 mm). The black pointers show some of the ovoid structures.](image)

Cutting agglomerates highlighted two main characteristic features:

Firstly, pellet type agglomerates as well as nucleus type agglomerates were present within the studied agglomerates. These two types of agglomerates can only be distinguished on the basis of their internal structure (Figures 3 and 4). For example, Figure 3 shows that the smallest agglomerates can also be of the nucleus type.

Secondly, ovoid structures mostly made of fine ore’s particles were also found inside the agglomerates. These structures, present within the two types of agglomerates (nucleus type and pellet type) are similar to the ones observed at the external part of the agglomerates. However, the mineralogy of these structures couldn’t be investigated for the moment.

![Figure 3. Section of an agglomerate (diameter of 5 mm). The white part is a rock nucleus around which fine particles or pellets are agglomerated (grey part of the agglomerate).](image)

Three agglomerates (one of each diameter) have also been studied by X-ray tomography. This technique allows imaging the internal structure of the agglomerates without mechanical disturbance. In the three cases, we observed that most of the particles within the agglomerate have the same density. In this way, it was difficult to distinguish pellet type agglomerates from nucleus type agglomerates. However, it was possible to observe several new structures inside the studied agglomerates as shown in Figure 5. The difference of porosity (which appears in black in the figure) between the middle and the edge of the agglomerate indicates the presence of a rock nucleus at the centre of the particle. Moreover small “pellets” at the edge of the agglomerate have also been noticed (e.g. at the top of Figure 5). They fit to the ovoid structures identified by microscopy analysis. These pellets may have derived from the different stages of agglomerate growth. Thus, fine particles can coalesce themselves into small pellets. If these pellets collide with a larger agglomerate, they can layer to that agglomerate into a bigger one.
2.2 Agglomerate structure

Figure 2. Those structures were mostly composed of fine particles. Figure 1. Those structures were mostly composed of fine particles.

2.1 Ore

A low-grade uranium ore from Niger has been used for this study. Processing of low-grade ore deposits is a low grade uranium ore, uranium oxides are probably not visible.

2.3 Porosity of agglomerates

Porosity influences heap leaching and agglomerates' quality. The porosity properties have been studied by mercury porosimetry. The agglomerates have been previously freeze-dried in order to remove the water within the samples without damaging their structure.

Mercury porosimetry consists in injecting mercury within the sample pore network in vacuum conditions. The mercury injection pressure can be related to the pore size by the Laplace law. Moreover, the injected fluid volume gives access to value of the porosity. Two mercury injections have been done: the first one shows total porosity within the agglomerate and the second one is used to evaluate the percentage of connected porosity. Results, presented in Tab. 1, suggest that the porosity is quite the same whatever the diameter or the type of agglomerate (pellet- or nucleus-type agglomerate). The connected porosity is quite low (around 3%). These results are unexpected, compared to the value of total porosity (around 18%). We can suppose that trapped porosity corresponds both to the porosity inside the nucleus and to the internal structures which are not connected to the edge of the agglomerates. Thus, the agglomeration of new pellets may close some pores. We assume that connected porosity correspond to the porosity of the edge of the agglomerates where the small pellets have been noticed in the previous analysis.

Moreover, we noticed that the trapped pores had a radius comprised between 0.01 µm and 5 µm (i.e. mesopores). Connected pores are either bigger or smaller and may correspond to fractures within the agglomerates or pores located at the periphery of the agglomerates. Note that the pore size distribution was also similar between the two sizes of agglomerates.

Table 1. Porosity of agglomerates (results obtained by mercury porosimetry)

<table>
<thead>
<tr>
<th>Diameter of the agglomerates</th>
<th>Total porosity</th>
<th>Connected porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mm</td>
<td>18.92 %</td>
<td>4.41 %</td>
</tr>
<tr>
<td>10 mm</td>
<td>17.95%</td>
<td>3.12%</td>
</tr>
<tr>
<td>20 mm</td>
<td>17.48%</td>
<td>2.16%</td>
</tr>
<tr>
<td>20 mm</td>
<td>17.61%</td>
<td>3.07%</td>
</tr>
</tbody>
</table>

Figure 3. Section of a pellet type agglomerate (diameter of 10 mm).

Figure 4. Section of a pellet type agglomerate (diameter of 10 mm).

Figure 5. Nucleus type agglomerate (diameter of 20 mm) observed by X-ray tomography. The white pointers and the black circle at the top of the figure highlight small pellets structures. The white circle highlights the nucleus. The white points inside the agglomerates are high density particles we supposed to be pyrites; however, their mineralogy has not precisely been determined for the moment. As the studied ore is a low-grade uranium ore, uranium oxides are probably not visible.

Figure 5. Nucleus type agglomerate (diameter of 20 mm) observed by X-ray tomography. The white pointers and the black circle at the top of the figure highlight small pellets structures. The white circle highlights the nucleus. The white points inside the agglomerates are high density particles we supposed to be pyrites; however, their mineralogy has not precisely been determined for the moment. As the studied ore is a low-grade uranium ore, uranium oxides are probably not visible.

Figure 6. Porosity distribution within an agglomerate with a diameter of 10 mm. The black line is the total porosity, the dark grey one is the trapped porosity and the light grey line represents the connected porosity. Between 0.01 µm and 5 µm most of the porosity is not connected.

3 Discussion and further tests

These first tests improved our knowledge of agglomerates before leaching. Our main conclusions are the following:

- The small pellets located at the edge of
agglomerates might come from the different stages of the agglomeration processes described by Janwong (2012) and Bouffard (2005). This allow proposing a chronology for agglomerate growth:

(i) Small pellets are formed within the drum from fine particles.

(ii) During the rotation of the drum, these pellets pack themselves with bigger agglomerates (pellet or nucleus type) to form a bigger one.

(iii) The layering of new pellets an agglomerate, associated to the rotation within the drum could abrade the last particles fixed on the agglomerate. This could close the mesopores and increase trapped porosity.

- We assume that the connected porosity mostly corresponds to the porosity of the last layered particles (fines particles or pellets) on the agglomerate.

This process might cause a problem for the leaching efficiency: the MIP measures showed that the agglomerates had a low porosity, which contradict some previous results found in literature explaining that good agglomerates should be strong and porous at the same time (Liu et al 2012).

In order to improve the agglomerate quality and to increase the porosity, further work is needed. First, the special pore distribution must be characterized by X-ray tomography data. Second the evolution of porosity and pore structure during soak or leaching tests must be evaluated.

Understanding the agglomerate evolution during soaking tests is a good way to understand the processes involved during column leaching of agglomerates.

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Iron Oxides Evolution along the Lateritic Profile of Mabounié Carbonatite (Gabon): a Key Point to Understand Magnetic Separation Processes

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Abstract. An extended research program on Mabounié ore (Gabon) focusses on developing a process to recover Rare Earth Elements (REE), Nb-Ta and U originating from a carbonatic laterite. The first step of this process is the ore beneficiation. In order to remove parts of the gangue minerals, a low intensity magnetic separation (800 Gauss) was performed. The QEMSCAN® characterization of feed material, magnetic and non-magnetic fractions helps to localize Nb and REE bearing minerals, such as pyrochlore and losses of these minerals. Among the gangue minerals, which are relatively easy to remove are magnetite (Fe₃O₄, ferrimagnetic) and hematite (Fe₂O₃, paramagnetic). These two minerals are difficult to distinguish by means of QEMSCAN® analyses, and the Satmagan® instrument was required to predict magnetite removal. Optical observations demonstrate that magnetite and hematite are not the only iron oxides present in the ore. Maghemite which is chemically not distinguishable from hematite (Fe₂O₃, ferrimagnetic) appears as a transition phase. Therefore, chemical characterizations of each oxide by microprobe analyses cannot help to distinguish magnetic from non-magnetic iron oxides. Along the lateritic profile, magnetic separation efficiencies change dramatically at one level, called “transition zone” between the banded and superficial ore. Correlations between QEMSCAN® modal mineralogy, iron speciation chemical analyses and the magnetite compound obtained by Satmagan® allow quantifying each iron oxide.

Keywords. Mabounié, Magnetic separation, Magnetite, Iron oxides, QEMSCAN®, Rare Earth Elements.

1 Introduction

The Mabounié deposit (Gabon) is a lateritic low grade rare earth elements and niobium-tantalum deposit developed on the uppermost altered part of a carbonatite. The lateritic profile is composed of two major zones: the apaticic zone and the banded/superficial zone. The superficial alteration led to its formation with increasing chemical concentrations of valuable elements in the upper part of the profile (Laval et al. 1988; Piantone et al. 1995; Boulingui 1997). The upper approximately thirty meters of the lateritic profile are composed of ferrisols and banded sandy horizons (Caia et al. 1994). The main ore mineral to be recovered is pyrochlore, containing the majority of both REE and niobium. This mineral exists in low concentration in carbonatite rocks (0.2 wt. %), and can be enriched up to 2.5 wt. %. Throughout the top 30 meters of the laterite, iron concentrations are very high, ranging from 40 to 80 wt. % Fe₂O₃. Iron, which is mainly related to oxyhydroxides, can be largely removed during beneficiation.

In the carbonatite, iron-bearing phases consist of oxides, sulfides, and a few silicates (Boulingui 1997) - such as chlorite, serpentine, and phlogopite - not considered in the following study due to their early alteration and their low amount. Magnetite (Fe₃O₄, ferrimagnetic), Ilmenite (FeTiO₃, paramagnetic), Pyrite (FeS₂, paramagnetic) and Pyrrhotite (Fe₁₋ₓS, ferrimagnetic) are the predominant contributors to the rock iron content. During alteration, sulfides disappear, and oxides (magnetite and ilmenite) are partly transformed into iron oxyhydroxides. None of the alteration products are sensitive to low intensity magnetic fields.

To design an industrial processing unit for the treatment of Mabounié ore, a precise quantification of ferro- and ferri-magnetic minerals are key factors. For this purpose, four fractions from top to bottom, S₁, S₂, R, R₂, respectively, were studied.

2 Analytical method

2.1 QEMSCAN®

QEMSCAN® analyses for this project were carried out at the ERAMET Research mineralogical service, using a FEI Quanta 650F SEM platform with two Bruker X flash 30mm silicon drift energy dispersive X-ray detectors. The software used included IMeasure v. 5.2 for the data acquisition and iDiscover v. 5.2 for the spectral interpretation and data processing. The PMA measurement mode was used to collect X-ray data every 2.5 μm across the polished sample surfaces, with X-rays acquired at 10,000 total X-ray counts per spectrum.

2.2 Satmagan®

Satmagan® (Saturation magnetization analyzer) measures indirectly ferro- and ferri-magnetic mineral quantities. It is used to quantify the magnetic moment of powder samples subjected to a sufficiently strong magnetic field (> 2.2 T) which allows magnetic saturation of minerals (Stradling 1991). A small plastic cell (1.2 cm³) is filled with the sample and introduced into a magnetic field induced by an internal coil. In a constant and saturated magnetic field, the ratio between gravitational force and magnetic force is proportional to the ferro- and ferri-magnetic mineral proportion in the sample. The magnetic moment of other minerals is insignificant compared to magnetic minerals. It is a non-destructive and fast method from which results depend on equipment calibration performed on ten certified standard samples.
2.3 Iron speciation analytical chemistry

A chemical analysis of the ore with respect to its Fe<sup>2+</sup> content was performed by means of an oxido-reduction method at ERAMET Research in the chemistry department.

Prior to the titration with potassium dichromate, samples were placed into a solution by means of an acid dissolution method in a non-oxidative environment (saturated in carbon dioxide).

The difference between the Fe<sup>2+</sup> values and the Fe<sub>tot</sub> values (Fe<sub>tot</sub> obtained by XRF determination) can be expressed as Fe<sup>3+</sup>.

2.4 Magnetic separation

Magnetic separation is a physical separation method applying a magnetic field and varying magnetic field strengths in order to separate magnetic, paramagnetic and nonmagnetic phases. The magnetic force (F<sub>m</sub>) is defined by the following equation (Gillet, 1991).

\[ F_m = \frac{1}{2} \mu_0 V_p \left( \frac{\kappa_p}{1 + D \kappa_p} - \kappa_f \right) \text{grad}(H^2) \]

Where \( V_p \) and \( \kappa_p \) are the volume and the magnetic susceptibility of the particle. \( \kappa_f \) is the magnetic susceptibility of the medium fluid. \( H \) is the strength of the magnetic field (A/m). \( D \) is the demagnetization coefficient.

A low intensity magnetic separator (LIMS) is used to recover the ferromagnetic iron oxides. It is composed of a drum, rolling around a magnet. The separation medium can be either water or air (Metso, 2013). In the present case study, the magnetic separation was performed at the GTK laboratory (Finland) with a 800 Gauss magnetic field. The first step, called roughing step, is performed by a Roxon D900 x L500 mm magnetic separator, and separates magnetic from nonmagnetic particles. The nonmagnetic product is conducted through a second Roxon D900 x L500 mm magnetic separator, during the scavenging stage, in order to clean it of remnant iron bearing minerals. The third stage is performed by a Sala D920 x L310 mm magnetic separator, produces an enriched magnetic product. All separators are of counter-current types.

3 Results: Mineralogy of the profile

The upper part of the lateritic profile is divided into two different kinds of ores, named superficial and banded ores. The distinction is mostly based on field observations (Laval et al., 1988). Therefore, the mineralogical study of these two ore types (Figure 1) shows major differences during QEMSCAN® measurements. Iron bearing mineral contents are similar in the superficial and the banded ores, 75.0 and 74.7 wt. % respectively. Iron oxides occur as hematite or magnetite and iron oxy-hydroxides such as goethite. Their respective content varies along the profile.

In the superficial ore, at the top of the profile, goethite is the dominant mineral and represents about 51 wt. % of the sample. Iron oxide represents 23.6 wt. % of the sample. The superficial ore shows high contents of silica (including quartz and amorphous silica) 8.62 wt. %, originating from the erosion of the surrounding sandstone and gneiss. The “other minerals” class (Figure 1) includes other present oxides (pyrolusite, ilmenite, etc.), all together representing about 16 wt. % of the sample investigated. Pyrochlore, rich in REE and niobium, represents less than 1 wt. % in the superficial ore sample.

In the banded ore, iron oxides are the dominant minerals and represent about 49 wt. % of the sample whereas goethite accounts for about 26 wt. %. As the banded ore is located stratigraphically underneath, quartz is barely observed (0.6 wt.%). Pyrochlore contents increase and reach up to 3.4 wt. %. The proportion of other minerals increases as well to amount to 21.3 wt. %.

![Figure 1](image)

Figure 1. Mineralogical composition along the lateritic profile calculated from QEMSCAN® measurements from which magnetite/maghemite is extracted and estimated by using Satmagan® analyses. Superficial ore occurs at the top of the profile, above the banded ore.

The high amount of iron oxides in the ores causes challenges in magnetic separation. To this point, it is important to identify the different mineral species. The QEMSCAN® analytical method cannot readily distinguish magnetite from maghemite as their X-ray spectra and BSE values are very similar. In order to differentiate these phases, reflected light microscopy has been applied on the magnetic fraction of each ore. Observations lead to the identification of textures that are typical for maghemitisation of magnetite. These replacements of magnetite are due to chemical and mineralogical transformation of magnetite (Fe<sub>3</sub>O<sub>4</sub>) to hematite (α-Fe<sub>2</sub>O<sub>3</sub>) through a transitional phase called maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>), which is crystallographically still cubic, like magnetite, but possesses chemically already a hematite composition. As shown in figure 2, in both superficial (Figure 2a) and banded (Figure 2b) ores, cores of the iron oxide crystals (outlined in white) are composed of magnetite altered to maghemite surrounded...
by hematite. It is important to note that maghemite, like magnetite, is ferromagnetic. Maghemite will therefore report to the ferromagnetic fraction during magnetic separation.

In order to confirm the presence of maghemite and hematite (Fe₂O₃), the amounts of total iron and ferrous iron were measured by means of ICP-MS and potentiometry, respectively. The difference between the total amount of iron and ferrous iron is an indication of oxidized species (ferric iron) in the sample. In the case of the study, the major oxidized phase is hematite. The results are compared to those values obtained by means of the Satmagan. The hypothesis is that if maghemite is a major ferromagnetic phase, the magnetite compound indicated by the Satmagan instrument should be higher than those measured using potentiometry.

Comparative measurements (potentiometry and Satmagan) show that iron in the ore measured by potentiometry ranges between 62 wt. % of Fe₃O₄ and 30 wt. % of Fe₂O₃ in the banded ore horizon, and between 58 wt. % of Fe₂O₃ wt. % and 30 wt. % of Fe₂O₃ in the superficial ore horizon (Table 1). However, the magnetite compound obtained by Satmagan is 62 wt. % of Fe₃O₄ for the banded ore and 63 wt. % for the superficial ore, thus 5% higher than the potentiometry measurement. This difference can be attributed to the maghemite compound.

Table 1. Results (mass percent) of iron speciation analyses and Satmagan values on magnetic products from banded and superficial ores. R MAG is a magnetic concentrate of banded ore and S MAG a magnetic concentrate of superficial ore. Fe₂O₃ [1] is obtained by chemical assay. Fe₃O₄ [2] is the magnetite compound obtained by Satmagan.

<table>
<thead>
<tr>
<th></th>
<th>wt.% Fe₂O₃</th>
<th>wt.% Fe(II)</th>
<th>wt.% Fe(III)</th>
<th>wt.% FeO₂</th>
<th>wt.% FeO₃ [1]</th>
<th>wt.% FeO₄ [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>R MAG</td>
<td>63.0</td>
<td>15.0</td>
<td>50.6</td>
<td>29.5</td>
<td>62.0</td>
<td>62.0</td>
</tr>
<tr>
<td>S MAG</td>
<td>63.0</td>
<td>14.0</td>
<td>49.0</td>
<td>30.1</td>
<td>57.9</td>
<td>63.0</td>
</tr>
</tbody>
</table>

The amount of magnetite and maghemite combined in both ores reaches 16.5 wt. % in the banded ore and 4.2 wt. % in the superficial ore. In comparison to QEMSCAN® iron oxides proportion analyses, hematite represents 32.4 wt. % and 19.4 wt. %, respectively.

4 Discussion

In order to evaluate the efficiency and the impact on the ores of a low intensity magnetic separation, banded and superficial ore horizons have been sampled in the high superficial sub-zone (S+) and the low banded sub-zone (R-) located at the bottom of the banded ore horizon. The curves displayed in figure 3 show the evolution of the recoveries as a function of the yield of nonmagnetic concentrates. The spacing between a curve and the “no-separation” line graphically shows the efficiency of the magnetic separation. The curve is on the no-separation line when the iron recovery is equal to the yield. If the curve is above the no-separation line, it shows an enrichment of iron in the magnetic concentrate. If the curve is under the no-separation line it shows a depletion of iron in the nonmagnetic concentrate.

As expected, the banded ore shows a better response to magnetic separation than the superficial ore: the spacing between the no-separation line and the R and R- curves is greater than between the no-separation line and the S+ and S curves (Figure 3). The two superficial samples (S+ and S) and the two banded samples (R and R-) show lower and higher efficiency during magnetic separation, respectively.
Table 2. Data used from figure 3. S+ = High superficial. S = superficial. R = banded and R- = lower banded. Mag = Magnetic and Non-mag = Nonmagnetic.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Yield (%)</th>
<th>Grade</th>
<th>Recovery</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S+</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed</td>
<td>100</td>
<td>37.2</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Mag</td>
<td>8</td>
<td>74.5</td>
<td>16.00</td>
<td>17.1</td>
</tr>
<tr>
<td>Non-mag</td>
<td>92</td>
<td>33.9</td>
<td>84.00</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed</td>
<td>100</td>
<td>41.3</td>
<td>100</td>
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<tr>
<td>Mag</td>
<td>11.5</td>
<td>73.6</td>
<td>20.50</td>
<td>22.0</td>
</tr>
<tr>
<td>Non-mag</td>
<td>88.5</td>
<td>37.1</td>
<td>79.50</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed</td>
<td>100</td>
<td>49.7</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Mag</td>
<td>29</td>
<td>75.0</td>
<td>43.70</td>
<td>51.1</td>
</tr>
<tr>
<td>Non-mag</td>
<td>71</td>
<td>39.4</td>
<td>56.30</td>
<td></td>
</tr>
<tr>
<td>R-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed</td>
<td>100</td>
<td>44.8</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Mag</td>
<td>32</td>
<td>70.6</td>
<td>50.50</td>
<td>51.5</td>
</tr>
<tr>
<td>Non-mag</td>
<td>68</td>
<td>32.6</td>
<td>49.50</td>
<td></td>
</tr>
</tbody>
</table>

This is in agreement with results from the mineralogical study, the content of magnetite and maghemite (ferromagnetic minerals) seems to increase with depth. This observation is confirmed by the yield versus iron recovery curves. The R- samples shows increasing efficiencies. The ratio between magnetite + maghemite and other iron bearing minerals of the banded ore is close to 4/1 whereas it reaches only 19/20 in the superficial ore. The higher the ratio, the more magnetic the iron bearing minerals.

Furthermore, with increasing depth, the mass recovery increases. This is explained by the greater mass of magnetic minerals that can be removed from the banded ore rather than from the superficial.

Magnetite is an inherited phase from the carbonatite, still present in the carbonatite protor. During the hydrothermal and superficial weathering of the rock magnetite underwent progressive oxidation to resulting in the presence of hematite, through an intermediate maghemitization stage. The superficial ore, located near the surface, is more subjected to weathering and in consequence more oxidized.

5 Conclusions

In order to predict the ore behavior during magnetic separation, it is crucial to determine the iron oxide varieties and their distribution along the ore horizon.

The presented results demonstrate that weathering has a great impact on the efficiency of magnetic separation. This efficiency can be controlled by mineralogical analyses combined with Satmag an measurements. Mass balance calculations are used to predict magnetic separation steps. The magnetic field strength is a function of the magnetic susceptibility and volume of the particle. One way to improve magnetic separation efficiency is to differentially increase the strength of the magnetic field by choosing a different technology such as medium intensity magnetic separator (MIMS).

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References

Comminution as an Economic Efficient Key for the Improvement of Metal Recovery from Low-Grade Kupferschiefer-Type Black Shale-Hosted Copper Ore from the Mansfeld Mining District, Germany

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Abstract. Comminution of low-grade, fine-grained ores represents a challenge in terms of cost-effective particle size reduction and ore liberation in the beneficication process of metal commodities. Kupferschiefer-type black shale-hosted low-grade ore deposited on dumps in the Mansfeld mining district since the beginning of the industrial mining era represents nowadays an economical resource. However, the Cu-Pb-Zn-mineralization is largely characterized by minute finely disseminated ore particles and complex intergrowths of base metal sulphides forming microscopic to mesoscopic, bedding parallel linear replacement fillings. In this study, comminution products of black shale-hosted low-grade ore generated by a ball mill, a vertical roller mill and a vertical impact crusher have been investigated. Comparative analyses of the particle size distribution and the degree of sulphide ore liberation reveal that both vertical roller mill and impact crusher produce a comminution product < 100 µm similar to a ball mill product, but containing enhanced liberation of sulphide ore particles. Moreover, the significantly lower specific power consumption of the vertical roller mill [7.2 kWh/t] and the impact crusher [3 kWh/t] illustrates that the application of alternative comminution methods can offer a substantial cost and energy-saving contribution for an additionally improved extraction of complex sulphide ores.

Keywords: Comminution, Kupferschiefer, black shale, vertical roller mill, impact crusher, copper

1 Introduction

The mining of Kupferschiefer-type black shale-hosted copper ore has left behind a significant legacy of mining and processing residues in the Mansfeld-Sangerhausen mining district. This comprises numerous historic small scale dumps, tabular dumps piled up from the beginning of the industrial mining age and huge conical dumps, which mark the youngest remnants of the local mining history during the socialist era of the GDR.

The mining of Kupferschiefer-type ore in the Mansfeld-Sangerhausen district was generally marked by winning of the Permian black shale horizon. Stratigraphically adjacent rock units, namely the hanging wall limestone/dolomite and footwall sandstone have been mined in several other Mid-European Kupferschiefer-type mining districts (Richeldorf, Lower Silesia/SW Poland), but were neglected in the mineral processing scheme of the Mansfeld processing facilities. Hence, also mineralized parts of the wallrocks were deposited within the large volumes of mainly limestone waste rock, derived from shaft sinking and raising stope level mining from the beginning of the industrial age. The processing of black shales to recover copper and byproducts was exclusively by pyrometallurgy, which has produced huge volumes of waste (silicate slags) and tailings (sludges).

Figure 1. Location of the Mansfeld-Sangerhausen mining district in Central Germany (from Jahn and Witzke 1999).

2 Petrological and mineralogical description

Lithological, the black shale is a finely laminated carbonaceous marl, mainly composed of quartz, carbonates (calcite/dolomite), clays (Fe-rich illites), organic matter (kerogen type II) and varying portions of Cu-, Pb-, Zn-and Fe-sulphides, depending on the ore zone. The sulphide assemblage contains mainly bornite, chalcocite, chalcopyrite, sphalerite, galena, pyrite and subordinate Cu-Ag-sulphides. Small-scale changes in the metals content of the ore are reflected by varying metal grades of the low-grade ore deposited on top of the barren wall rocks. Reliable average metal contents are difficult to ascertain, but representative sampling techniques of lumpy low-grade black shale ore reveal an average copper content of 0.6 % (Kamradt et al. 2012). Moreover, the main part of the ore mineralization occurs in the finely disseminated portion, in which sulphide minerals or aggregates of few to several tens of µm in size commonly occur intensely intergrown and form complex ore textures. Apart from the very fine-grained
sulphide ore, bedding parallel vein fillings of up to 0.2 cm thickness are common and mostly associated with. In order to introduce these ores to an improved mineral processing route, it is important to use effective processing methods. Comminution, comprising crushing and grinding, is the most cost and energy consuming treatment step in the entire processing route. Estimations of the energy consumption assume that 30-50% of the total mining operation costs are related to comminution (Wills and Napier-Munn 2006; Sadrai et al. 2006). The transfer of raw ore to a recoverable state is controlled by the achievement of suitable particle sizes and the liberation of the valuable minerals.

4 Conminution of low grade
Kupferschiefer-type black-shale-hosted ore

4.1 Conventional comminution

Generally, the challenge in processing of ores starts with the reduction of the grain sizes to a liberation degree, in which the desired mineral can be extracted (e.g. flotation, leaching or gravity concentration). A well-established and applied comminution of sulphide ore is a multi-stage process of crushing and grinding, in which the raw ore is fed initially to a primary jaw crusher and subsequently processed by a secondary cone crusher in order to produce a pre-crushed, several mm-sized product, which is in the most cases too coarse-grained for the following extraction process. The required fineness of the comminuted ore is commonly achieved by grinding with ball mills.

Ball mill grinding has to struggle with potentially serious issues. Most prominent and known is the overgrinding effect, in which an undesirable part of the comminution product has been crushed to very fine particles < 5 µm that are usually not recoverable by e.g. froth flotation. Economically, it means that considerable portion of the feed material can be lost, because the mass of the particles becomes very low at simultaneous enlargement of specific particle surface and thus, not accessible to be trapped by air bubbles (Chander 1978). Moreover, fine-grained particles below 10 µm tend to stick together because of adhesive forces, in particular when the feed contains clays or micas. Agglomerated particles, particularly if built up by a mix of gangue and sulphides, will be lost for subsequent processing too, because the sulphide particles are shielded by gangue particles, unable to attach to the air bubbles in a flotation pulp.

Grain size distribution curves of ball mill products from low-grade black-shale-hosted ore reveal that more than 60% of the comminution product ranges in the grain size range below 20 µm. It is questionable, if such fine-grained material can be processed satisfactorily in conventional flotation cells, especially if one has to consider that a part of the sulphides were not liberated. Otherwise, with the slowly established column flotation it is economically possible to recover of fine particle by flotation (Abd El-Rahim 2014).

4.2 Improvements by alternative comminution techniques

In order to process the run-of-mine ore more cost- and energy-saving, it is advisable to operate the comminution circuit with lowest grinding stages as possible.

Vertical roller mills (VRM) can comminute material up to 150 mm feed grain sizes. The application of VRM is traditionally established in the concrete production. Generally, the decrease of the grain size is achieved by shear stress affecting the mill feed between the roller and the roller bed. The grinding pressure is a function of gravity, centrifugal force, spring tension and hydraulic pressure and controls the desired particle size of the mill product.

Grinding tests on Kupferschiefer-type black shale-hosted copper ore have been carried out on a vertical roller mill produced by Loesche GmbH equipped with tilted conical rollers (15° to the roller bed/grinding track). Main advantages of roller mills are represented by the selective grinding of waste and ore and the accumulation of the value minerals in distinct grain size.
classes, mostly in the finer grain size classes. A downstream classifier secures a constant grain size range of the mill product and thus, prevents overgrinding. Furthermore, residual moisture can be eliminated simultaneously by friction heat that is produced during the grinding process. Vertical roller mills are said to be low wear- and low energy-consuming.

Another single-stage comminution technique is represented by impact crushers. Classic impact crushers have a horizontal working axis. The feeding material is crushed by impacts onto the moving rotor as well as mutual impacts of feed particles.

For grinding tests onto an impact crushing platform, low-grade Kupferschiefer-type black shale-hosted ore has been comminuted by the VeRo Liberator of a German start-up company based in Hamburg. The VeRo Liberator is a new development on the impact crusher market and the main difference compared to established impact crushers is the vertical working axis that can be variably operated by motors turning three stacked levels of impact tools at very high speeds. These levels turn clockwise and/or anticlockwise, doubling the impact forces on the materials. Preliminary tests have shown that the black shale-hosted ore can be sufficiently comminuted in a single pass.

The most favourable effect of VRMs and the VeRo Liberator impact crusher, respectively, is the lower energy consumption for the entire comminution process, in which the necessity of an additional comminution stage is not applicable if the generated comminution product has the desired properties for an effective extraction of the value minerals. Furthermore, both crushing techniques operate dry, whereas in classical ball mills wet milling has to applied to reach a fineness level suitable for the following beneficiation process. The use of additional resources (water, energy, etc.) manifests disadvantages in the overall balance by causing high drying costs.

Calculations of the Bond Work Index for comminuted low-grade black shale-hosted ore have been carried out for grinding products <100 microns (pre-crushed < 11 mm) generated by dry operation of ball mill and VRM, respectively. The impressive energy efficiency of the VRM is expressed by considerably lower energy consumption [7.2 kW h⁻¹] of substantially more than 50 % in respect to the ball mill [17.1 kW h⁻¹] (Kamradt et al. 2012).

The particle size distribution curves (PSD) of both, ball mill and VRM products reveal that a larger proportion of finer particles in the range of 40 to 60 µm is expressed by a slightly steeper slope in the PSD curve for the VRM product. However, the comminution product < 100 µm contains, similar to the ball mill product, more than 50 % of particles < 10 µm. The optimum particle size for sulphide flotation has been localized at 30 micron, whereas sulphide particles in the range of 10 to 100 microns are accessible for the flotation process (Trahar and Warren 1976).

PSD analyses on previous comminution tests with the VeRo Liberator aggregate on various ores have shown that 50 % to 95 % of the feed (mostly < 100 mm) can be crushed to particle sizes < 250 µm at a single pass without using a primary crusher. VeRo Liberator products contain between 35 to 65 % particles < 100 µm, fully liberated in the most ore types and thus, can be directly fed to the subsequent beneficiation route. Ongoing tests with the impact crusher on Kupferschiefer-type black shale-hosted ore indicate that a single-pass with only few seconds operation time produce a slightly coarser comminution product in which d₅₀ is < 100 µm at significantly lower energy demand [3 kW h⁻¹]. Additionally, the PSD-curve reveal that the portion of particles < 10 µm is lower compared to the ball mill- and VRM-product.

![Figure 3: PSD-curves for the comminution product < 100 microns show that the ball mill- and VRM-product are similar and slightly coarser product for the VeRo Liberator impact crusher.](image)

5 Particle liberation of sulphide ore in the comminution products

The significant factor for sufficient recovery rates of the beneficiation in e.g. froth flotation processes is the degree of liberation of the valuable minerals. Hence, it has to be considered, in which grain size range the desired value minerals occur within the ore. Consequently, the recovery depends on the grain size range of the comminution product, in which the ore particles exist in a liberated state.

The fine-grained sulphide ore in the black shale necessitates that the crushing process effectively expose particles free of gangue in a grain size range between 5 and 100 µm.

Particle analyses have been executed on ball mill-, VRM- and VeRo Liberator-comminution products of Kupferschiefer-type low-grade dump material.

Microscopic studies on grain mounts of the ball mill fraction < 100 µm of the black-shale-hosted ore show that sulphide particles occur both, intergrown with gangue (dolomite/quartz/clay) and also in a completely liberated state. It has been recognized that copper sulphides are commonly partially exposed but the majority of their surface is covered by gangue minerals or interlocked with other sulphides. Additional investigations on ball mill product of more limestone-dominated low-grade ore indicates that the amount of completely liberated sulphides is markedly higher, which indicates that the breakage behaviour is more plastic if the carbonate content in the ore increases and the carbon-clay proportions decreases, respectively. The shape of liberated particles is commonly irregular, angular and break lines are straight to slightly concave.
Single-phase sulphide particles that are completely liberated can be found, but in particular bornite, chalcopyrite or sphalerite appear commonly intergrown with pyrite, galena or gangue. SEM-based mineral liberation analyses of the ball mill product (< 100 µm) have shown that 67 wt.% of the copper sulphides can be liberated completely and that approximately 20 wt.% of the sulphides remain intergrown with gangue covering more than 50 % of the sulphide particle surface, which usually cannot be extracted by froth flotation.

The < 100 µm VRM-product of low-grade black shale-hosted ore have been also investigated by automated SEM-based particle analysis. Mineral liberation data show that at least 72 % of the copper sulphides have been completely liberated, 18 wt.% of the copper sulphide particles represent particles occupied over 50% with intergrowths onto the particle surface. Thus, the degree of liberation of copper sulphides in the VRM-product appears slightly higher in comparison with the ball mill product.

SEM-based investigation on the fine grained fractions of the VeRo Liberator product (<63, <125, <250 µm) show a significant portion of completely liberated sulphide particles in particular for sulphide clasts larger than 30 µm, apparently crushed at the mineral boundaries or crystallographic-defined breaks and exhibit completely liberated clasts. Sulphide minerals with grain sizes below 30-40 µm appear mostly unaffected by impacts and are still enclosed and intergrown in-situ association with gangue forming extremely finely intergrown textures.

4 Conclusion

Investigations on various comminution products show that a sufficient reduction of the ore particle size can be achieved more economically by the application of alternative methods. Compared to ball mills products, the VRM-products show higher liberation of the sulphide ore at much lower energy consumption and thus can be deployed for the recovery of very fine-grained base metal sulphides. The comminution product of the VeRo Liberator impact crushe contain 50 % particles < 100 µm that reflect a slightly coarser particle size distribution and could be effective methods for the comminution and particle liberation of Kupferschiefer-type low-grade ore. Generally, the current study reveals that the application of alternative crushing/grinding techniques can reduce significantly the operational cost by lower specific power consumption, which could represent immense savings in the budget of any processing facility. However, further studies, in particularly on the new VeRo Liberator platform are needed and will be carried out in the near future.

Acknowledgements

The author is grateful to Loesche GmbH and PMS GmbH for providing tests on their comminution platforms. Prof. Dr. Gregor Borg is thanked for review and helpful hints. Juliane Schaefer is acknowledged for providing granulometric data. Furthermore, this study has been supported by the German Federal Ministry for Education and Research (BMBF) in the funding priority "R²-Innovative Technologies for Resource Efficiency: Resource-Intensive Production Processes" as well as is currently promoted in the running joint project "EcoMetals", which is part of the BMBF R&D programme "Raw materials of strategic economic importance for high-tech made in Germany".

References

Surface Chemistry of Ore-Binder Mixture System in Relation to Iron Ore Pelletisation

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Abstract. The surface property of single and multi-minerals (hematite and gangue) with bentonite binder was investigated to produce quality pellets by properly controlling the surface properties of minerals and to beneficiate low grade fine iron ores. The results showed that zeta potential of hematite-bentonite mixture did not change with the bentonite dosage. On the other hand, the type and amount of gangue minerals greatly affected the zeta potential of the mineral mixture with bentonite. Specifically, the amount of silica presented in the system governed the changes in zeta potential due to the bentonite adsorption on silica surface and its charge while alumina had no effect. This is due to their nature of the charges and interaction with bentonite. This study indicated that the mineral composition of iron ores significantly affected the surface charge of the ore, and can noticeably influence the quality of pellets formed by iron ores with the binder.

Keywords. Low grade ore; gangue mineral; zeta potential; mineral-binder interaction

1 Introduction

Agglomeration is commonly performed when coarse particles are required for improving the particle beneficiation performance, in terms of ease of handling, suppressing dust generation, densifying the product for convenient storage, shipping or preparing the final products as tablets, granules (Pandey and Kumar 2012). The agglomeration process in iron ore industry is mainly applied in pre-production process, i.e. pelletisation and sintering to produce porous furnace feeds with certain physical strength and chemical components.

Pelletisation is an important iron ore agglomeration process. It is significantly beneficial in dealing with fine iron ore than sintering and other possible agglomeration techniques because pelletisation requires a smaller capital cost. Pelletisation is an industrial process that produces green balls with the desired size, e.g. 9-16 mm (Sivrikaya and Arol 2012), by rolling fine iron ore with the addition of critical amount of water, binder, and any other additives if required. After pelletisation, the iron ore pellets with the enough compressive and drop strength become the desirable feed of industrial furnaces, such as, Corex furnace and blast furnace (Pandey and Kumar 2012).

Qiu et al. (2004) studied the interfacial characteristics of iron ore concentrates with different binders and the functions and molecular structure of organic binders in relation to iron ore pelletisation. They focused on investigating the difference between their organic binder and conventional bentonite binder with a high Fe content magnetite ore, not a low grade hematite ore we investigated in this study.

Qiu et al. (2003) also discussed the essential functions and the preferred binder structure for iron ore pelletisation. Functionally, good organic binders should improve the wettability of iron ore particles, and possess great adhesive force to iron ore surface. Thus, in order to achieve a better understanding of mineral surface properties appropriate for iron ore pelletisation, zeta potential measurement can be performed to investigate the mineral-binder interactions.

According to two previous studies, the combination of coarse and fine particles provides a more compact structure, and thus achieved the higher compressive strength and drop strength of iron ore pellets (Maeda and Shimizu 2009, Kawachi and Kasama 2011). Kawachi and Kasama (2011) reported that the strength of dried pellets was varied by the amount of micro-particles in the ore. With the greater amount of micro-particles, at the beginning of drying the higher strength of pellets was obtained due to the increase of granule condensation. In the case of hematite pelletisation, the compressive strength of green pellet can be determined by the adhesion forces between hematite particles by liquid bridge of water. On the other hand, the strength of pellets after drying can be maintained by the adhesion force created between intertwined particles and gives the stronger structural integrity (Kawachi and Kasama 2011). Both those two studies reported the importance of gangue minerals on the compressive strength of pellets, but the mechanism behind that was not studied in detail (Maeda and Shimizu 2009; Kawachi and Kasama 2011).

Although there are valid arguments discussing about iron ore pelletisation in terms of the optimization of the pelletiser operating parameters, the effect of surface properties and gangue minerals on pelletisation of low grade iron ores are still rarely investigated by previous studies.
Bentonite is hydrated aluminosilicate clay mainly composed of montmorillonite with layered structure loosely bound by counter ions (Sivrikaya and Arol 2010). In aqueous solution with mineral particles, bentonite behaves as a binder to bridge mineral particles. This can be explained by the electrostatic interaction between bentonite and mineral particles as shown in Fig. 1. Positively charged edge of bentonite is attracted to the negatively charged mineral surface and bridge mineral particles.

This study aims to identify the surface properties, specifically surface charge of iron oxides and gangue minerals in iron ores and their mixtures to produce quality pellets with a binder. The properties of iron ore pellets are varied depending on the amount and type of gangue minerals. One of the key components making this change is the surface property of existing minerals since particle-particle interactions play significantly important role in creating pellets.

The outcome of this study gives us a better understanding of the surface chemistry of iron ore pelletisation. This useful information greatly help us produce quality iron ore pellets by properly controlling the surface properties of mineral components to beneficiate low grade/fine iron ores that are becoming more important due to a limited access to high grade/coarse ores.

2 Materials and Methods

2.1 Reagents and Samples

Potassium nitrate (99.5%, CHEMTECH) was used as an electrolyte. The four chemicals, hematite (Iron (III) oxide, BDH Laboratory Supplies), silica (Silica powder 200 mesh, Chem-supply), alumina (analytical reagent, Ajax chemicals) and bentonite (Sodium bentonite, Chem-supply) were used as samples for the experiment.

2.2 Analytical equipment

Malvern Zetasizer Nano-Z (ZEN2600) was used in the zeta potential analysis whereas the mortar-pestle and laboratory sieves were used in comminution and size classification of samples during the sample preparation process. Laboratory pH meter (AQUA-pH, TPS) was used to monitor pH of aqueous suspension. A stop watch was used to measure the time during sample suspension preparation. Moreover, necessary laboratory glassware was used in handling solutions, and suspensions.

2.3 Analytical methods and procedures

2.3.1 Sample preparation procedure

In zeta potential measurement, 4 sample powders were separately dried at 105 °C for several hours in an oven, dry pulverized in a ring mill and screened to obtain -38 μm size fraction for the experiment.

In mixed mineral systems, 3 different series of tests were performed. They were (1) hematite-bentonite mixture, (2) hematite-silica-alumina-bentonite mixture where silica and alumina mass% was 10% in total solid, and (3) hematite-silica-alumina-bentonite mixture where silica and alumina mass% was 24% in total solid. The silica and alumina dosage was determined by assuming two cases dealing with high grade (i.e. less gangue minerals) and low grade hematite ore (i.e. high gangue minerals).

3 Results and Discussions

3.1 Zeta potential of single minerals and binder

Table 1 shows the zeta potential of single minerals and bentonite at natural pH (i.e. 7-8). The results indicated that silica and bentonite have high negative charge while hematite and alumina have the small charges in water. The values agreed with the previously reported values (Rao 2004).

Table 1. Zeta potential of single minerals and bentonite at natural pH.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Zeta potential (mV) at natural pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>4.1</td>
</tr>
<tr>
<td>Silica</td>
<td>-54.9</td>
</tr>
<tr>
<td>Alumina</td>
<td>-1.6</td>
</tr>
<tr>
<td>Bentonite</td>
<td>-32.3</td>
</tr>
</tbody>
</table>

3.2 Zeta potential of minerals and binder mixture

Figure 2 shows the zeta potential of hematite-bentonite mixture at natural pH. Here bentonite dosage was varied to investigate any effect on the surface charge of the mixture. There was not much change at higher than 1 wt.% bentonite addition observed. In other words, the results showed that addition of more than 1 wt.% bentonite does not change the surface property of the hematite at all. It is agreed well with the fact that the common bentonite dosage is in between 0.5 - 1.0 wt.% (Kawatra and Halt 2011). The results can be explained by the saturation of bentonite adsorption on the hematite surface due to small charge exist on the hematite.
The ratio between silica and alumina (SiO$_2$/Al$_2$O$_3$) was also varied to investigate their contributions. In 10 wt.% silica + alumina dose, significant change in zeta potential appeared at 10 SiO$_2$/Al$_2$O$_3$ ratio while slight change was observed up to 4 SiO$_2$/Al$_2$O$_3$ ratio. The contribution of alumina presence was almost negligible in terms of surface charge of the mixture. On the other hand, at the highest SiO$_2$/Al$_2$O$_3$ ratio of 10, bentonite adsorbs onto silica to make the surface charge more negative close to the surface charge of bentonite (Table 1). This result agreed with the bentonite adsorption onto glass beads observed by Kawatra and Ripke (2002).

In higher silica and alumina addition of 24 wt.%, opposite trend from 10 wt.% composed of silica and alumina was obtained. It can be explained by the more negatively charged silica available in the system. With less amount of silica (2 and 4 SiO$_2$/Al$_2$O$_3$), there is less interaction with bentonite; but the surface charge of the mixture is dominant by the surface charge of silica (Table 1). On the other hand, with higher amount of silica available (10 SiO$_2$/Al$_2$O$_3$), the more bentonite adsorbs on the mineral surfaces, and changes the surface charges to less negative, which is close to the surface charge of bentonite (Table 1). Based on the results in Fig. 3, silica dosage significantly affects the surface charge of the mixture with bentonite while alumina dosage does not affect the surface charge. It is due to their nature of the charge and interaction with bentonite. This explains the mineral composition of iron ores significantly affect the surface charge of the ore. It can influence the quality of pellets formed by iron ores. For example, with large amount of silica present in the iron ore, the pellet structure can be more rigid and stronger due to stronger silica-bentonite interaction and existence of hard silica in the structure. On the other hand, less amount of silica in the iron ore can lead the loosely bound and weak pellets due to weak interaction between hematite and bentonite and fragile hematite presence without much structural support from silica.

4 Conclusions

Iron ore pelletisation is vital to the steel making industry since quality pellets can provide a good furnace operation condition. The surface properties of iron ore and its gangue with a binding mineral are important to be investigated. There are literatures mentioned the importance of the surface properties of each single mineral on iron ore pelletisation; however, the interactions of mineral-binder mixtures from the surface property point of view were rarely investigated experimentally.

This study aimed to identify the surface properties, specifically surface charge of iron oxides and gangue minerals in iron ores and their mixtures with a binder to produce quality pellets. Zeta potential of mineral mixture (hematite, silica, and alumina) with bentonite binder was measured for this purpose.

The results showed that zeta potential of hematite-bentonite mixture did not change as increasing the bentonite dosage. On the other hand, the type and amount of gangue minerals significantly affected the zeta potential of the mineral mixture with bentonite. Specifically, the amount of silica presented in the system governs the changes in zeta potential due to the bentonite adsorption on its surface and its charge while alumina had negligible effect. This is due to their nature of the charges and interaction with bentonite. This study indicated that the mineral composition of iron ores significantly affect the surface charge of the ore, and can noticeably influence the quality of pellets formed by iron ores with binder.

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SESSION 14
Geometallurgy

Convenors
Dee Bradshaw, Pertti Lamberg, Eric Pirard, Sven Sindern
Geometallurgical Assessment: Beneficiation of Rare Earth Minerals as a Possible By-Product from the Vergenoeg Fluorite Mine, South Africa

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Abstract. A systematic geometallurgical study of the rare earth mineralogy and beneficiation potential as by-product was carried out at the Vergenoeg Fluorite Mine, South Africa. For this purpose, a representative suite of samples was collected from a mining block prior to blasting. After mining, this material was tracked through the beneficiation plant by sampling all crucial steps. Whole rock geochemical analyses, quantitative mineralogical and microstructural analyses (by MLA), complemented by mineral chemistry data for relevant REE minerals, were obtained for undisturbed and processed samples. These data were used to assess the deportment of REE and to track the route of REE minerals within the beneficiation process.

Microcrystalline xenotime and monazite were found to be the two most abundant REE minerals, with all other REE minerals of only very minor quantitative importance. Process samples from the flotation circuit illustrate that the material from the cleaner circuit (B) tailing, being usually considered as waste, is strongly enriched in both monazite and xenotime. The REE minerals are well liberated, thus leading to the conclusion that it may be feasible to produce REE minerals as a future by-product by only slight modification of the current flow sheet.

Keywords. REE, MLA, mineral processing, geometallurgy

1 Introduction

SEM-based automated mineralogy is a key tool in geometallurgy, as it provides quantitative data on mineralogy and microstructure such as modal mineralogy, mineral associations, mineral locking and liberation, particle- and grain sizes, etc. Automated mineralogy has been commonly applied in the mining industry during the last 10–15 years for quality control of processing intermediates and products. The software for both MLA and QEMSCAN is particularly designed to analyse granular samples. However, information on mineralogy and fabric relationships in the undisturbed ore is lost when the material is crushed, milled and beneficiated. The value of studying undisturbed samples has been recently documented by Hoal et al. (2009), Voordouw et al. (2010), Birtel et al. (2011, 2013), Gregory et al. (2013) and Kern (2013). It is also a goal of this study to critically assess the value of examining undisturbed ore in conjunction with process samples.

The present study was carried out on the open pit and processing plant of the Vergenoeg Fluorite Mine, South Africa. The ore of this deposit is known to contain considerable concentrations of REE (Graupner et al. 2015) with an as yet unexplored beneficiation potential. The aim of this study is to assess the processing characteristics for a potential extraction of rare earth minerals from the existing flotation circuit at Vergenoeg Mine and to examine aspects of the rare earth mineralogy.

2 Methods

For this study, 13 individual hand specimens were collected to represent all macroscopically recognizable structural and mineralogical lithotypes identified in a single mining block, measuring ca. 10×10×10 m in dimensions (sample set A). Sample set A was complemented by a single composite sample representing a mixture of equal amounts of drill core cuttings from all blast holes drilled in the respective mining block (sample A-D-Mix).

Subsequently, the studied mining block was blasted, then processed as a single feed material through the existing comminution and flotation circuit that produces a fluorite concentrate. The beneficiation circuit was sampled in three surveys (9 samples each = sample set B), according to their residence time in the prevailing flotation stage. Fig. 1 shows the sampling spots along the flow sheet.

Figure 1. Flow diagram of the processing plant with sampling spots: A = mined block, D = Conditioner input, E = Rougher concentrate, F = Cleaner circuit (A) concentrate, G = Cleaner circuit (A) tailing, H = Cleaner circuit (B) concentrate, I = Rougher tailing, J = Scavenger tailing, K = Scavenger concentrate, L = Cleaner circuit (B) tailing, M = Magnetic separation concentrate, N = Magnetic separation tailing, O = Tailings dumps.
Geometallurgical Assessment: Beneficiation of Rare Earth Minerals as a Possible By-Product from the Vergenoeg Fluorite Mine, South Africa

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Geometallurgy 1383
Polished blocks (40 mm diameter) and sample powders were prepared for MLA and electron microprobe analyses from the hand specimens of sample set A. Polished grain mounts (30 mm diameter) and sample powders were prepared for all granular samples (A-D-Mix, process samples of sample set B). Sample powders were used for bulk chemical analyses supplied by ACME Ltd. (Vancouver). Polished blocks were subject to mineralogical studies. In preparation for MLA analyses, three individual process samples were used to test, whether data obtained on unsized samples would be comparable to those obtained for sized sample materials (4 different particle size fractions). Particle size distributions for these three samples were further characterized by laser diffraction. Results illustrated that particle size distributions and quantitative data on mineralogy and microfabric were very similar for unsized sample material and for bulk information reconstituted from particle size fractions. It was thus decided to limit analysis to unsized grain mounts.

Polished blocks of samples A and B were analysed with a mineral liberation analyser (MLA) Quanta FEG 600, an FEI field emission scanning electron microscope equipped with two Bruker EDX detectors. The instrument is equipped with MLA software supplied by FEI for automation and data processing (Gu, 2003; Fandrich et al., 2007).

Instrument settings for this study were 25 kV (acceleration voltage) and 230 μA (emission current). In order to determine mineralogy, the XBSE mode was used to map the entire sample at a magnification of 175× times, 300× or 500× if needed to detect smaller grains. For refinement, 20 selected samples were also analysed in GXMAP mode, where minerals of a selected grey range were analysed in a closely spaced grid (X mapping) to avoid misidentification of minerals with same or similar grey values.

Electron microprobe analyses were performed with a J EOL JXA 8900 on 4 selected samples of sample set A (3 polished blocks) and one grain mount sample with randomly picked fluorites from sample set B, in order to accurately determine the mineral chemistry in particular of fluorite as a major mineral and possible host of REE. Acceleration voltage was 20 kV, the probe current 30 nA and the beam diameter between 10 and 20 μm. Counting times varied between 10 and 60 s on the peak and 5 and 30 s on the background.

In an effort to validate the results of MLA analysis, modal mineralogical data in combination with mineral chemistry for the ore-forming minerals was used to calculate a modal chemical composition. This was compared with chemical analytical data determined on a representative fraction of each sample, being in good agreement.

3 Results

The results presented focus on the mineralogy of the REE in the studied mining block and the potential to beneficiate the identified rare earth minerals as a by-product within the scope of the current fluorite processing plant. The data are also used to track significant and systematic changes of important characteristics, such as REE mineral concentration, association and liberation.

3.1 Modal composition of starting material and products

MLA data of undisturbed samples (sample set A) reveal that the three major phases iron oxide (representing magnetite and hematite, as well as minor goethite), fluorite and quartz together add up to 96–99 wt. % of the total ore (Fig 2A). The remaining 1–4 wt. % comprise REE minerals (Fig. 2B) and other, quantitatively insignificant minerals (i.e., apatite, sulfides).

Figure 2. Modal mineralogy: (A) major phases, (B) minor phases for sample set A, selection of 11 out of 13 samples. Sample A-D-Mix represents the average composition of the block. Processed samples from set B: major phases (C), minor phases (D): REE minerals are accumulated in the rougher tailing and highest rare earth mineral contents are in the Cleaner A and B tailing, this material is presently considered as waste.

Microcrystalline xenotime and monazite in approximately equal amounts are the only important REE minerals in the studied mining block (Fig. 2, B, Fig. 3). Other REE minerals were identified (i.e., bastnäsite, fluorcerite, florencite) but found to contribute only limited amounts to the total REE content of the ore (less than 4 %).

157 randomly chosen fluorite grains were analysed for their REE contents by EMPA. Nd was found in 47 of 157 grains with an average composition of 543 ppm (limit of detection 364 ppm). Ce and Dy were only detected in 19 and 3 grains, respectively, with average compositions of 733 ppm for Ce (limit of detection 497 ppm). In contrast to these low amounts, Y is the dominating REE found in 146 of 157 analysed grains.
with an average content of 1579 ppm (in the range of ≥198 ppm to 4798 ppm, limit of detection 198 ppm).

Process samples from the flotation circuit illustrate that rare earth minerals are enriched in the rougher tailing (3.6 wt. %) and depleted in the rougher concentrate (2.1 wt. %, Fig. 2D). Iron oxide minerals are the main phases in the cleaner A and B tailing (Fig. 2C). The enrichment of iron oxides is accompanied by the highest rare earth mineral contents (Fig. 2D) of all process samples by up to 4.2 wt. %.

3.2 Mineral association and liberation

Mineral association (Fig. 4) considers the sum of the contact surfaces of one particular mineral with the associated mineral – compared to the entire contact surface of this mineral, mineral liberation by free surface (Fig. 5) considers the exposed surface of a certain mineral contained in particles of a particular granular sample. Liberation classes with a step size of 10 % are usually defined and plotted in area charts (see Fig. 5 for the case of xenotime, upper row). The mineral distribution (Fig. 5, lower row) indicates the amount of minerals in a particular liberation class.

REE minerals are enriched in the rougher tailing and depleted in the rougher concentrate. The mineral associations and mineral liberation by free surface reveal a crucial difference between the particles in the two products; whereas the tailing accumulates REE minerals associated with iron oxide minerals, liberated particles preferably enter into the concentrate. This concentrate feeds the cleaner circuit (A), where the fluorite is concentrated and the liberated REE minerals are separated to the tailing.

This series of separation steps is responsible for the formation of two distinct tailing products regarding their REE minerals contents: REE minerals in the scavenger tailing are mostly intergrown with iron oxide minerals. Liberated REE minerals are accumulated in the cleaner (B) tailing.

Figure 5 shows the scavenger tailing compared to the cleaner circuit (A) tailing, as the cleaner circuit (B) showed inconsistent flotation behaviour during the sampling campaign. The two charts (Fig. 5) show the same patterns for mineral liberation (Fig. 5 upper row); however, the mineral distribution (Fig. 5 lower row) reveals the difference between the two waste products: (a) After passing the scavenger, in the scavenger tailing the vast majority of REE minerals is associated with other minerals (>50 wt. % of xenotime in the liberation classes between 0 and 30 %). (b) With respect to the cleaner circuit (A), the tailings contain 54 wt. % of fully liberated REE minerals which is favorable for subsequent concentration. In the cleaner circuit (A) the REE minerals are separated to the tailing, where the content increases by 53 % compared to the initial value (Fig. 5). Approximately 54 wt. % of xenotime and monazite grains in this tailing stream are fully liberated (Fig. 5), i.e., easy to separate during a following mineral separation step.

4 Implications and conclusions

Monazite and xenotime are the two most abundant rare earth minerals in the mining block that was subject of
this investigation. They occur in approximately equal amounts and are microcrystalline, they are densely intergrown with each other, occur in a matrix of iron oxide minerals or quartz, and are rarely associated with fluorite.

Flotation circuit - REE mineral concentrations

Figure 6. Flow diagram of the flotation circuit with REE mineral concentration numbers indicated in wt. %. See Fig. 1 for abbreviations. Cleaner circuit (B) was subject to irregularities, the two products (L and H) are not representative.

With respect to the flotation behaviour, the cleaner circuit (B) tailing contributes together with the scavenger tailing (Fig. 6) directly to the final tailings, which are considered as waste and stored in the tailings dam on the mine property. Without any changes to the present configuration of the flotation circuit, the cleaner circuit (B) tailing can be considered as potential starting material for REE beneficiation. It contains an estimated average of 1.07 wt. % REE$_2$O$_3$, similar to or even exceeding rare earth contents reported for many current exploration projects worldwide. The particles in this concentrate are well liberated and favor a subsequent enrichment in an additional flotation stage. There are several reasons for this:

a) Monazite and xenotime have quite similar flotation characteristics.

b) Monazite and xenotime are enriched in the rougher tailing and depleted in the rougher concentrate. The mineral associations and mineral liberation by free surface reveal a crucial difference between the particles in the two fractions; whereas the tailing accumulates REE minerals associated with iron oxide minerals, liberated particles preferably enter into the concentrate.

c) The results from Kern (2013) indicate that particle sizes smaller than 125 µm show sufficient liberation for the successful flotation of both fluorite and REE minerals.

d) The rougher concentrate feeds the cleaner circuit (A), where a final fluorite concentrate is produced. In this flotation step, the REE minerals report to the tailings, where the content increases by 53 % compared to the initial value. Approximately 54 wt. % of xenotime and monazite grains in this tailing stream are fully liberated, i.e., easy to separate during a following mineral separation step.

Acknowledgements

We greatly acknowledge the support and funding of this project by Vergenoeg Mining Company (Pty) LTD and also the kind permission for publishing. We thank Sabine Hauer and Bernhard Schulz from TU Bergakademie Freiberg for MLA analyses and professional help with data processing. The study also benefited from discussions within the NorDorsk funded Network ProMinNET.

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Clay Mineral Characterization on Ni-Laterite: Qemscan Imaging of Alteration Processes

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Abstract. Weda Bay (Indonesia) nickel lateritic ores have a very fine textured complex mineralogy. In order to obtain a comprehensive mineralogical identification, three types of equipment have been used iteratively. Powder XRD analyses on oriented thin sections with different kinds of treatments displayed crystal structures present in the sample. Qemscan® mapping was used to classify chemical homogeneous phases, named using XRD identification. On homogeneous particles, precise microprobe chemical analyses have been performed, to calibrate both Qemscan® and XRD databases. Nickel saprolites are principally composed of serpentine, smectite and iron hydroxides. With this recognition methodology, 3 different serpentines (Mg-rich / Ni-poor, Mg-rich / Ni-rich, and Mg-poor / Ni-poor), and 3 different smectites (nontronite, saponite, stevensite) were characterized. Quantification of each phase was performed for the purpose of resource estimations. The size of crystallites was less than the analytical resolution of Qemscan®, so a database has been compiled to account for treatment of mixed EDX spectra. XRD quantification has also been calibrated with other external analyses: chemistry of whole rocks and minerals (by microprobe), calcimetry, and cation exchange capacity. Mineral quantification by means of both Qemscan® and XRD gave similar results. Mineralogical mapping of samples across the lateritic profile allows imaging appearance and disappearance of each mineral during alteration processes. Nickel concentration can be explained by the succession of three different generations of serpentine, with one of them enriched in nickel by fluid circulation.

Keywords. Weda Bay, nickel, lateritic ore, smectite, serpentine, Qemscan®, XRD

1 Introduction

Eramet Research has conducted numerous hydrometallurgical pilot campaigns to develop the treatment of nickel and cobalt found in lateritic ores from Weda Bay (Indonesia) and to test the efficiency of the Ni and Co recovery with different ore feed blends (Berthomieu et al. 2012). A precise knowledge of the mineralogical composition of these ores is a key factor for treatment processes.

Lateritic nickel deposits are commonly represented as superposed horizons resulting in different degrees of weathering. From the bottom to the top, they are:
- Rocky-saprolite, with mineral dissolution along cracks in the peridotitic protolith,
- Earthy-saprolite, where serpentine and other silicates are replaced by clay minerals and iron hydroxides,
- Superficial limonite, composed of iron hydroxides without any relic silicate.

The Qemscan® software is a pertinent and statistically powerful tool to perform phase and mineral characterization studies with respect to mineralogical and textural properties. The Qemscan® methodology allows mineral identification and classification by using the EDX (Energy Dispersive X-ray) spectra in combination with BSE (Back-Scattered Electron) values of minerals. The Qemscan® has been used for lateritic Ni-ores, where very fine grained (<1µm) clay minerals, texturally associated with serpentine and iron hydroxides, prevent a positive identification by means of optical microscopy (Andersen et al. 2009; Swierczek et al. 2012; Boni et al. 2013). Features below 1 µm in size are difficult to analyse by automated EDX systems. Qemscan® analysis and mineral recognition are therefore challenging. X-ray diffraction used for mineralogical quantification is an independent methodology that can be used to control and calibrate Qemscan® analyses.

In this study, five earthy-saprolite samples from different localities of the Weda Bay deposit (Kao Rahai, Sake River, Sake West, Nuspera and Uni Uni) were studied. After sieving the samples, chemical analysis were done on each fraction, leading to grouping them to chemically similar ranges. These three different granulometric fractions (<33µm, 63-500µm and 500-2000µm) were chosen and polished sections and these fractions (respectively 1, 3 and 5) were manufactured to obtain a reasonable representativeness for these samples.

2 Method

2.1 Qemscan

QEMSCAN® analysis for this project was carried out at the ERAMET Research mineralogical service, using a FEI Quanta 650F SEM (Scanning Electron Microscope) platform with two Bruker Xflash 30mm silicon drift energy dispersive X-ray detectors. The software used included iMeasure v. 5.2 for the data acquisition and iDiscover v. 5.2 for the spectral interpretation and data processing. The PM A measurement mode was used to collect X-ray data every 2.5 µm across the polished sample surfaces, with X-rays acquired at a total of 2,000 X-ray counts per spectrum.

Geometallurgy 1387
2.2 XRD

XRD (X-Ray Diffraction) patterns were recorded from randomly oriented powders and from oriented samples (prepared from suspensions of clays in deionised water) in order to identify the clay minerals. This second type of record was made with an air dried sample and a second pattern was recorded after ethylene glycol saturation of the oriented sample. A Bruker D8 Advance A25 diffractometer (Cu Kα radiation) equipped with a LynxEye detector was used. Analytical parameters are 40 kV and 40mA. The treatment of data was performed with softwares of the Diffrac.Suite package (Bruker).

2.3 Microprobe

The EPMA apparatus used in this study was a CAM ECA SX.100 electron microprobe also situated at ERAMET Research. Column conditions used were 15kV and 20mA. Standards used were apatite (Ca), chromite (Cr), nickel (Ni), hematite (Fe), albite (Na), olivine (Mg), alumina (Al) and quartz (Si). The precision was fixed to be around 0.1wt% on oxides.

3 Results

3.1 Mineral identification

XRD analyses performed on oriented sections resulted in the characterization of clay minerals. On Weda Bay samples, the complex mixture of phyllosilicates, mainly serpentine and smectites (Figure 1), as well as their chemical variations, decreased the definition of their characteristic peaks making a positive identification of phases rather difficult. Microprobe analyses on each identified Qemscan® chemical homogeneous phase were needed to choose the best XRD interpretation. Names of mineral phases thus identified help with the assignment of precise names and chemical composition in the Qemscan® database.

![Figure 1. Qemscan mapping of serpentine-smectite intergrowth in Weda Bay ore](image)

Nontronite, iron-saponite and stevensite, which are three different smectites, have been identified in Weda Bay samples. Structural formulae determined from microprobe analyses confirm the identification of these minerals (Table 1), with a very specific chemistry: no alumina was found in clay minerals; the measured chemical compositions, although rather different from the theoretical compositions, are similar to already published data (see Newman 1987, for example).

### Table 1. Microprobe analyses of smectites. All Fe is assumed to be Fe<sup>3+</sup>.

<table>
<thead>
<tr>
<th></th>
<th>nontronite</th>
<th>Fe-saponite</th>
<th>stevensite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2O</td>
<td>0.10 &lt;dl</td>
<td>0.1 &lt;dl</td>
<td>&lt;dl</td>
</tr>
<tr>
<td>MgO</td>
<td>8.11 7.07 6.60</td>
<td>10.4 10.0</td>
<td>14.2 17.4</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.70 0.68 0.64</td>
<td>0.3 0.3</td>
<td>0.2 0.3</td>
</tr>
<tr>
<td>SiO2</td>
<td>58.31 56.08 49.18</td>
<td>43.3 42.9</td>
<td>44.3 43.4</td>
</tr>
<tr>
<td>CaO</td>
<td>1.47 1.35 0.81</td>
<td>0.1 0.1</td>
<td>&lt;dl 0.1</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>23.84 22.74 21.14</td>
<td>17.0 18.2</td>
<td>11.7 9.8</td>
</tr>
<tr>
<td>NiO</td>
<td>2.01 2.23 2.11</td>
<td>1.4 1.6</td>
<td>1.4 1.7</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.06 0.22 0.09</td>
<td>0.1 0.2</td>
<td>0.1 0.1</td>
</tr>
<tr>
<td>Total</td>
<td>94.60 90.40 80.59</td>
<td>72.65 73.22</td>
<td>71.90 72.87</td>
</tr>
</tbody>
</table>

### Table 2. Modal mineralogy of the 5 earthy-saprolites: Qemscan estimations in bold, XRD in normal.

<table>
<thead>
<tr>
<th></th>
<th>nontronite</th>
<th>Fe-saponite</th>
<th>stevensite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>4.01 4.03 3.89</td>
<td>3.88 3.80</td>
<td>3.85 3.72</td>
</tr>
<tr>
<td>Al</td>
<td>0 0.06</td>
<td>0.03 0.03</td>
<td>0.02 0.03</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>0.05</td>
<td>0.09 0.17</td>
<td>0.13 0.25</td>
</tr>
<tr>
<td>Tetra</td>
<td>4.01 4.03 4.00</td>
<td>4.00 4.00</td>
<td>4.00 4.00</td>
</tr>
<tr>
<td>Al</td>
<td>0.06 0.06</td>
<td>1.40 1.33</td>
<td>1.84 2.24</td>
</tr>
<tr>
<td>Mg</td>
<td>0.84 0.76 0.78</td>
<td>1.05 1.04</td>
<td>0.63 0.38</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>1.23 1.23 1.20</td>
<td>1.0 1.11</td>
<td>0.10 0.11</td>
</tr>
<tr>
<td>Ni</td>
<td>0.11 0.13 0.13</td>
<td>0.00 0.00</td>
<td>0.00 0.00</td>
</tr>
<tr>
<td>Cr</td>
<td>0.00 0.00 0.00</td>
<td>2.24 2.18</td>
<td>2.55 2.48</td>
</tr>
<tr>
<td>Octa</td>
<td>2.24 2.18 2.12</td>
<td>2.55 2.48</td>
<td>2.57 2.74</td>
</tr>
<tr>
<td>Ca</td>
<td>0.11 0.10 0.07</td>
<td>0.01 0.01</td>
<td>0.00 0.01</td>
</tr>
<tr>
<td>Na</td>
<td>0.01 0.00 0.00</td>
<td>0.01 0.00</td>
<td>0.00 0.00</td>
</tr>
</tbody>
</table>

3.2 Mineral Quantification

XRD mineral quantification was applied using a calibration of XRD estimations by Bertrand calcimetry, C.E.C. (Cation Exchange Capacity), whole rock chemistry and mineral microprobe chemistry. This combined quantification methodology for clay minerals is described in Calvert et al. (1989). Qemscan® mineral quantifications were calculated by means of surficial proportions of each mineral and their assumed densities. Because clay minerals, serpentine and iron hydroxides are very finely mixed, around 25% of pixels represent rim analyses of two or three minerals. Estimations of end-member proportions in each pixel are therefore a key parameter to obtain a precise quantification.

A comparison between these two modal mineralogies shows the reliability of both methodologies to quantify clay minerals (Table 2). Nevertheless, for the other minerals, the reliability is not as good. For example, in the Sake West and Nuspera samples, iron hydroxides are over-estimated and serpentine under-estimated. The chemistry of goethite, containing variable amounts of alumina, and adsorbed silica, disturbs quantification of these two minerals.
4 Discussion

In the earthy-saprolites, mineral quantifications show very different and heterogeneous results. Saprolite from Kao Rahai contains predominantly serpentine (around 70 wt%), minor Fe-oxides (around 12 wt%) and smectites in small amounts (less than 10 wt%), whereas ore from Sake River contains no serpentine, Fe-oxides up to 45 wt% and smectites up to 45 wt%. Between these two extreme compositions, are the three other ore localities:
- Sake West, is close to the composition of Kao Rahai, with less serpentine (30-50 wt%), more Fe-oxides (30-45 wt%) and smectite (9 wt%). This sample has the highest content of quartz (6 wt%).
- Nuspera is close to the composition of Sake River with 15-20 wt% serpentine and 28 wt% smectite,
- and Uni Uni contains more serpentine (32 wt%), more smectite (24-29 wt%), and less Fe-oxides than Nuspera.

The supergene alteration profile of saprolite starts with an almost pure serpentinite that constitutes the proto-rock (Butt and Cluzel, 2013), as seen in the Kao Rahai earthy saprolite. Serpentinite alters progressively, with the typical development of large serpentine crystals. In the upper part of the profile, the breakdown of serpentine leads to the appearance of Fe-oxides. This transition coincides with the formation of smectites, a phyllosilicate with a structure close to that of serpentine, but containing more Si and Fe. This mineral appears in poorly drained profiles (Butt and Cluzel, 2013), were Mg is the only element that undergoes leaching by externally derived fluids. Subsequently, smectite is also dissolved, and the rock becomes desilicified resulting in the formation of limonite.

Serpentine also has variable chemistries. Qemscan® mapping of sample blocks (Figure 2) shows the succession of three generations of serpentine:
- the first one is Mg-rich and Ni-poor, growing directly at the expense of pre-existing Mg-silicates, forsterite and enstatite,
- the second one is Mg-rich and Ni-rich, and appears with the dissolution of Ni-bearing silicates in the upper part of the profile, and pervasive fluid interaction,
- the last one is Mg-poor and Ni-poor. It represents the last phase of serpentine crystallisation and is located in fissures with quartz and opal.

5 Conclusions

Clay mineral quantification can be performed by means of Qemscan® and an XRD based methodology. Their combined use increases the confidence in the results. Amounts of each of the major phases (serpentines, iron hydroxides and smectites) are strongly variable, depending on geological parameters and alteration processes.

For the purpose of an improvement in Ni recovery, it is not sufficient to consider only the total amount of serpentine and smectite (main Ni-bearing phases), but also to identify and quantify the different species of each phase, as they may contain different but mineral specific Ni contents.

Acknowledgements

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Boni M et al. (2013) Quantitative mineralogical characterization of karst bauxite deposits in the southern Apennines, Italy, Econ Geol 108:813-833
The Value of Ore Body Knowledge for Mining Operations

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Abstract. The world's demand for metals is ever increasing and ore deposits available for processing and extraction are becoming, lower grade and more complex, often containing deleterious elements that require tailored treatment so that a multifaceted and sustainable approach is needed. Appropriate ore body knowledge, through geometallurgical assessment, including process mineralogy, is increasingly providing the critical information that stands between failure or collapse and survival or success of some mining operations. Operational teams include geologists, mineralogists, samplers, mineral processors and often others, working together. The degree of cross-training, communication and trust dictates the potential capacity of the team and where an appropriate work dynamic is fostered, in which relationships flourish as much as does the ethic of technical excellence, it is possible to develop technical capabilities that surpass those of conventional teams. The valuable role of tools, including those of 'process mineralogy' being used to provide the platform for innovative technology development and economic benefits is presented.

Keywords. Ore body knowledge, process mineralogy

Introduction

Minerals and metals are essential for modern life and their reliable and responsible supply is critical to maintain and develop a sustainable world. However, the global mining industry currently faces multiple, multifaceted internal and external challenges. These include: technical challenges such as declining ore grades, more complex and remote ores; financial and economic challenges with cost blow outs and delays in the development of new projects and rising operating costs with lower productivity; and social and environmental challenges which include, heightened competition for water, energy and land, growing scrutiny of the industry’s social and environmental performance and an increasingly complex policy and regulatory environment (Hajkowicz et al. 2012; World Economic Forum Scoping Paper 2014; Mining Company of the Future 2014).

The success of the mining and extraction process from rock breakage, feed preparation and classification to separation into streams of various mineral concentrations for sale or disposal implies knowledge of the minerals themselves. The key attributes to be considered include: the element deportment in the minerals in the ore, the bulk modal mineralogy, the mineral grain size, texture and association. For design purposes, this knowledge defines the entitlement and potential recovery of an ore and impacts the choice of the metallurgical flowsheet.

As lower grade deposits are mined, one of the limits to potential exploitation is provided by the mineralogical complexity. Figure 1 illustrates the mineralogical barrier between current operations on the right and the increased number of potential lower ore grade mining operations on the left. The bimodal distribution is representative only. For any deposit to be economically viable, the project revenue from payable metal extracted has to exceed the associated costs of mining and processing. The limits of current technology on successful beneficiation of the ore types impose the barrier. Thus the adoption and implementation of new technologies is the key to accessing the lower grade deposits in the future.

A mineralogical barrier identified was dramatically overcome over 100 years ago when the flotation process was developed at the Broken Hill Lead-Silver-Zinc mines in Australia in the early 1900s (Woodward 1952; Clark et al. 2005; Lynch et al. 2007). The mines had started in the mid-1800s directly smelting oxide ores to produce lead silver bullion. As the oxide ores were depleted and sulphide ores became available, gravity separation of the dense lead-silver component was adopted in the 1890s although in this process considerable revenue was lost as the silver and lead were recovered but the zinc was lost to the tailings. Facing financial ruin and after the failure of the use of magnetic separation in 1901, the potential of an ‘academic curiosity’ was considered and after significant effort, the world’s first industrial flotation process was developed. Initially a bulk concentrate was obtained and later with the incorporation of chemistry (copper sulphate addition) by Bradford, (1913) selective lead and zinc concentrates were produced. As the flotation process was adopted more ore types of lower grades could be processed.

Figure 2 shows the effect on the lowering of the average world copper grades that could be treated with the invention and widespread incorporation of the flotation process. The correlated increase in copper

Figure 1. A conceptual illustration of the mineralogical barrier potential to processing lower grade ore bodies facing the mining industry (adapted from Mudd 2013 in Bradshaw, 2014).
production is exponential. Figure 2 also shows that biological leaching is used as copper grades being processed approach 0.5%. What this figure doesn’t show is the increased complexity introduced by ores of similar grades containing different copper minerals and gangue matrices. This will result in changes in ore hardness and thus mill throughput as well as and recovery potential from flotation.

**Case Study: Nickel Flotation**

An excellent example of the effects of ore variability on the beneficiation process is given by Lawson et al., 2014. They showed that in order to identify the potential for improved pay-metal recovery in a particular, operation it is necessary to characterise the nickel deportment and gangue mineralogy to understand the reason for the losses. In particular any Ni in silicates cannot be recovered in the sulphide flotation process and any talc present has strong negative effects on Ni sulphide flotation.

The four different ore domains indicated by the dotted lines in Figure 3 show 1) economic levels of Ni, Cu and PGMs in a pyrrhotite bearing sulphide deposit with low pyrrhotite (Po) to pentlandite (Pn) ratios. 2) economic levels of Ni, Cu and PGMs in a pyrrhotite bearing sulphide deposit with moderate to high pyrrhotite (Po) to pentlandite (Pn) ratios. 3) uneconomic high pyrrhotite - low tenor deposits and 4) low grade low sulphide, high MgO and PGM deposits which can sometimes be economically mined and processed.

They showed that the processing improvement opportunities were dependent on the geological occurrence of the deposit as well as the gangue and valuable phases present and required to be exploited into either combined or individual concentrates.

In the design and commissioning of the Montcalm concentrator (Type 2 ore in Figure 3) mineralogical characterisation identified three ore types that required different and process treatment (Charland et al. 2006; Lotter 2011). By identifying the appropriate operating conditions it was possible to exceed a ‘Type 1’ start up (using McNulty’s classification from McNulty (1998), where Type 4 is the least desired) as shown in Figure 4.

**Figure 2:** Copper production increase and copper grade decrease showing the significant decrease in grades that could be treated when flotation was developed (from US Geological Survey 1900-83, Brook Hunt 1984 onwards)

**Figure 3.** Ni as Ni sulphide vs Ni head grade showing four types of deposits with differing processing potential (adapted from Lawson et al. 2014)

The four different ore domains indicated by the dotted lines in Figure 3 show 1) economic levels of Ni, Cu and PGMs in a pyrrhotite bearing sulphide deposit with low pyrrhotite (Po) to pentlandite (Pn) ratios. 2) economic levels of Ni, Cu and PGMs in a pyrrhotite bearing sulphide deposit with moderate to high pyrrhotite (Po) to pentlandite (Pn) ratios. 3) uneconomic high pyrrhotite - low tenor deposits and 4) low grade low sulphide, high MgO and PGM deposits which can sometimes be economically mined and processed.

**Figure 4.** Montcalm startup curve compared to compiled types by Mackey and Nesset (2003) (from Lotter 2011 in Bradshaw 2014).

Figure 5 shows the value of investing in appropriate ore body knowledge and that the initial investment and higher costs are recovered at the time of commissioning and in the longer term greater long term benefits are obtained. Process mineralogy, as part of a geometalurgical assessment, although associated with some capital investment, is a valuable risk reduction tool for any mining company, not only in terms of finances but also in terms of human and intellectual capital (Bradshaw 2014). When the economic losses caused by
poor ore characterization, insufficient hardness profiling, excessive reagent consumption, underperforming flowsheets and related costly post start-up 'de-bottlenecking' (or a combination thereof) are considered, the expenditure is a small price to pay (Baum 2014).

Figure 5. The nett project cash flows for mine start ups with and without process mineralogy (adapted from Lotter and Arrué 2006)

Acknowledgements

This paper is distilled from discussions and insights gained from colleagues and especially students from universities and research institutions around the world, as well as from various mining companies, equipment and reagent suppliers and the author would like to thank them all for their support, partnerships and collaboration through the years.

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A New Approach to Drill Core Scanning by Combination of Mechanical and Optical Tests: Preliminary Results

Xavier Decamp, Godefroid Dislaire, Pierre Barnabé, Eric Pirard
University of Liège, Applied sciences, GeMMe. Belgium
Christophe Germay
EPSLOG S.A. Belgium

Abstract.
Mineralogy, geological textures, porosity, rock resistance, grain size distribution, etc. are all becoming essential data contributing to geometallurgical modelling of ore deposits. Nevertheless, most of these rock properties are measured on punctual core plugs while, nowadays, thousands kilometres of cores are drilled every year. It is therefore necessary to develop new tools to better take advantage of this gold mine of information. With this in mind, this research investigates the potential of combining mechanical and optical tests during drill core scanning in order to provide several continuous data along the core. The mechanical test used for this study is a scratch-test that measures absolute rock resistance values with a centimetre resolution. This provides a continuous rock strength profile that could be linked to hardness of rock, which would be useful for developing comminution indice. Thereafter, these values can also be related to petrophysical properties such as porosity or permeability. Another advantage of this technique is that it provides a fresh surface consisting of a 1cm width groove.

The optical tests consist of laser surfometry and hyperspectral imaging in shortwave infrared range (wavelengths from 1000 to 2500nm) on the groove resulting from the scratch-test. The laser surfometry (obtained by triangulation) brings granulometry information and a digital elevation model (DEM). Finally, the principal contribution of hyperspectral acquisitions is the possibility to create mineralogical maps.

Keywords. Geometallurgy, Core scanning, Mining exploration, Scratch-test, Hyperspectral, SWIR, Laser triangulation.

1 Introduction
As it has always been necessary to know exactly what ore deposits are composed of, several tests and techniques have been developed to better understand mineral resources and increase their recovery.

In the same way, the goal of this research is to enable the creation of new indices of metal recovery and the prediction of the variability in rock response to comminution by investigating combination of continuous mechanical and optical tests on drill cores.

The mechanical test consists of a scratch test and the optical tests are laser surfometry and hyperspectral imaging. This provides a continuous rock strength profile that could be linked to hardness of rock, which would be useful for developing comminution indice (good correlation with UCS and Equotip tests already exists – Fig. 4 and 5).

2 Methods
2.1 Scratch Test
The principle of the scratch test is to control and monitor the continuous shearing action induced by the motion of a diamond (PDC) cutting tool on the surface of a rock core sample (Fig. 1). The continuous high resolution profile of rock strength (UCS) along the core sample is derived from the force acting on the cutter.

Figure 1. The last generation of the core scratcher. A PDC cutter is shearing the surface of cores that are firmly tightened on the bed of the machine.

Experimental results have consistently confirmed a universal relationship between the volume of rock sheared away and the energy provided to the cutter (Fig. 2 and 3) (Germay 2009). The coefficient of proportionality is a direct measure of the mechanical strength of the rock.

The failure process mobilised ahead of the cutter is similar to the shear process mobilised along the plane of failure developed during Uniaxial Compressive Test. The rock strength derived from the scratch test is therefore strongly correlated with the UCS (Fig. 4). This result combined with the intrinsic continuous nature of the test yields one of the most interesting outcomes of the scratch test: the ability to rapidly produce robust high resolution (1cm) profiles of rock strength along core samples.
A New Approach to Drill Core Scanning by Combination of Mechanical and Optical Tests: Preliminary Results

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1 Introduction

As it has always been necessary to know exactly what ore deposits are composed of, several tests and techniques have been developed to better understand mineral resources and increase their recovery.

In the same way, the goal of this research is to enable the creation of new indices of metal recovery and the prediction of the variability in rock response to comminution by investigating combination of continuous mechanical and optical tests on drill cores. The mechanical test consists of a scratch test and the optical tests are laser surfometry and hyperspectral imaging. This provides a continuous rock strength profile that could be linked to hardness of rock, which would be useful for developing comminution indice (good correlation with UCS and Equotip tests already exists – Fig. 4 and 5).

2 Methods

2.1 Scratch Test

The principle of the scratch test is to control and monitor the continuous shearing action induced by the motion of a diamond (PDC) cutting tool on the surface of a rock core sample (Fig.1). The continuous high resolution profile of rock strength (UCS) along the core sample is derived from the force acting on the cutter.

Figure 1. The last generation of the core scratcher. A PDC cutter is shearing the surface of cores that are firmly tightened on the bed of the machine.

Experimental results have consistently confirmed a universal relationship between the volume of rock sheared away and the energy provided to the cutter (Fig. 2 and 3) (Germay 2009). The coefficient of proportionality is a direct measure of the mechanical strength of the rock.

Figure 2. Forces acting on a sharp cutter.

Figure 3. Energy applied to the cutter versus the volume of rock destroyed for different rock types.

The failure process mobilised ahead of the cutter is similar to the shear process mobilised along the plane of failure developed during Uniaxial Compressive Test. The rock strength derived from the scratch test is therefore strongly correlated with the UCS (Fig. 4). This result combined with the intrinsic continuous nature of the test yields one of the most interesting outcomes of the scratch test: the ability to rapidly produce robust high resolution (1cm) profiles of rock strength along core samples.
Correlation between the intrinsic specific energy $\varepsilon$ and the uniaxial compressive strength (92 sandstones, 86 limestones, 19 shales, 4 chalk).

Figure 4.

Correlation between specific energy from scratch test and hardness response of rock from Equotip test.

Figure 5.

2.2 Laser surfometry

The laser surfometry is based on triangulation which means the measurement of distance by calculating the angle. The principle is quite simple: an emitter projects a laser spot onto the sample. The light is then reflected onto a CCD sensor at a certain angle depending on the distance with the sample. The distance to the sample can therefore be calculated on the basis of the position of the light spot in the sensor.

The system used for this study is composed of a laser (emitter) and a CCD sensor (receiver) arranged with a 20° angle from one to another.

2.3 Hyperspectral imaging

The main characteristic of the hyperspectral imaging technique is the impressive number of bands used to build the reflectance spectrum. Although it is impossible to directly observe sulphides in VNIR and SWIR, this technique allows identifying other minerals as muscovite, biotite, chlorite, calcite, etc. and, in some case, correlate it to specific lithology containing the sought-after metals (Linton et al. 2011). For the purpose of our study, a SPECIM camera and a spectrograph with 256 bands active in shortwave infrared range (wavelengths from 1000 to 2500nm) were chosen to identify and quantify most of the carbonates, oxides and hydrated silicates. At the same time, a macro lens was added in front of the camera to reach a high spatial resolution with a pixel size of 30x30µm, thereby enabling a mineral mapping of the groove resulting from the scratch test.

3 Preliminary results

3.1 Scratch test

Preliminary tests on mining drill core samples present good results and visually show a strong link between rock strength and mineralogy (Fig. 5 and Fig. 6).

Figure 6. Rock strength profile along the core. There is a strong correlation between limestone (on the left, in green-yellow tints) and sulphides (in blue).

Figure 7. RGB pictures matched with the rock strength profile.

3.2 Laser surfometry

The laser acquisition occurs directly after the scratch test and allows building surfometry maps of the core (Fig. 7).

Figure 8. Rock strength profile along the core. There is a strong transition between limestone (on the left, in green-yellow tints) and sulphides (in blue).

Then automatic proceedings individualise the groove and calculate a grain size distribution (Fig. 9 and 10). Indeed, as the pixel size is 20x20µm it is necessary to have a minimum grain size of 80-100µm to be able to identify them. The main tools used to do it are Black Top Hat and Watershed segmentation (Beucher and Meyer 1992, Thurlery and Ng 2008).

Surfometry data will also be useful to look further into the interpretation of the interaction cutter/rock during the scratch test. Finally, during spectroscopy proceeding,
these data may also help as groove DEM (Digital Elevation Model) given that it is assumed that roughness or slopes influence reflectance values.

Future research will focus on the characterisation of absorption features in terms of position, depth, (a) symmetry or width in order to analyse degree of crystallinity, grain size and finally produce better mineral discriminations (example in Fig. 11) (van der Meer 2006; Zaini et al. 2012).

4 Conclusion and perspectives

The combination of mechanical and optical tests on drill core scanning (Fig. 12) could improve modelling of ore deposits and enable computing new kinds of geometallurgical models.

On the one hand, the scratch test brings continuous rock strength profile which could be linked to rock breakability during crushing/grinding.

On the other hand, laser surfometry allows measuring grain size distribution and computing DEM for next image processing while hyperspectral imaging identifies and quantifies mineralogy (not sulfides) as well as mineral crystallinity.

Combining laser surfometry and hyperspectral data enables to identify geological textures such as fractures or lineaments with specific orientations and compositions. Moreover, it could also permit to predict the size of metal liberation to be reached after the comminution process.

Finally, crossing data from mechanical and optical tests will allow the creation of new metal recovery indices that can be used in ore deposit modeling thanks to continuous information along drill cores.

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Geometallurgy 1397
From Plant to Mine: a Reverse Approach to Help Resource Estimation and Geometallurgical Modelling
Quentin Dehaine, Lev Filippov
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Abstract. This paper presents a reverse approach using characterisation results on samples from the output of a kaolin processing plant to study the by-product potential of LREE (La, Ce, Nd), Nb and Sn. Statistical analysis on chemical assays allow building of regression models to predict Nb and LREE content as a function of major elements (TiO$_2$, SiO$_2$). These predictive models have been verified for all the material streams in the plant and thus for the ore itself. The purpose of this study is first complete a database of core sample analyses using regression models calibrated by ICP analyses on core samples. And then to use data to determine mineral quantification using chemical compositions obtained by microprobe analyses on process samples. The results will be used to estimate the kaolin grade of core samples and help in geometallurgical modelling of the deposits to assess the by-product potential of the metals of interest.

Keywords. Rare earth, rare metals, binary correlation, mineral quantification

1 Introduction
This study focuses on a china clay deposit of SW England which lay on the St Austell biotite granite which represents 70% of the outcrop (Manning et al. 1996). As a consequence of the kaolinisation process, the accessory minerals of the host granite have been partially liberated in the clay matrix which enables their pre-concentration in the hydrocyclone underflow of the kaolin plant. This leads to a pre-concentration of rare-metals (Sn, Nb, W) and light rare-earth (LREE) in a micaceous residue which is considered as a potential source for these metals as a by-product of kaolin production (Dehaine and Filippov 2014).

A previous study on samples from every output of a kaolin dry mining plant, including the final product and all the wastes/residues, has shown that there is a strong binary correlation between Nb and TiO$_2$ (Dehaine and Filippov 2014):

\[ \text{Nb (ppm)} = 179.87 \times \text{TiO}_2 \% \] (1)

A similar approach using multiple linear regression gives the following formula for the LREE (La, Ce, Nd) content:

\[ \text{LREE (ppm)} = 105.87 - 1.26 \times \text{SiO}_2 \% + 111.93 \times \text{TiO}_2 \% \] (2)

These relationships are related to the mineral associations. Nb is hosted by rutile, whereas the LREE are hosted by monazite which is commonly associated with or included in rutile as shown by mineralogical study by Dehaine and Filippov (2014). These formulas are linear and verified for every output of the plant. Thus, they can be extrapolated for the feed of the plant, i.e. the ore itself.

Core sample analyses for industrial mineral deposits are usually limited to major elements by XRF. This is the case for the majority of the core samples of the studied deposits but some of the core samples were analysed for trace elements during an XRF trace analysis campaign. The methodology used in this study is presented in Figure 1. It follows the two main objectives which are:

1. To populate a core sample database using estimates determined from regression models similar to (1) and (2), calibrated by ICP analyses on core samples,
2. To determine mineral quantification which can be used as a tool for geometallurgical modelling of the deposit to help in assessing the by-product potential of the metals.
From Plant to Mine: a Reverse Approach to Help Resource Estimation and Geometallurgical Modelling

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![Figure 1. Outline of the methodology used in this study.](image-url)
2 Estimation of trace elements in core samples using major elements

2.1 Testing prediction models on existing trace element data

Figure 2 shows the binary correlation between Nb analysed by XRF analysis and Nb estimated using formula (1). This result is encouraging as it shows a correlation with a $R^2=0.7$ between the Nb analysed and estimated on core samples.

XRF analysis is a fast and relatively cheap analysis technique which is often used for major element analysis. However XRF analysis even when calibrated appropriately is not very accurate for trace element analysis and suffers large analytical errors. This is even more pronounced for LREE because of overlapping between peaks especially for Ce and La with the K$_{a1}$ ray peak of Ti.

Thus it is necessary to use a more reliable analysis technique to calibrate our prediction models.

![Figure 2. Log-Log Binary plot between Nb analysed by trace XRF analysis an Nb predicted by prediction formulas.](image)

2.2 Sub-sampling of core samples to calibrate prediction models

From the formulae (1) and (2) it is clear that TiO$_2$ can be used as a “tracer” for Nb and LREE. TiO$_2$ is also well quantified by XRF analysis. Thus it has been decided to select 30 samples among all the available core samples based on their TiO$_2$ content. The logarithmic transformation of TiO$_2$ values has a normal distribution and 30 sub-samples were selected at random. To do so the cumulative distribution of Log(TiO$_2$) is calculated in order to take 30 uniformly distributed samples (Figure 3).

Results from the ICP analyses for the 30 selected samples were used in the formulae (1) and (2) and the estimates produced used to correct/complete LREE and Nb contents in the database.

![Figure 3. Cumulative distribution of Log(TiO$_2$) for the 700 ProTrace core samples and example of a random selection of 30 sub-samples uniformly distributed in the [0;1] interval.](image)

3 Mineral quantification

However knowing the grade of metals within the deposits is not enough to estimate their by-product potential. What is required is to know if the zones of interest for metal recovery are also interesting for kaolin recovery. This can be done using mineral quantification which will give an estimate of the mineral composition including the estimated kaolin (i.e. kaolinite) grade or iron-oxide minerals grade which have an influence on final product brightness.

3.1 Principle

The principle of mineral quantification using bulk sample chemical analysis was first introduced by Isnard and de La Roche (1968) for a 2-mica granite, and was later formalised by (Mallet 1979). Since then many studies have tried to apply this theory to the case of clay minerals (e.g. Johnson et al. 1985; Yvon et al. 1990). The methodology consists of modelling a sample as a mineral mixture, each mineral having its own chemical composition. This can be expressed as:

$$T = SX$$

where T is the bulk analysis vector containing the elemental weight fractions of the sample obtained by chemical analysis (XRF, ICP, etc.), S is the stoichiometric matrix containing the elemental weight fractions in the minerals, obtained by microprobe analysis (or a reference database) and X is the mineral composition vector, unknown, containing the weight fractions of each mineral in the sample.

Many studies have proposed techniques to resolve equation (3) and develop automatic resolution procedures (Zangalis 1991; Paktunc 1998; Posch and Kurz 2007; Whiten 2007) but only a few studies have shown the potential of this tool for geomeetallurgical
modelling (Lund et al. 2013).

In this study we use the resolution method proposed by (Johnson et al. 1985), consisting in reducing, by the mean square methods, the residue \( r \) defined as follows:

\[
r = \sqrt{(SE)_T}
\]

where \( E \) is an estimate of \( X \), obtained by XRD analysis or microscope observations. In our case these estimates are initially set as a uniform distribution with the same weight for each mineral. The purpose is then to minimise the residual using simultaneous linear equations to derive a new estimate for \( E \). This is realised using an iterative process detailed in Johnson et al. (1985) which is performed on both \( E \) and \( S \) by successive iterative processes:

a. A new estimate of \( E \) is calculated by the gradient method,
b. A new residual is calculated, if it is lower than the previous one and the convergence criterion is not reached, the iteration is repeated,
c. When the convergence criterion is reached a similar iteration process is applied to the element with the highest individual residual \( r_i \) in order to derive a new estimate of \( S \) with respects to its mineralogical constraints,
d. The steps a and b are repeated with the new \( S \) matrix, then step c and so on until the global convergence criterion is reached.

3.2 Application to core samples

Table 1 gives the mean chemical composition of the main minerals of the St Austell biotite granite, obtained by microprobe analysis. It corresponds to the \( S \) matrix defined in equation (3). The minimum and maximum values are also recorded to constrain the modification of the matrix \( S \) during the iterative process. In addition to kaolinite (Kln), the main gangue minerals are quartz (Qtz), K-feldspar (Kfs) mainly orthoclase and microcline, biotite (Bt), which display a composition varying from siderophyllite to anite, and muscovite (Ms). The main accessory minerals are rutile (Rt) and tourmaline (Tur) which varies from schocl to dravite.

This iterative process will be applied to the corrected core samples data to estimate their mineralogical composition. If successful this reverse approach will show how it is possible to use mineralogical characterisation results on process samples to build tools for resources estimation and geometallurgical modelling.

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The ongoing downturn within the mining industry has resulted in the issues facing the industry becoming more visible. Some of the current challenges the industry faces centre around the decreasing grade and increased depth of discoveries, mineralogical variability, and increased costs. To combat these challenges, it is proposed that during exploration a greater emphasis needs to be applied to the understanding of the metallurgical response downstream.

Current techniques provide routine analysis of samples collected during the recovery circuit, but their application, the current techniques provide routine application, the current techniques provide routine application. Taking this a step forward, data integration and understanding of the metallurgical response downstream. Successful geometallurgical studies therefore result in the issues facing the industry becoming more visible. Some of the current challenges the industry faces centre around the decreasing grade and increased depth of discoveries, mineralogical variability, and increased costs. To combat these challenges, it is proposed that during exploration a greater emphasis needs to be applied to the understanding of the metallurgical response downstream.

Recent development, and the release of the latest analytical techniques; one such technique is in automated quantitative mineralogy. Acquisition of this type of mineralogical data using ZEISS Mineralogic Mining automated mineralogy with LA-ICP-MS analysis to help calibrate vector mineral solution which, from an exploration stage, can be successfully employed in target generation. Where this is employed as a workflow solution is also being rapidly developed. One example of this is the correlation from multiple systems as workflow solutions is also being considered. The utilization of AM is considered one of the tools available to collect mineralogical and textural data automatically generated from samples collected from the ore body, the additional volume, variety and quality of the data can greatly reduce downstream costs. Exploration and pre-feasibility studies, this front end cost may be deemed costly during early stage exploration and pre-feasibility studies. This allows valid comparisons of data, and reproducible and robust data is generated from every degree of experience, ensuring that repeatable, such automated systems by removing the subjectivity of the results. Various opportunities outline the methods require technological development on possible. Successfully developing and applying these methods must be utilized to acquire the relevant data to make this type of analysis can also give an early indication of the likely metallurgical response during geometallurgical modelling. At each stage, a clearer understanding of the deposit, its mineralogy aids decision making, reducing risk and understanding of the metallurgical response downstream. In order for this to become successful, thorough and complete mineralogical studies may be deemed costly during early stage exploration and pre-feasibility studies. This paper aims to describe the innovations in AM techniques through developing the quality of the ZEISS and Mineralogic Mining) has built on existing processes.

During the pre-feasibility stage of a mine development technological innovation and also limited application of mineralogical studies, there has been limited analysis of samples collected during the recovery circuit. Despite their success, they provide (e.g. Gu et al. 2014). The volume, variety and quality of the data which, from an exploration stage, can be successfully employed within mining industry for over 20 years. Numerous Energy Dispersive Spectrometers (EDS) have been successfully employed within mining industry for over 20 years. The majority of the issues focus on the deposit, its mineralogical complexity and/or variability, and the ability to use AM on a SEM-EDS ruggedized (and mobile) platform. These innovations now mean that AM techniques through developing the quality of the ZEISS and Mineralogic Mining) has built on existing processes. During the pre-feasibility stage of a mine development technological innovation and also limited application of mineralogical studies, there has been limited analysis of samples collected during the recovery circuit. Despite their success, they provide (e.g. Gu et al. 2014).
Advances in Mineral Characterisation Techniques: Emerging Tools and Workflows

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Abstract. Some of the current challenges the industry faces centre around the decreasing grade and increased depth of discoveries, mineralogical variability, and production and exploration costs. To combat these challenges, it is proposed that during exploration a greater emphasis needs to be applied to the geometallurgical model. In order to successfully create and understand this model, more advanced techniques must be utilized to acquire the relevant data to make this possible. Successfully developing and applying these methods requires technological development on analytical techniques; one such technique is in automated quantitative mineralogy. Acquisition of this type of mineralogical data using ZEISS Mineralogic Mining during mineral exploration can help provide the volume and variety of data required in such an application. Taking this a step forward, data integration from multiple systems as workflow solutions is also being rapidly developed. One example of this is the correlation of Mineralogic Mining automated mineralogy with LA-ICP-MS analysis to help calibrate vector mineral exploration. The volume, variety and quality of the data provided by ZEISS Mineralogic Mining thus provides a solution which, from an exploration stage, can be successfully employed in target generation. Where samples are collected from the ore body, the additional mineralogical and textural data automatically generated from this type of analysis can also give an early indication of the likely metallurgical response during geometallurgical modelling. At each stage, a clearer understanding of the mineralogy aids decision making, reducing risk and down-stream costs.

1 Introduction

Automated Mineralogy (AM) techniques based on a Scanning Electron Microscope (SEM) platform with numerous Energy Dispersive Spectrometers (EDS) have been successfully employed within mining industry for over 20 years.

The most widely used and valuable application is when they are applied to process mineralogy. In this application, the current techniques provide routine analysis of samples collected during the recovery circuit to monitor physical, mineralogical and chemical variation. Recent studies have begun to quantify the value of these solutions in terms of the value of the data they provide (e.g. Gu et al. 2014). Despite their success, and the paradigm shifting impact they have on mineralogical studies, there has been limited technological innovation and also limited application during the pre-feasibility stage of a mine development cycle.

Recent development, and the release of the latest generation of automated mineralogy solutions (namely ZEISS and Mineralogic Mining) has built on existing AM techniques through developing the quality of the mineralogical data collected, usability and flexibility (Graham et al 2015a). Additional developments also include the ability to correlate with other techniques and the ability to use AM on a SEM-EDS ruggedized (and mobile) platform. These innovations now mean analytical quality SEM-EDS data can now be provided in the field (i.e. exploration camps and mine sites).

This paper aims to describe the innovations in AM and outline how these advances can benefit mineralogical characterisation during early stages of the mining value chain.

2 Industrial Trends, Related Issues and Opportunities

The ongoing downturn within the mining industry has resulted in the issues facing the industry becoming widely publicised and discussed, such as; decrease in ore grade, decrease in minimum grind size, more variable ore, more unfavourable ore containing deleterious elements and phases, increase in depth, cost of discovery and increase in the cost of operation (i.e. energy costs).

The majority of the issues focus on the deposit, its mineralogical complexity and/or variability, and understanding of the metallurgical response downstream. To counter these issues, there is a potential paradigm shift occurring towards a greater appreciation and application of geometallurgical modelling during early stage exploration and pre-feasibility studies.

In order for this to become successful, thorough and quantitative characterisation is required. The utilization of AM is considered one of the tools available to collect this data. Successful geometallurgical studies therefore would provide valuable mineralogical information earlier in the process to make informed decisions and add value downstream. Conversely, the studies can also help deter developing unfavourable projects. Whilst such studies may be deemed costly during early stage exploration and pre-feasibility studies, this front end cost can greatly reduce downstream costs.

There is also a big advantage to be gained in using such automated systems by removing the subjectivity of mineral identification by individuals with varying degrees of experience, ensuring that repeatable, reproducible and robust data is generated from every sample. This allows valid comparisons of data, and therefore increasing confidence in decision making based on more and better data.

Furthermore, additional opportunities outline the potential to reduce exploration costs and improve discovery success when exploring undercover. One example is through using trace element contents of epidote and chlorite to act as vector minerals to direct exploration of undercover porphyry deposits (Cooke et al. 2014).
3 Mineralogic mining: An introduction and automated mineralogy innovations

ZEISS, with the development of Mineralogic Mining, builds on existing AM technologies (Graham et al. 2015a). Quicker and more accurate mineral identifications and better textural quantification have been made possible by developing the acquisition of high resolution Backscattered Electron (BSE) images, advanced image processing and fully quantitative EDS mineral classification system. The system works on a modularised/recipe based protocol whereby aspects of the analysis are saved (i.e. SEM analytical operating conditions, mineral classifications etc.) and can be recalled, edited, reassigned to other analyses which reduces the need for highly experienced instrument operators.

The key innovations in AM are fully quantitative EDS analysis capability; the ability to correlate across platforms; and the capability to use the solution on a ruggedized and mobile system. These are described below;

- **Fully Quantitative EDS Mineral Classifications** - Mineral classification is done by using a fully quantitative EDS. The EDS spectrum is gathered, quantified and the weight % proportions of the elements detected is provided on a per EDS pixel basis. As such, each EDS pixel (or analysis point) is classified using a mineral classification recipe which is based on the minerals stoichiometry. Typically millions of data points are measured to build up a highly accurate picture of the mineralogy and texture of a sample. A suitable example is sperrylite (PtAs2) that has a stoichiometric composition of 57% Pt and 43% As. The sperrylite mineral composition within Mineralogic would thus contain a minimum and maximum range of Pt and As for that sperrylite classification. There is also the flexibility to adjust the number of counts per analysis and the beam acceleration voltage (3,000 is recommended; Graham et al. 2015b). The quantified nature of the spectrum with higher counts provides further advantages in terms of mineral discrimination and improvements in the measured assay and deportment data.

- **Correlation of AM with other Techniques** - With the mineral maps from AM it is now possible to correlate these with other imaging tools and analytical techniques. Analytical techniques all provide certain pieces of the puzzle, and integrating data from multiple sources can be used to provide the most comprehensive sample characterisation in the most optimal manner. Examples include the ability to take, using a Light Microscope (LM), an automated large area image, then correlate this with the sample once it is placed in the SEM. The LM image can then be used to identify key areas of interest and then as a navigation tool to move around the sample in the SEM (Graham et al. 2015a). AM can also be carried out on areas of interest to produce a fully correlated workflow from LM, to SEM and then AM.

- **It is also possible to correlate between SEM, AM and X-ray microscopy (XRM).** Numerous studies have used XRMs in economic geology for ore characterisation (Holwell et al. 2012; Godel 2013) and also process mineralogy for 3D liberation analysis and heap leach studies (e.g. Miller et al. 2009; Dhawan et al. 2012). Developments using ZEISS XRM (Versa and Ultra) for oil and gas applications outline this capability to generate 3D information and correlate this with 2D mineralogical data.

As highlighted previously, the development and application of LA-ICP-MS analysis of trace element contents within vector minerals can be used to target deposits (Cooke et al. 2014). Work carried out by Harman et al. (2015) has begun to develop a workflow and a correlation whereby AM is used to locate suitable minerals (epidote and chlorite) using an AM analysis. These minerals are then identified where a high quality EDS spot is carried out and provides the mineral locations and the co-ordinates of the high quality EDS analysis. Taking the samples from the SEM to the LA-ICP-MS, it will be possible in the future to import the mineral locations and coordinates and correlate to ensure the laser analysis is taken from the exact location the EDS spot was taken from.

- **A Ruggedized SEM for On-Site Automated Mineralogy** - ZEISS, has developed a ruggedized and mobile SEM that comes on wheels in a fitted travel case for use outside traditional laboratory environments. This platform has been extensively used by the military in various applications, being deployed rapidly around the world and used in a range of harsh environments. It has also been used as a well sites for automated mineral analysis to provide valuable information to make assessments on 2D porosity and bulk mineralogy of drill chips during oil and gas exploration (Pfau and Oliver 2011). More recently, this ruggedized SEM platform has been converted for use with Mineralogic, and is therefore available for use on mine sites and within exploration camps.

4 Discussion

The challengers facing the industry in terms of declining ore quality and increased depth of discovery outline the need for innovation and change. The application of thorough geometallurgical studies is viewed as a way to combat these challengers. However, this potential paradigm shift would require an adoption of more advanced mineral characterisation techniques. The outlined innovations by ZEISS with Mineralogic Mining demonstrate how AM is able to provide the necessary quantitative mineralogical data.

The technological and methodical developments of Mineralogic represents the introduction of the 2nd generation of AM. The inbuilt flexibility and ease of use in creating mineral classifications and creating automated analyses mean a full time experienced mineralogist is not required to operate the solution. In addition, with no post-processing of data required, the time to results from preparing the sample to receiving the data is dramatically reduced. Therefore, a variety of valuable information is provided to the user quickly and efficiently.

The combination of the flexibility and ease of use with the ability to place this analytical capability on a ruggedized platform offers an exciting new application area for AM solutions. This means the analytical
capability can now be present on mine sites and in exploration camps delivering valuable mineralogical data. A whole swathe of data is now available to geologists on the ground to use and interpret to help direct exploration efforts and understand the deposit. As exploration continues to be carried out in search for undercover deposits, drill core will become a more valuable window offering limited insights into the deposits where as much information as possible must be gathered. The oil and gas industry with the ruggedized platform already apply this level of AM analysis during exploration through analysis of rock chips from drilling (Pfau and Oliver 2011).

The correlative aspect of the AM solution now means analytical workflows are much simpler with data that can be overlapped and compared. Examples include the acquisition of 3D data using an XRM with a 2D mineralogical data set and the ability to correlate large area LM images with the analytical capability on the SEM. Another exciting workflow is the continued development of AM to be used with LA-ICP-MS for the analysis of vector minerals (Harman et al. 2014).

5 Conclusion

AM has had a long and successful history of collecting quantitative mineralogical data. However, until recently the technique lacked the suitable platform, ease of use and flexibility to be widely employed during the early stages of the mining value chain. ZEISS, with Mineralogic, has developed the latest generation of AM technology that makes the utilization of such techniques more appealing and feasible. The ruggedized platform brings this analytical capability to the mine site or exploration camp. Whilst the ability to correlate with other techniques offers exciting new sample characterisation workflows in both research and industry applications. As such, it is now possible to produce the volume, variety and quality of data required for mineralogical characterisation studies during early stages of the mining value chain.

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Geometallurgy
Abstract. Non-destructive micro-CT techniques were employed to illustrate in-situ the three-dimensional distribution and morphology of gold particles within a most exceptional specimen of Witwatersrand ore from the 2.87 Ga Basal Reef (lower Central Rand Group), which is depicted on the cover of Mineralium Deposita’s 50th Anniversary volume. These images confirm unambiguously the dominance of isolated rounded gold particles which define, as heavy mineral concentrates, three foresets and one bottomset of an overall cross-bedded structure on top of a palaeosurface. Local mobilization of this detrital gold generation by post-depositional fluids is evident from minute, micrometre-scale secondary gold in the immediate vicinity of the, on average, 0.14 mm large micro-nuggets. The study provided not only strong support for the modified palaeoplacer hypothesis for the Basal Reef (and by analogy for most other Witwatersrand ore bodies), but it also revealed that micro-CT is most suitable for unveiling the 3-dimensional distribution and shape of gold particles in ore with a resolution of as good as a few micrometres.

Keywords. Gold, Witwatersrand, micro-CT, Basal Reef

1 Background

The cover page of the 50th anniversary volume of SGA’s flagship publication, Mineralium Deposita, in 2015 is decorated by an image depicting part of a most remarkable specimen of Witwatersrand gold. This specimen (Fig. 1) has become world-famous not only for its exceptional gold content in the form of macroscopically visible concentration of gold particles defining delicate cross-bedding structures but also for its significance on our understanding of the genesis of Witwatersrand gold. The genesis of the Witwatersrand ores, the largest known accumulation of gold in the continental crust, has been regarded as “the most debated issue in the history of economic geology” for decades (Davidson 1965). It is safe to say that the above specimen, which represents the footwall contact of the c. 2.87 Ga Basal Reef in the Johannesburg Subgroup (Central Rand Group) and which was collected by Mike Lain at the Free State Geduld gold mine in the Welkom goldfield, provided the most critical clues as to the mode of gold emplacement in the host conglomerates. It was first described by Minter et al. (1993), who dissolved a slab of it in hydrofluoric acid and thus released over 5000 gold particles, 75% of which had rounded, spherical to toroidal forms and 25% irregularly jagged and branched, dendritic forms. The morphology of many of these particles was further documented by scanning electron microscopy. These morphological studies revealed the coexistence of two generations of gold, one of which has been interpreted as detrital and the other as secondary products of local gold mobilization by post-depositional fluids on the scale of a few micro- to millimetres (Frimmel et al. 1993). Thus they provided a key argument in favour of the modified palaeoplacer hypothesis for the genesis of the Mesoarchaean Witwatersrand ores.

Those workers who favour an epigenetic hydrothermal introduction of the gold into the host conglomerates (Barnicoat et al. 1997; Phillips and Law 2000) questioned the reliability of the above morphological studies and suspected the obtained shapes to be artifacts of sample preparation. To overcome this problem, non-destructive techniques that permit the 3-dimensional characterization of the gold particles in-situ are called for. Radiography using X-rays is a means to achieve this goal. A first radiograph of the said specimen was presented by Minter et al. (1993). Since then, major advances were achieved in industrial X-ray computed tomography, including very high spatial resolution (μ-CT), and the applicability of this technique to geological materials (e.g. Ketcham and Hildebrandt 2014).

Thus it seems timely to revisit the said specimen and analyze it once more using state-of-the-art instruments. To this effect the sample was investigated at the Development Center X-ray Technology (EZRT) of the Fraunhofer Institute for Integrated Circuits in Fürth, Germany.
The Cover of Mineralium Deposita’s Anniversary Volume Uncovered

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2 Methodology

2.1 Principles of X-ray imaging

The principle of X-ray imaging is based on the attenuation of the radiation by the penetrated matter. Radioscopic X-ray images of specimens (radiographs) are often generated by digital detector arrays (DDA). Intensity and contrast of the images depend on the sensor material and the detector characteristics on the one hand and on the applied X-ray spectrum on the other hand. X-ray images reveal internal structures of the specimen. As all structures are projected onto the active area of the detector, they may superimpose each other in the radioscopic image. Depth information is not available in the projection.

In computed tomography (CT) the full three-dimensional information is numerically reconstructed based on a set of projected images of the specimen from various angular directions.

For planar objects, computed laminography (CL) is often used and 3D image reconstruction is performed through the so-called tomosynthesis. Thus higher spatial resolution can be achieved but at the expense of imaging artifacts, which may alter the apparent morphology of particles or pores in the sample. For this reason we applied standard µ-CT to a region-of-interest (ROI) in this sample. Advantages and disadvantages of the techniques are discussed in Voland et al. (2015).

2.2 Experimental setup

For our experiments we used an X-ray system that has been optimized for high-resolution scans. The main components of the system are the microfocus X-ray tube and the DDA with an active area of 40 x 40 cm². The imaging itself is based on a cone beam geometry; a geometrical magnification factor of 26.3 was selected to achieve a sufficient spatial resolution. This results in an effective pixel size of 5.6 µm in the projective images as well as in the reconstructed volume (spatial resolution 11 µm at best according to Nyquist-Shannon theorem). Additional system requirements that arise for high-resolution systems are found in Salamon et al. (2009). An attenuation radiograph of the scanned sample region is shown in Fig. 2.

2.3 Post-processing

Small artificial movements of the sample axis which may cause considerable imaging artifacts, if high-absorption particles are present in a less-absorbing matrix, were corrected by an approach following Mayo et al. (2007): an iterative method of alternating filtered back projection (FBP) and forward projection steps has been applied on downsized radiographs. The results of ten iterations are then used for an improved full-resolution reconstruction.
3 Results

Due to the large difference in density between gold and effectively all other minerals in the specimen, which comprise mainly quartz and phyllosilicates with accessory apatite, zircon, monazite, rutile, chromite, and sulphides (mainly pyrite), the individual gold particles can easily be distinguished in radiographs (Fig. 2). The only other mineral which could be confused with gold because of its high density is uraninite and this is, although common in many Witwatersrand reefs, conspicuously absent in the given specimen.

The 3-D rendering of the two subsets (marked a and b in Fig. 2) is shown in Figure 3. These images leave no doubt that the gold in the given sample represents heavy mineral concentrates along delicate sedimentary structures (foresets and bottomset of cross-bedding). Two generations can be clearly distinguished both by their form and size: (i) a predominating larger grained population with mainly disk-shaped to toroidal forms (Fig. 3b, 4), and (ii) an extremely fine-grained, dusty, irregularly shaped population that is observed only in a few places in the immediate vicinity of the former population (Fig. 3a). The former population comprises discrete particles, many of which are not in mutual contact. Their distribution and lack of connectivity rule out any formation through precipitation from an infiltrating fluid/solution. The rounded surfaces of these grains reflect mechanical abrasion during transport and confirm that these particles are detrital.

In contrast, the second population is far too fine-grained to have been transported mechanically. Its irregular, dendritic morphology strongly points to precipitation from a hydrothermal fluid/solution. Its spatial distribution provides clear insights into the source of the Au in that fluid/solution: If the source had been external to the host pebbly arenite, this population of secondary gold should follow fractures, micro-shears or any other potential fluid pathway; thus it should occur as veinlets. This is not the case. Instead it is spatially restricted to few isolated domains in the vicinity of some accumulations of detrital gold particles. Consequently, the source of the Au for this 2nd population must be due to very local remobilization of some of the detrital gold particles over not more than a few millimetres by post-depositional fluids/solutions.

4 Conclusions

All in all two main conclusions can be drawn from this study:

1. The two morphological types of gold previously recognized after sample digestion in HF (Minter et al. 1993) are a real feature and not an artifact of sample preparation. They represent undoubtedly placer gold and secondary gold that formed by very short-range mobilization of the placer gold by post-depositional fluids/solutions. Thus this study confirms the hypothesis.
of the modified palaeoplacer origin for much of the Witwatersrand gold.

2. μ-CT is a powerful method to document, quantify and characterize the 3-D spatial and size distribution as well as morphological features of ore phases (in this case gold) that show a sufficient density difference to other ore and gangue minerals. This opens up the possibility of detailed geometallurgical studies on (gold) ores that will help to improve the efficiency of ore processing and beneficiation in the future.

Figure 4. Magnified 3D view onto a 150 μm long single gold micro-nugget as revealed by μ-CT, from the top foreset of the Basal Reef specimen shown in Figure 1.

Acknowledgements

We thank Mrs. Thomas, the wife of the late Mike A.S. Thomas, for making available a slab of the unique Basal Reef specimen.

References


Data Collection and Testing for Geometallurgy: Getting More from Drill Core

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Abstract. Potential problems in treating an ore can be identified early with routine, methodical collection of geometallurgical data from drill core. Ideally the data collected will be quantitative and spatial to allow use in geometallurgical modelling for the definition of spatial variation in processing behaviour. Early recognition of spatial domains that may influence, for example, blasting, crushing, grinding, recovery, and environmental treatment of an ore allow the effective design of a suitable testing regime for more precise and expensive bankable tests. Rapid and inexpensive geometallurgical tests for drill core include non-destructive and destructive measurements. Non-destructive tests include high resolution imaging, mineralogy (e.g. spectral data), elemental analysis (e.g. portable XRF) and strength measurements (e.g. rebound hardness, petrophysics). Destructive tests include elemental analysis (e.g. assay data) and rock strength (e.g. constrained crushing and size analysis). The routine collection of quantitative, spatial data is very important for predictive geometallurgical modelling and requires an approach to core logging that includes logging support methods and tools in addition to traditional visual logging.

Keywords. Geometallurgy, testing, data collection, spatial domainning

1 Introduction

Geometallurgy provides ore-body knowledge for development and mining purposes, plus closure and rehabilitation. The principle aims are to identify and quantify spatial variations in processing behaviour, for example comminution, liberation, recovery and environmental treatment. Early recognition of spatial domains that may influence, for example, blasting, crushing, grinding, recovery (beneficiation), and environmental performance of an ore allow the effective design of a suitable testing regime. If geometallurgical data is available during prospect evaluation it can be used to assist with decisions about preferred mine and mill design, tailings facilities and storage. During mine life, geometallurgical data can be used for mine optimisation and planning and ultimately to assist with mine closure. This is achieved through a practical integration of geological, mining, metallurgical, environmental and economic information to maximize the value of an ore body while minimizing technical and operational risk (e.g. Dunham et al. 2011; Ehrig 2011; Lamberg 2011; Turner-Saad 2010; Walters 2011).

What is needed is a holistic approach to identify attributes that contribute to the realised value of a resource. This includes traditional attributes such as grade as well as less traditional factors including: concentration of deleterious elements, hardness, grindability, mineral species and abundance, and mineral liberation. A first indication of at least some of these attributes can be obtained by data collection carried out directly on drill core and includes non-destructive and destructive testing. The methodology is iterative and the aim is to obtain the necessary geometallurgical information as rapidly and cost effectively as possible from the minimum number of test types.

2 Drill core data collection and testing

Listed below are some examples of non-destructive and destructive data collection and testing suitable for geometallurgy.

2.1 Non-destructive

High quality images: The collection of high quality photographs is an essential first step in collecting geometallurgical data from drill core. High resolution images should be collected under controlled lighting and the drill core should preferably be clean, whole, wet and free of markings (except depth and orientation marks). Good quality photographs can be used to improve manual core logging and in some cases automated logging of core texture and colour may be possible. If the core has orientation marks then the images can be used to generate geotechnical data (Fig 1).

Figure 1. Example of a high quality image of oriented drill core, showing orientation marks.
Mineralogy: Spectral data (e.g., infra-red (IR), thermal IR (TIR)) can be collected from clean, dry drill core using hand held (e.g. TerraSpec) or more automated techniques (e.g. Hylogger, Corescan, Sisu-Rock). This data provides information on mineralogy especially alteration minerals and can also be used to provide extra constraints to improve estimation of modal mineralogy from assay data (see below).

Elemental analysis: Portable X-ray fluorescence (pXRF) data can be collected systematically from drill core to give an estimation of elemental content. Care must be taken to avoid sampling errors. Automated systems are being developed for drill core and drill chips (e.g., O’Hanlon and Lewis 2014).

Rock strength: To help determine probable comminution behaviour it is helpful to have an indication of rock strength from drill core at an assay scale. Impact hardness (Fig 2) and sonic velocity measurements (Fig 3) are non-destructive and can be rapidly collected from drill core giving continuous down-hole information (Fig 4).

Elemental analysis: Multi-element assay data for regular intervals (e.g. 1m, 2m) of drill core, not composite samples, is critical. Samples should be analysed for a complete suite of elements, i.e. rock forming elements as well as metals and deleterious elements, using a method that provides as complete a digestion of the sample as possible.

The Assay results give the first indication of the distribution of likely penalty elements (e.g. As, U, Bi) and can be used to calculate mineralogy for each assay interval. Mineralogy calculation generally works best if constrained by (semi) quantitative X-ray diffraction (qXRD) data (and/or IR data; Berry et al. 2011). Collection of qXRD data is recommended for every tenth assay sample to support the estimation of mineralogy for each assay interval.

Rock strength: Low cost destructive tests for use on drill core to determine rock strength include the GeM comminution index (GeM Ci) test and point load testing. The GeM Ci test was designed to be inserted into routine assay sample preparation and is based on constrained jaw crushing protocols linked to analysis of size distributions (Fig 5; Kojovic et al, 2010). The test produces two indices that act as proxies for crushing and grinding hardness suitable for variability mapping, domaining and selection of large composite samples for more precise testing (Kojovic et al. 2013).

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Methodical collection of geometallurgical data from drill core will be determined for each assay interval. Mineralogy calculation generally works best if constrained by (semi) quantitative X-ray diffraction (qXRD) data (and/or IR data; Berry et al. 2011). Collection of qXRD data is recommended for every tenth assay sample to support the estimation of mineralogy for each assay interval.

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Figure 2. Example of an impact hardness tool.

Figure 3. Example of a device for collecting sonic velocity data.

Figure 5. Example of a Jaques crusher used for GeM Ci testing.
Point load testing (Fig 6) is routinely carried out on drill core, largely for geotechnical work but results can be a useful guide to comminution behaviour (Kojovic 2008).

Quantitative information is very important for predictive geometallurgical modelling and this requires an approach to core logging that includes logging support methods and devices in addition to visual logging. Ideally geometallurgical parameters for drill core will be determined for each assay interval.

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3 Summary

Methodological collection of geometallurgical data from drill core provides an early indication of potential problems. It adds to the geometallurgy data base and provides a more robust dataset (e.g. for use in modelling). Importantly, all measurements taken from drill core are spatially located (i.e. not composites) thus they can be related to other properties within a deposit model. Early collection of geometallurgy data aids bulk sample selection that is needed for larger scale, bankable tests.

Geometallurgy data helps in the management and minimisation of risk. It can be used in prospect evaluation and comparison. Is useful during feasibility to help determine plant design (e.g. crushers, SAG, HPGR) and processing options (e.g. flotation, leaching) and can be used to aid mine optimisation (e.g. short and long term block models) and scheduling.
Chalcopyrite, as well as tellurobismuthite (Bi₂Te₃), are produced in large quantities at low cost. Gold, galena and stable, and furthermore, the components are already urea. DESs are environmentally benign, yet chemically choline chloride with hydrogen-bond donors such as are a form of ionic liquid that are mixtures of salts such as dissolution and recovery. Deep eutectic solvents (DES) electrolytes with potential for high selectivity in both liquid at low temperature. They are powerful solvents and selectively dissolve native gold and tellurium, sulphides and tellurides. Ionic liquids are anhydrous salts that are compatible methods. Here, we show that ionic liquids are developed more energy-efficient and environmentally-cost and an associated CO₂ footprint, both of which it safely disposed of, and this waste treatment requires solid form, which require treatment before they can be processes often produce wastes, in gaseous, liquid or acids or bases that require energy to produce. These high temperature, or the use of large quantities of strong-intensive process, requiring either smelting or leaching at 1 Introduction

The extraction of metals from ores is often an energy-intensive hydrometallurgical treatments, most notably cyanidation, oxidation or high-T hydrometallurgy. The processing of ore by hydrometallurgy or dissolution, deep eutectic solvent, ionic liquids to Ore Processing – Dissolution Rates for Gold and Other Minerals. The Application of Deep Eutectic Solvent Ionic Liquids

Abstract

The question is whether it is possible to develop new, compatible metallurgical processes for the mining industry on a planet of over 9 billion people? The advent of heap-leaching and biohydrometallurgy have made significant advances in this direction, but there remain many ores for which the most economic, or only, option operations must secure. The increasing intolerance of the “social licence to operate” that all mining

Our thesis is that ionic liquids can provide new, low-energy, low-cost and more environmentally-compatible methods. Here, we show that ionic liquids are...
The Application of Deep Eutectic Solvent Ionic Liquids to Ore Processing – Dissolution Rates for Gold and Other Minerals

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Abstract. The processing of ore by hydrometallurgy or pyrometallurgy typically has a high energy demand and large associated CO₂ footprint. This thus is a need to develop more energy-efficient and environmentally-compatible methods. Here, we show that ionic liquids are one such method, and that they can be used to selectively dissolve native gold and tellurium, sulphides and tellurides. Ionic liquids are anhydrous salts that are liquid at low temperature. They are powerful solvents and electrolytes with potential for high selectivity in both dissolution and recovery. Deep eutectic solvents (DES) are a form of ionic liquid that are mixtures of salts such as choline chloride with hydrogen-bond donors such as urea. DESs are environmentally benign, yet chemically stable and, furthermore, the components are already produced in large quantities at low cost. Gold, galena and chalcopyrite, as well as tellurobismuthite (Bi₂Te₃), are soluble in DES by oxidation at 45-50°C at rates that are very favourable in comparison to cyanidation, bio-oxidation or high-T hydrometallurgy.

Keywords. Gold, dissolution, deep eutectic solvent, ionic liquid, ore processing.

1 Introduction

The extraction of metals from ores is often an energy-intensive process, requiring either smelting or leaching at high temperature, or the use of large quantities of strong acids or bases that require energy to produce. These processes often produce wastes, in gaseous, liquid or solid form, which require treatment before they can be safely disposed of, and this waste treatment requires further energy. The energy input equates to a significant cost and an associated CO₂ footprint, both of which it would be desirable to reduce. Furthermore, some hydrometallurgical treatments, most notably cyanidation, have poor public acceptability and can negatively impact on the "social licence to operate" that all mining operations must secure. The increasing intolerance of cyanidation has resulted in its being banned from use in a number of countries and states (Roth 2010).

The question is whether it is possible to develop new, low-energy, low-cost and more environmentally compatible metallurgical processes for the mining industry on a planet of over 9 billion people? The advent of heap-leaching and biolymetallurgy have made significant advances in this direction, but there remain many ores for which the most economic, or only, option is energy-intensive hydrometallurgical or pyrometallurgical treatments.

Our thesis is that ionic liquids can provide new environmentally-friendly approaches to processing a variety of ores, in particular those that are difficult and energy-intensive to treat. Whilst there is now a large literature and extensive application of these liquids in the recovery of metals from scrap and metal oxides (Abbott et al. 2011a, b), as well as applications across a range of chemical processing (Wasserscheid et al. 2008), there has been only limited attention paid to the possibility of using ionic liquids to process ores (Whitehead et al. 2004, 2007, 2009; Luczak et al. 2008; Dong et al. 2009).

There is a vast array of different types of ionic liquids and many are unsuitable to large-scale applications such as mineral processing due to high cost, lack of availability or toxicity. We proceed here by explaining what ionic liquids are, and then showing that a group of ionic liquids known as deep eutectic solvents fulfil the requirements for industrial application. We then demonstrate that these ionic liquids can be used to rapidly dissolve a variety of ore minerals, including gold, at low temperatures.

2 A new type of chemistry - ionic liquids

Ionic liquids are salts that are liquid at low temperature, typically <100°C. These anhydrous liquids are composed of ions and, like high temperature molten salts, are electrolytes and powerful solvents. In contrast to aqueous liquids, where the solubility of metals is limited by the tendency for water to combine with metal ions and precipitate oxides and hydroxides, in water-free ionic liquids much higher metal concentrations can be achieved. High ligand concentrations are possible allowing much greater control on metal speciation in solution, whilst recovery from solution can be by electrowinning, cementation, ion exchange or precipitation (Abbott et al. 2011b). These features provide potential for high selectivity in both dissolution and recovery. The high concentrations of metals that can be achieved, together with the fact that ionic liquids can be reused in a closed circuit, means that high volume/low concentration aqueous wastes are not produced.

In order to be suitable for a large-scale metallurgical process a reagent must be low cost, readily available in

Geometallurgy
large quantities, chemically stable to allow prolonged reuse, have good environmental compatibility, and have no registration requirements (i.e. be a common, simple chemical with well-known characteristics). Unfortunately all the ionic liquids that have previously been tested for dissolution of ore minerals (Whithead et al. 2004; 2007, 2009; Luczak et al. 2008; Dong et al. 2009) fail to meet one or more of these criteria. Ensuring that all these industry-necessary criteria are met from the outset led to the development at the University of Leicester of the deep eutectic solvents (DESs). These are mixtures of salts, such as choline chloride, with hydrogen-bond donors such as urea or citric acid (Abbott et al. 2004). The eutectic mixtures have melting points that are significantly lower than their individual components, giving a room-temperature ionic liquid. DESs are not an ionic liquid sensu stricto, since they are a mixture rather than a single salt, nevertheless they are anhydrous liquids made of ions and share many properties with ionic liquids sensu stricto, although also exhibit some significant differences (Smith et al. 2014). The solvent properties of DESs can be adjusted by changing the hydrogen-bond donor, giving 10^4 possible different liquids and allowing the possibility of tailoring the properties of the liquid to a specific process (Abbott et al. 2004). DESs are environmentally benign, yet chemically stable. Their components are common, cheap chemicals, e.g. choline chloride (vitamin B4) is mainly used as an animal-feed additive, being already produced in large quantities (forecast to exceed 500 kt choline chloride p.a. in 2017; Global Industry Analysts 2014) at low cost (~€2/kg). Urea is a common nitrogen fertilizer (2012 worldwide production capacity was ~184 Mt; Ceresana 2012) that is non-flammable and completely biodegradable, retailing at ~€0.5/kg. The behaviour of d-block metals and group IIIA-VA metals and semi-metals in DESs is well-understood (Abbott et al. 2011b). It has previously been shown that metal oxide extraction by DESs is economically viable even for low value metals (Abbott et al. 2009).

3 Dissolution rates of gold and other minerals in a deep eutectic solvent

Here we demonstrate how a variety of minerals can dissolved from ore samples using iodine (I₂) as an oxidising agent within a DES. We show how the dissolution rates can be rapidly estimated using a new micro-leach technique with an optical profiler, and compare these rates to those of existing techniques. We investigate a quartz vein-hosted orogenic-type gold ore with relatively fine gold particles (90% <100 µm, most <40 µm; Dominy & Platten 2008) because high efficiency of extraction of gold from such ores typically demands a hydrometallurgical step (often involving cyanidation), pyrometallurgy, or both. In addition we investigate native tellurium and a telluride mineral, because telluride-bearing gold ores typically present issues for metallurgists (Spry et al. 2004; Zhang et al. 2010). In hydrometallurgy gold tellurides may be refractory to cyanide solutions and so lost to tailings. Alternatively the ores may need to be roasted to make them amenable to cyanidation (Zhang et al. 2010). In either case tellurium (increasingly sought after for solar photovoltaic panel construction; Woodhouse et al. 2013) is lost and becomes a potential environmental contaminant. Thus approaches that might liberate and recover gold and valuable associated elements from ores could both increase the value gained from an ore and reduce environmental legacies.

3.1 Experimental

All samples were mounted in resin, cut, and polished to produce the flat surface of a standard polished block used for reflected light microscopy. The electrum, chalcopryite, galena and pyrite investigated were all in the same sample - gold ore from the Cononish gold deposit, Scotland, (Curtis et al. 1993; Spence-Jones 2013; Hill 2014) courtesy of Scotgold Resources Ltd. Gold-rich sample CGJ CON 002 consists largely of pyrite, with lesser galena and chalcopryite, in a quartz matrix. The electrum grain that was leached was silver-rich, measured as approximately 50 wt.% Au(Au+Ag) by SEM-EDX.

Samples of native tellurium (BM 31691, Zlatna, Transylvania, Romania) and tellurobismuthite (Bi₂Te₅) were obtained as polished blocks from collections at the Natural History Museum, London. The ionic liquid used was Ethaline, a DES mixture of 1 mol. eq. choline chloride and 2 mol. eq. ethylene glycol. Ethaline containing 0.1 mol dm⁻³ iodine was prepared following the procedure of Abbott et al. (2015). Polished blocks were etched by suspending them in a well-stirred solution at either 45°C (tellurium, tellurobismuthite) or 50°C (electrum, galena, chalcopryite, pyrite). The etch time was 10 minutes for sample CJG CON 002 (electrum, galena, chalcopryite and pyrite). For the tellurium and tellurobismuthite there was an initial 5 minute leach, at which point the etch depth was measured. This was then followed, without re-polishing, by an additional 10 minute leach at which point the etch depth was measured again at an integrated leach time of 15 minutes.

2D and 3D optical images of the samples pre- and post-dissolution were captured on an optical profiler. This instrument captures a reflected light image of the sample surface identical to that given by a conventional reflected light microscope used for ore microscopy (Fig. 1A, B). However, in addition, images are constructed by determining the features of an image that are in focus at different heights. These are then analysed to produce a reconstructed 3-D topography of the surface. Line profiles were measured across grains where the dissolution rate was being measured using a flat surface of a non-soluble phase (resin, quartz) to provide a reference height. Only the relatively flat base of an etch pit was measured, away from grain boundaries or inclusions that retard dissolution by partly shielding the grain from the solution. Using distinctive features on the sample surface, care was taken to position the line profiles in precisely the same position pre- and post-dissolution so that an accurate estimate of the difference between the profiles could be measured.
3.2 Results

Reflected light images of CJG CON 002 pre- and post-dissolution show that the ~30 x 15 µm electrum grain was completely dissolved after the 10 minute leach (Fig. 1B). Galena and chalcopyrite were also etched, but pyrite appears unreacted and only mildly tarnished in some places. Both native tellurium and tellurobismuthite were also observed to dissolve, with the tellurium showing an increase in surface roughness during dissolution.

Figure 1. Reflected light image of gold ore. A. before, and B., after reaction with a deep eutectic solvent for 10 minutes at 50°C. The electrum (el) grain in A has been completely removed in B whereas pyrite remains unreacted.

The etch depths measured versus time are shown for the different minerals in Figure 2, Galena shows the fastest dissolution rate of ~0.74 µm/min, with chalcopyrite next at half that rate. The electrum appears to be next, but note that in 10 minutes the electrum grain had been completely dissolved and thus this represents a minimum dissolution rate of 0.17 µm/min. Tellurium is just a little slower than this, and tellurobismuthite slower still. Tellurobismuthite is strongly anisotropic with a perfect (0001) basal cleavage. Observing the etching rates in two adjacent grains with different orientations suggests that the dissolution rate is ~45% faster parallel to the c-axis (perpendicular to the cleavage) compared to parallel to the cleavage. Where etch depths have been measured at two different times the dissolution rate appears to be broadly linear, although the tellurium rate may have increased by 50% after 5 minutes (Fig. 2), perhaps due to increased roughness of the surface. There was no measurable dissolution of the pyrite, in line with the observation that it appeared unreacted, with fine polishing scratches preserved on the surface.

Figure 2. Etch depth for different minerals versus dissolution time. The electrum dissolution rate is a minimum.

3.3 Dissolution rates and industrial feasibility

The observation of broadly linear dissolution rates suggest that, apart perhaps from the tellurium, there is no major biasing of our data over these time and length scales by, for example, enhanced early dissolution due to surface damage by polishing, increasing dissolution rate due to the development of surface roughness and hence increased surface area, or later retardation of the reaction due to depletion of the liquid boundary layer. Nevertheless, these are questions that can be investigated further using this technique.

One question is whether the dissolution we have demonstrated will take place on a feasible timescale for industrial implementation. Our measured rates can be used to make a simple calculation of the lifetime of a gold grain dissolving under these conditions. Figure 2 shows that the electrum (and tellurium) grains should dissolve approximately 2.4 µm in 15 minutes. A pyrite grain to a 100 µm diameter grain dissolving in a well-mixed solution suggests that dissolution should be complete in ~5.25 hours. Given that our electrum dissolution rate is a minimum, it is likely that this time could be shorter. This dissolution rate compares very favourably with the timescales used in many current ore metallurgical processes (e.g. bio-oxidation of pyrite - a 100 µm grain would take 300 hours to dissolve; Climo et al. 2000; e.g. hydrothermal transformation of calaverite to gold - a 100 µm grain would take 24 hrs at 200°C; Zhao et al. 2009). The dissolution rate also compares very favourably to cyanidation, for example, our (minimum) electrum dissolution rate translates to 2.8 x 10^-4 mol m^-2 s^-2, which is ~40 times greater than the maximum gold dissolution rate in cyanide determined by Wadsworth et al. (2000) of 0.69 x 10^-5 mol m^-2 s^-2. Our dissolution rate is at 50°C vs. 25°C used by Wadsworth et al., but room temperature dissolution at realistic rates looks perfectly feasible.

These results show strong selectivity in the dissolution process with ore minerals going into solution...
and pyrite remaining undissolved. In many gold ores pyrite represents the major gangue in a sulphide float concentrate and thus there is potential to separate gold from pyrite. Of course the gold grains must be exposed at the surface of pyrite grains and not "locked" as inclusions. Dissolution of chalcopyrite and galena from the gold ore means that there is the potential to also recover Cu and Pb from the same sample, simultaneously adding value to the ore and removing environmental contaminants from the waste. Dissolution of tellurobismuthite suggests that other tellurides may be soluble and there may be routes to recovering a wider range of components in complex ores.

4 Conclusions

Deep eutectic solvent ionic liquids meet all the criteria for a reagent that can be used in large-scale metallurgical process, being cheap, readily available, chemically stable, environmentally compatible and free of registration requirements. A micro-leach technique we have developed using an optical profiler allows us to rapidly measure dissolution rates in a sample and compare different minerals. Results demonstrate that electrum, native Te, tellurobismuthite, galena and chalcopyrite are all soluble by oxidation with iodine at low temperatures in a DES solvent. Dissolution rates vary between minerals with galena showing the fastest dissolution rate and tellurobismuthite the slowest. The dissolution rate of electrum is very favourable compared to current industrial processes, including cyanidation. Pyrite is notably insoluble under the same conditions.

Given that ionic liquids contain no water, it is not appropriate to refer to their application to ore and metal processing as hydrometallurgy. Instead, ionometallurgy (Abbott et al. 2011a) with deep eutectic solvents would seem to offer a new set of environmentally-benign tools for metallurgists that could both augment existing processes and ultimately replace some.

Acknowledgements

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References


How to Build a Process Model in a Geometallurgical Program?

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Abstract. This work presents a literature review on ways to acquire relevant experimental data for the process model of a geometallurgical program. It identifies the needs in several unit models and proposes ideas for future developments.

Keywords. Geometallurgy, process model, magnetic separation, flotation, gravity separation.

1 Introduction: Approaches in geometallurgy

Geometallurgy is defined as a multi-disciplinary science that links geology, mineral properties and behavior of the material in metallurgical operations, more specifically in minerals processing (McQuiston and Bechaud 1968; Lamberg 2011; Vann et al. 2011).

A geometallurgical program is the industrial application of geometallurgy in a mining operation context. It includes a spatially-based model that forecasts how the ore will behave in mineral processing operations (Alruiz et al. 2009; Lund et al. 2013; Schouwstra et al. 2013; Aasly and Ellefmo 2014). It usually consists of two main sub-units:

- Geological model: 3D block model in which geological and geometallurgical data is available.
- Process model: A flow sheet model in which data from geological model is used to forecast the metallurgical performance. Depending on the approach, this model can predict the recovery rate, the element grade of mineral grade in the concentrate and tailings, particle size distribution, water and energy consumption.

Combining the two models the information can be used for data management, visualization, for production planning and to test different production scenarios.

Depending on the approach taken for geometallurgy and the level of geometallurgical information needed, the program describes the sample collection and characterization, the nature and number of tests needed for the process model, the definition of ore-types and domains and the validation of the models based on case studies.

Usually one of the following approaches is used:

- Traditional: the geological and process models are based on chemical grades from drill core assays. Variability testing is used to develop functions to predict metallurgical performance parameters.
- Proxies: the process model is based on a large number of small-scale tests that describe the metallurgical response of the ore in the process more or less indirectly.

- Mineralological: the geological and process models are based on quantitative mineral characterization. This approach has three levels of information:
  - Unsized (1D): Phases, chemical and modal composition
  - Sized (2D): Chemical and modal composition by particle size (class).
  - Liberation (3D): Chemical and modal composition, liberation distribution by particles size classes

A review of the use of geometallurgy in current operations can be found in Lishchuk et al. (in prep.).

2 Process models used in geometallurgical programs

The simulation of ore dressing circuits historically derives from the simulation of chemical processes. Early works Keat and Shacham 1973; Ford 1979; Ford and King 1984 were focused on the theoretical design of simulators, the classification of different simulation systems but also the design principles for a simulation environment to be used in a production context.

Table 1 presents the most common computer simulation environment types. Nowadays, most of the commercial software seems to be based on unit operations working either in a static (steady state) or dynamic mode.

The level of information required to feed the unit models depends directly on the approach selected for the geometallurgical model: there is no need for mineralogical information if the global model relies on elemental grade only.

<table>
<thead>
<tr>
<th>Hypotheses</th>
<th>Specific simulator</th>
<th>Section based simulator</th>
<th>Unit operation based simulator</th>
</tr>
</thead>
<tbody>
<tr>
<td>The flow sheet is fixed</td>
<td>Sections of the flow sheet are fixed</td>
<td>Usually steady state process</td>
<td></td>
</tr>
</tbody>
</table>

3 Experimental requirements

To model and simulate a process at any above listed levels, experimental data is needed where the streams are described on corresponding level. For developing and calibrating models the experimental data must be mass balanced. This gives challenging when aiming to
liberation level since the mass balancing must be done also on mineral liberation level.

### Table 2. Assumptions in unit models using different level of information.

<table>
<thead>
<tr>
<th>Chemical elements</th>
<th>Unsized</th>
<th>Sized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minerals</td>
<td>-Mineralogy is fixed -Particle size distribution (PSD) is fixed</td>
<td>-Mineralogy is fixed -PSD varies</td>
</tr>
<tr>
<td>Behavioral classes : minerals by floatability components</td>
<td>-Liberation distribution is fixed -PSD is fixed</td>
<td>-Liberation is fixed -PSD varies</td>
</tr>
<tr>
<td>Particles</td>
<td>(not applicable)</td>
<td>-Association varies -Shape is fixed -Micro-textural information could be used (Pérez-Barmúevo et al. 2013)</td>
</tr>
</tbody>
</table>

Experimental data is acquired by performing 3 types of tests:

- Geometallurgical tests: small-scale tests using a limited number of samples designed to predict the particles behavior.
- Variability tests: small-scale tests using a simplified flow sheet, an extensive number of samples and duplicates designed to describe how variations in the process impact the products.
- Laboratory tests: small to medium scale tests using a limited number of samples, designed to build a flowsheet that will be up-scaled first to the pilot level, then used in a full-scale process.

The following section details the tests available so far for each level, provides a short literature review of each of them. Some tests might not be included in this work due to the abundance of various proprietary tests.

### 3.1 Comminution

The basic test for comminution is the Bond test (Bond and W ang 1950; Bond 1961) that gives a measure of the Bond Work index (BWI). However, despite its wide acceptance and use, several limitations have made it less attractive (Powell and Morrison 2007).

For AG and SAG mills variability and laboratory testing, the Julius Kruttschnitt Mineral Research Centre (J K M R C) has been developing a drop-weight test (J K D W T) to describe accurately the breakability of the ore. The test provides an abrasion breakage parameter (ta) as well as impact breakage parameters (A and b) (J K T e c h 1992; Napier-Munn et al. 1996). A second test called the JK Rotary breakage test (JK R B T) can measure the specific breakage energy (Ec) and the amount of material passing 10 % of the size of the initial material (t10; J K T e c h 2014). Another test called SM C can provide similar results to the J K D W T based on the same principles (M orrell 2004).

A model for AG and SAG mills has been proposed by M innovex to measure a SAG power index (SPI) and a crushing index (CI) based on small-scale SAG mills (Amelunxen et al. 2014).

For geometallurgy purposes M wanga et al. 2014 has proposed the geometallurgical comminution test (GCT) that combines small-scale ball mill tests with product characterization. The author also provides an in-depth literature review of comminution tests and suggested guidelines for comminution tests in a geometallurgical program (M wanga 2014).

### 3.2 Magnetic separation

The use of dry low intensity magnetic separators (dry L I M S) like the M örtsell (1955) and wet low intensity magnetic separators (wet L I M S) for variability and laboratory testing is well established but magnetic deportment has also been integrated in geometallurgical models as a bulk property (Philander and Rozendaal 2013; Philander and Rozendaal 2014).

The Davis tube is another test that can be used as a proxy to describe the behavior of ore in magnetic separation (M uraiu and Svoboda 2003; N iiranen and B öhm 2012). It operates by creating a divergent magnetic field in a glass tube through which the sample is poured (dry or as a slurry).

### 3.3 Gravity separation

Several methods can be used at variability testing or laboratory testing level to reproduce gravity separation units: jigs, shaking tables, small-scale spirals, dense/heavy media separation and centrifugal methods (K nelson). Dense media separation (D M S) tests have been applied to choose a gravity separation method according to the density of the ore (M ils 1980).

However, the use of these tests in a geometallurgical context seems to be limited. Possible development in this area could include a gravity separation step coupled with a real-time characterization method like flow-cell multispectral measurements (L ero y et al. 2014). This could allow a fast acquisition of both mineralogical and liberation data at a particle level, based on gravity separation.

### 3.4 Flotation

For variability and laboratory testing, flotation tests are repeated with a large number of samples under various experimental conditions (changes in collector, frother concentration, particle size distribution, pulp density, pH, Eh, air flow and agitation speed) using a simplified sequence similar to the full scale process. These tests can be done either as one batch or in a cycle mode, closer to the plant operating conditions but time consuming and prone to errors (W ils 2011).

Several testing procedures have been developed to standardize these tests and ease their up scaling as summarized in following chapters. A detailed review of variability and laboratory test procedures can be found in Yianatos et al. (2010).

JK Floatability Index test (JK F I T, developed at the J K M R C) uses a sum of the floatability component of each mineral (fast, slow or non-floating) weighted by their mass proportion in the sample to compute a floatability index that can be scaled up. The basic test is
at the unsized mineral level but can be improved by integrating particle size distribution and liberation data from MLA measurements. As a result, this test is suitable for laboratory and variability testing but can also be linked with a geometallurgical model using JK SimMet and J K SimM et.

MinnovEX Flotation Test (MFT, developed by SGS) uses a continuous flotation rate distribution (k distribution) to distribute pulp particles of different sizes and degree of liberation into several classes. Once the k distribution is known by doing a small-scale test, it can be scaled up. Based on a mass conservation relation, one k distribution propagates from the feed to the other streams in the process. Since the test is at the sized mineral level, changes in the particle size distribution can be reproduced in simulation (Dobby and Savassi 2005). A similar test has been developed by (Amelunxen and A melunxen 2009). Since liberation data is not explicitly taken into account, this test is suitable for laboratory and variability testing.

Efforts have been done to build geometallurgical tests for flotation. One of them was based on a shaker test in which a test container the pulp is shaken by a pneumatic device (Chudacek and Fichera 1991). Vos et al. 2014 proposed a new small-scale test to determine flotation performance based on that principle: JK M ineral Separation Index (JK MS I). The results were consistent with the overall performance of batch flotation tests and plant processes, despite challenges to achieve a high recovery on the test case samples.

In flotation, collectors are fixed to the minerals to make their surface hydrophobic. Hydrophobicity is related to the liquid-mineral contact angle θ (measured between the liquid-air interface and the solid-liquid interface) by Young's equation.

During flotation the contact angle between water and the mineral should decrease and the air-mineral contact angle should increase as the surface of a floatable mineral is hydrophobic. Therefore, proper contact angle measurements could be related to the floatability of a given mineral and provide a proxy for flotation in a geometallurgical context. However, this kind of measurement is often done by optical instruments and in non-ideal conditions (non-smooth and non-flat surface, reactive minerals) resulting in an apparent contact angle rather than the actual (intrinsinc) one (Chau 2009).

A nother technique called Time-of-flight Secondary ion mass spectrometry (TOF-SIM S) is based on the bombardment by a primary ion beam resulting in the detachment of secondary ions at the surface of the particle. The main issue with this method is the collection and storage of samples which are required to be degassed with nitrogen then frozen in liquid nitrogen (Brito e Abreu and Skinner 2011; Chehreh Chegani and Hart 2014). For geometallurgical purposes, a possible flotation proxy could be developed through reliable optical contact angle measurement technique which could then be validated with TOF-SIM S.

3.5 Sensor-based tests for particles

Developments in sensor technology and improved computational power increase the use of real-time signal processing to classify particles. A wide range of the electromagnetic spectrum can now be measured either as a transmitted, diffracted, reflected or polarized signal (Wotruba and Harbeck 2012). Further extensions to sensors might be expected in the Terahertz range as well in a near future (Yu et al. 2010).

Limitations for a laboratory use include the high costs and dimensions of the equipment. So far, the main purpose of sensor-based equipment has been to track changes in the streams and adapt process parameters adequately. As such, they cannot be regarded as laboratory nor variability testing methods.

These techniques are in between characterization of particles and separation tests and are de facto suitable for geometallurgical testing if they provide reliable online measurements.

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Small-scale tests</th>
<th>Variability tests</th>
<th>Laboratory testing</th>
<th>Scale-up factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Communion</td>
<td>GCT</td>
<td>SPI, JKRBT, JKDWT</td>
<td>Bond test, simplified Bond test</td>
<td>Test-specific</td>
</tr>
<tr>
<td>Gravity separation</td>
<td>-</td>
<td>DMS</td>
<td>DMS, jigs, spirals, shaking table variants</td>
<td>Test-specific</td>
</tr>
<tr>
<td>Flotation</td>
<td>JKMSI, Contact angle measurement</td>
<td>MFT, JKFIT</td>
<td>Traditional flotation test work</td>
<td>Between 1.5 and 3 for classical tests</td>
</tr>
<tr>
<td>Magnetic separator</td>
<td>Davis tube and Frantz isodynamic test</td>
<td>Frantz, Small-scale LIMS</td>
<td>Small-scale LIMS</td>
<td>Not needed</td>
</tr>
</tbody>
</table>

4 Conclusion

Despite a trend towards standardization of variability tests and various laboratory scale devices, the actual number of tests satisfying the requirements of low costs and ease of use for geometallurgy is very limited. This shows an urgent need for developing such tests. Alternative approach is to use particle approach where both ore and process models are taken to particle, i.e. mineral liberation level. In testing this means that laboratory tests must be analyzed in mineral liberation level. Thereafter in modeling and simulation a validated assumption that similar particles behave in process in similar manner regardless of their origin, can be used.

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1422 MINERAL RESOURCES IN A SUSTAINABLE WORLD • 13th SGA Biennial Meeting 2015. Proceedings, Volume 4

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Abstract. Mineral resource estimates of metallic ores use traditionally elemental grades when describing the quality of the deposit. This information is very defective as it does not take into account how much of metal is recoverable. When considering the processing properties of an ore, i.e. geometallurgy, more comprehensive picture could be received if the resource model would report mineral grades rather than elemental grades. This is because minerals define the value and possible processing options of the deposit. Techniques commonly used for an analysis of mineral composition, i.e. modal analysis, are either tedious or poor in quality. This paper shows with few examples how reliable modal analysis can be done by combining diagnostic analysis methods with element to mineral conversion.

Keywords. Geometallurgy, modal analysis, element to mineral conversion, mineral resource estimate

1 Introduction

Mineral resource estimates of metallic deposits use traditionally elemental grades when describing the quality of the deposit. This information is very defective as it does not take into account how much of metal is recoverable. When considering the processing properties of an ore, i.e. geometallurgy, more comprehensive picture could be received if the resource model would report mineral grades rather than elemental grades. This is because minerals define the value and possible processing options of the deposit.

The reason for using elemental grades rather than mineral grades is not in international standards. For example the JORC code defines that the grade is: “any physical or chemical measurement of the characteristics of the material of interest in samples or product” In addition the code says that the term quality has special meaning only for diamonds and other gemstones (JORC Joint Ore Reserves Committee 2013). Therefore it is up to the companies to select appropriate grade used in reporting.

Elemental grades are used because their analysis techniques are commonly available in reasonable price and quality control is easy to implement. Techniques for analysing mineral grades in ore samples on a contrary are either tedious or cannot be regarded as reliable.

This paper shows through case studies why mineral grades would give better information and how analyses for mineral grades could be done with low costs.

2 Motivation for Using Mineral Grades

Geometallurgy combines geological and mineral processing information to create spatial based model for production management in mines (Lamberg 2011). Geometallurgical approaches can be classified in three groups (Lishchuk et al. 2015): traditional, proxy and geometaly based. The traditional approach uses elemental analyses in both the geological and process model.

An example of traditional approach and its’ challenges is from a skarn iron ore deposit in Northern Europe containing besides magnetite also sulphides: chalcopyrite, pyrite and monoclinc magnetite (Arvidson et al. 2013). The iron analysis therefore includes not only iron from magnetite but also iron from sulphides and to lesser extend to mafic silicates.

Based on Davis tube (Schulz 1963) magnetic separation tests the iron recovery model was established against iron content of the sample. The correlation is positive but there is quite big scatter in the metallurgical results for given iron grade (Fig. 1). Therefore the iron recovery model would include large error bars. When the iron recovery is studied against the mass proportion of iron carried by magnetite and monoclinc pyrrhotite the correlation is linear and much better defined (Fig. 1).

Other deposit types where mineralogy is crucial for evaluating metallurgical response of ore are for example nickel sulphide ores and supergene porphyry copper ores (Lamberg et al. 1997).

3 Analysis Techniques for Mineral Grades

Automated mineralogy is state of the art technique for determining mineral grades in ore and process samples (Fandrich et al. 2007). When considering the number of samples to be analysed for a mineral resource estimate, the method is however far too tedious and expensive.

Quantitative X-ray diffraction with Rietveld is faster and therefore lower cost method but the main problem in the analysis of metallic ore deposits is the detection limit which is about 0.5 wt% (Gonzalez et al. 2003). Therefore method is not suitable alone to be used in analysing of mineral grades in metallic ore samples.

Element to mineral conversion is simple and low cost method for analysing mineral grades. Basically it uses chemical analyses of samples and chemical composition of minerals and converts this information to mineral grades using following formula

\[ A^*x = b \]  \hspace{1cm} (1)

Where A is a matrix of chemical composition of minerals, x is a vector of mineral grades (unknown) and b is a vector of chemical composition of a sample received from a chemical analysis (Lamberg et al. 1997; Lund et al. 2013; Whiten 2007). The number of minerals which can be solved from the equation is equal or less...
than the number of chemical components analysed. In many cases this limitation excludes in practice the usability of simple element to mineral conversion in getting mineral grades for mineral resource estimate. In nickel sulphide deposits it is very important to distinguish sulphidic and non-sulphidic nickel. For this a number of wet chemical methods have been suggested and according to Klock et al. (1986) the bromine-methanol leaching is the most reliable (Penttinen et al. 1977). The bromine-methanol method has one additional usage. As only 7% of pyrite dissolves in the methods whereas the other common Fe bearing sulphides are fully decomposed in the treatment, the method can be used in evaluation of the ratio of iron sulphides, i.e. pyrite and pyrrhotite (Lamberg et al. 1997).

Diagnostic leaching techniques exist also for zinc and molybdenum to distinguish sulphidic and oxidic carriers of the metal (Lamberg et al. 1997). Even diagnostic leaching methods are very useful the problem with them is their availability. Very few laboratories offer these assays on regular basis.

4 Combining Different Methods and Challenge in Overdetermination

As diagnostic leaching may not be available or may not solve a specific case a more common approach by combining X-ray diffraction and chemical assays in element to mineral conversion has been suggested (Lamberg et al. 2013; Parian and Lamberg 2013). The combined method takes the information of mineral grades from quantitative X-ray diffraction and uses that besides the chemical assays to have more knowns. In favourable case this leads to a situation where all the minerals with more than 1 wt% receive a preliminary estimate by X-ray diffraction and elemental analyses can be used to determine the trace minerals and to refine the mineral grades against chemical assays.

The combined method was tested with complex iron ore samples against simple element to mineral conversion, simple quantitative X-ray diffraction and automated mineralogy by (Parian et al., submitted). The combined method was recommended as the most suitable for geometallurgical programs.

5 Discussion

Using combined method by Parian et al. (submitted) one can receive mineral grades and therefore one could ask whether elemental grades are needed at all in the resource estimate. Basically elemental grades could be back calculated any time when wanted from the mineral grades and the A matrix (chemical composition of minerals). Before abandoning chemical assays one needs to make sure that the chemical assays and back calculated chemical composition matches exactly for the commodity elements. To reach this match one may need to introduce weighting in the mathematical solution of the equation (1). Another option is to run the calculation in several rounds as done by Lund et al. (2013). When calculation is done in one round one quite often needs to use non-negative least squares solutions which tends to leave non-negative residual to all elements. When calculation is divided into rounds, it is possible to have a better control on residuals and set that for commodity elements the residual will always be zero.

As the mineral grades matches perfectly with the
5 Conclusions

Mineral resource estimate based on its name should describe the quality and quantity of the deposit. The quantity is best described by minerals, i.e. mineral grades rather than elemental grades. This can be done in a cost effective way by combining information from chemical assays and quantitative X-ray diffraction. The benefits of using mineral grades rather than elemental grades in mineral resource estimate are as follows:

- The deposit modelling with lithologies and domains can be done more comprehensively as the analysis data gives minerals and there is a direct match with geological and quality analysis data.
- Geometallurgical domaining, sampling and modelling will be easier to do since the ore body model gives minerals which are directly linking the deposit information to minerals processing.
- Some of the metallurgical data may become easier to explain. For example grindability may find correlation with mass proportion of hard minerals.
- The value of the deposit is better described decreasing the geometallurgical risk.
- The value of the ore resource increases as the data is better quality.

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Geometallurgy
Rapid Resource Characterisation of Cu-Chlorides and Sulphates in Porphyry Cu Deposits using Reflectance Spectroscopy

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Abstract.
Porphyry copper deposits typically comprise various ore domains, including primary and secondary sulphide zones as well as oxidised horizons. The mineral assemblages associated with respective zones typically require different processing methods, thus a comprehensive understanding of the spatial distribution of the various ore domains is crucial. Our preliminary study shows that important indicator minerals for oxidised ore domains, such as the Cu-chloride atacamite and the Cu-sulphate antlerite display characteristic absorption bands at visible and infrared wavelengths that can be identified with hyperspectral drill core scanning technologies such as the HyLoggingTM system. This creates the potential for a rapid resource characterisation of major parts of porphyry copper deposits across the world.

Keywords.
Porphyry Copper, atacamite, antlerite, HyLoggingTM

1 Introduction
Porphyry copper deposits are often characterised by various ore domains that require different processing routes. Oxide ores are typically processed via acid leaching since many of the Cu species are acid soluble, but do not respond to flotation, where their presence may in fact be detrimental. Whilst various analytical methods are available for identifying copper oxides, they may be slow, expensive and poorly defined spatially (as a result of compositing). Therefore, a rapid, spatially precise method for characterisation of the resource is required.

Oxide zones often include copper species which are detectable with reflectance spectroscopy. At the Porphyry Copper deposit of Radomiro Tomic (Northern Chile), for example, the ore body can be separated into four different geometallurgical zones, namely 1) primary sulphide, 2) secondary sulphide, 3) a lower oxide and 4) upper oxide zone (Cuadra and Rojas 2001). The lower oxide zone is characterised by an extensive zone of the Cu-chloride atacamite and associated weak argillic alteration. At other porphyry copper deposits, like Chuquicamata, oxide ores contain the Cu-sulphates antlerite and brochantite in addition to atacamite and chrysocolla (Ossandon et al. 2001).

Whilst a number of infrared active minerals which do not host Cu can be key indicator minerals for hydrothermal alteration and subsequent oxidation stages, it is the Cu bearing phases such as Cu-chlorides and sulphates, which have the greatest potential to impact upon processing. In general, Cu-related electronic transitions are present in the visible-near infrared (VNIR, 400 to 1000 nm), hydroxyl related absorption features in the shortwave infrared (SWIR; 1000 to 2500 nm), and fundamental sulphate and hydroxyl vibrations in the thermal infrared (TIR; 6000 to 14500 nm).

This paper tries to summarise the diagnostic absorption features in the VNIR, SWIR and TIR of some of the key indicator minerals for oxidation subsequent to hydrothermal alteration. For this, HyLoggingTM data from trial samples sourced from Chile were compared with literature data.

2 HyLoggingTM
HyLoggingTM is a drill core scanning technology that enables rapid acquisition of contiguous reflectance spectra from drill cores, covering the visible near (VNIR, 400 to 1000 nm), short wave (SWIR; 1000 to 2500 nm) and thermal infrared (TIR; 6000 to 14500 nm) wavelength regions (Cudahy et al. 2009). The HyLoggingTM system uses a computer-controlled X-Y table moving in a serpentine path under a fixed spectrometer and illumination system. Test samples of Cu-chlorides and sulphates were scanned with CSIRO's HyLoggingTM system located at the Advanced Mining Technology Center (AMTC) - University of Chile. Resampling of the collected spectra to 8 nm spectral resolution and 1 cm spatial resolution as well as mineralogical interpretation was done using The Spectral Geologist software (TSGTM). From each sample group one representative sample was chosen to discuss the main diagnostic absorption features described in this abstract.

HyLoggingTM has been used for routine mineral mapping in a variety of mineral deposits, including Archean Au deposits in the Eastern Goldfields of Western Australia (Cudahy et al. 2009), the Olympic Dam deposit in South Australia (Tappert et al. 2013) as well as Tertiary Channel Iron Deposits (CID) in the Hamersley Basin Province in Western Australia (Haest et al. 2012a, b).
Rapid Resource Characterisation of Cu-Chlorides and Sulphates in Porphyry Cu Deposits using Reflectance Spectroscopy

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3 Geological setting, and Electronic and Vibrational Spectroscopy of Cu-chlorides and sulphates

3.1 Atacamite

Atacamite (Cu₂(OH)₃Cl) is a major component of the lower oxide zone at the porphyry copper deposit of Radomiro Tomic (Northern Chile) (Cuadra & Rojas 2001). This Cu-chloride and associated weak argillic alteration formed in situ during extensive oxidation of the secondary sulphide enrichment of the primary sulphide zone. Lateral migration of copper-rich solutions, accompanied by strong argillic alteration, led to further enrichment of copper in the upper oxide zone.

VNIR-SWIR reflectance spectra acquired with the HyLogging™ system from a natural sample that is partly covered with small atacamite crystals (< 1cm) show a broad absorption feature between 650 and 1600 nm (Figure 1). Electronic transition bands related to divalent copper in atacamite are located at 672, 971 and 1179 nm (Frost et al. 2010). In addition to the three electronic transition bands, a fourth absorption feature centred at around 928 is evident from the HyLogging™ spectra, which remains unassigned at this stage. Minor narrow absorption features in the 1400 to 1600 nm wavelength region can be assigned to overtones of the hydroxyl related stretching fundamental in atacamite, but could in this natural sample also be due to hydroxylated silicates, such as kandites, that are common components of argillic alteration in porphyry copper deposits.

Figure 1 Atacamite (Cu-chloride); band assignments according to Martens et al. (2003), Frost et al. (2010), and this work.

3.2 Antlerite

The Cu-sulfates antlerite (Cu₃SO₄(OH)₄) and brochantite represent together with atacamite and chrysocolla the primary oxide ores in the porphyry copper deposit of Chuquicamata, Chile (Ossandon et al. 2001). The Cu oxide formed during in situ oxidation of one or more supergene chalcocite horizons and can contain remnant chalcocite.

VNIR-SWIR reflectance spectra of a natural sample that contains layers of antlerite in between quartz and other supergene minerals display a broad absorption...
Geometallurgy

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Figure 1

A number of distinct features are evident in the 1800 to 2500 nm region, which is typically occupied by combination bands of hydroxyl-related fundamental stretching and bending vibrations. However, calculation of the wavelength position of the combinations bands from hydroxyl-group fundamentals of atacamite (Martens et al. 2003), suggest that only the absorption bands in the 2264 to 2381 nm region are related to the Cu-chloride. The remaining features are probably related to other hydroxylated silicates.

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VNIR-SWIR reflectance spectra of a natural sample that contains layers of antlerite in between quartz and other supergene minerals display a broad absorption

Figure 2. Antlerite (Cu-sulphate); band assignments according to Ruma Suba Reddy et al. (2002), Frost et al. (2010), Lane (2007), and this work.
feature between 700 and 1300 nm (Figure 2a). Electronic transition bands of antlerite are located at 910, 1060 and 1180 nm (Reddy et al. 2002; Frost et al. 2010). Narrow absorption bands at around 1430 and 1470 nm are tentatively assigned to overtones of the hydroxyl related stretching fundamentals in antlerite. A minor, but distinct feature at 1724 nm was allocated by Reddy et al (2002) to the bending vibration of the hydroxyl group bonded to Cu.

Similarly to the atacamite, a multitude of absorption features are observed in the 2100 to 2500 nm wavelength region. However, only the narrow absorption bands at 2243 and 2307 nm could be correlated to combinations of hydroxyl related stretching and bending fundamentals at longer wavelengths. The latter bending fundamentals are evident in the 11200 to 13300 nm region shown in the TIR spectrum (Figure 2b). In the displayed TIR spectrum, S-O stretching fundamentals can be identified at 8554, 8766 and 9056 nm, which is in agreement with band assignments by Lane (2007). However, the same wavelength region is populated by the Si-O stretching fundamentals, which will cause more ambiguous results in samples with lower amounts of Cu-sulphates and higher amounts of silicate mineral groups, such as kandites or feldspars.

4 Conclusions

Hyperspectral drill core scanning technologies, such as the HyLogging™ system have a sufficient spectral resolution to identify indicator minerals for hydrothermal alteration as well as subsequent oxidation based on their respective diagnostic absorption features. Reflectance Spectroscopy has the potential to rapidly characterise mineral assemblages across different ore domains of Cu porphyry deposits, requiring only simple sample preparation (i.e. clean and dry drill core surfaces). This rapid resource characterisation may allow the mining industry to better plan feeding of ore to different processing plants, which may impact on the overall budget of the mining operation.

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Classification of Geometallurgical Programs Based on Approach and Purpose

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Abstract. Geometallurgy is a rapidly developing holistic approach for combining geological and metallurgical information for production management purposes in mining operations. The industrial application of geometallurgy is called a geometallurgical program and one of the largest challenges within geometallurgical programs is to select appropriate methods for resource characterization. Aim of such characterization is the prediction of metallurgical performance of different ore types and geometallurgical domains with the required accuracy. More than 25 geometallurgical programs from mining operations around the world were reviewed and a classification system developed with aim to clarify how geometallurgy is used and what methods are applied. The result is summarized as a two-dimensional classification which illustrates what geometallurgical approaches are used and how collected data is applied. In addition the proposed classification system gives a perspective of what are the minimum requirements for a geometallurgical program at different levels of application and who are the main participants that should be engaged in a geometallurgical program. The classification system can also be used as a reference system for benchmarking of different geometallurgical endeavours.

Keywords. Geometallurgy, data model, classification, geometallurgical program, traditional approach, proxies approach, mineralogical approach.

1 Introduction

Geometallurgy has primarily emerged as a team-based approach (Bayraktar 2014) combining geological and metallurgical information for production management (Lamberg 2011). Application of geometallurgy is usually justified by high variability within the ore body (e.g., Kojovic et al. 2010; Williams 2013). Global decrease of mineral grades (Curry et al. 2013) and commodity price fluctuations contribute to the increasing demand for geometallurgy.

The implementation of geometallurgy at a mining project relies on the development of geometallurgical models first and then conducting a geometallurgical program. A geometallurgical program provides comprehensive knowledge of the geological variation within an ore body and how such variability affects the processing properties of the ore. If metallurgical variation is not considered, the utilization of the ore body remains deficient, whereas properly applied geometallurgy improves overall ore utilization results and lowers operational risks.

This paper reviews the approaches and aims of geometallurgical programs that are currently being carried out by industry in Europe, Africa (Fig. 1) and introduces a classification system. The classification system was developed as basis for benchmarking geometallurgical programs qualitatively and quantitatively. The aim for the classification system was to analyse the data structure and identify different ways to link geological information with metallurgical responses. Such approach will help to identify gaps in the methods applied in geometallurgy and thus show areas where development is needed.

2 Survey

An on-line survey was developed in order to collect information on geometallurgical programs and models used in different mines. The survey was sent globally to industry representatives and in addition data was collected through literature survey.

In addition to basic information such as deposit type, commodities and production volumes, survey was asking about the level of geometallurgical program, depth of implementation of the geometallurgical information and application of the collected geometallurgical data in details. A total of 27 cases were collected and used to develop the classification system described below.

3 Classification system

The classification system aims to answer two important questions regarding geometallurgical program in a mine:

- What type of data is used (approach)?
- How data is used (application)?

The two-dimensional classification system covering approach and depth of application is visualized in the table shown in Figure 1.

3.1 Geometallurgical approaches

The type of approach is defined by the type of data used in the geometallurgical program. Based on survey three different geometallurgical approaches could be distinguished: traditional, proxies, mineralogical.

In the traditional approach chemical assays form the basis of the program. Metallurgical response is calculated from the chemical composition of the ore collected by chemical assays. Simple recovery functions are used for this purpose, i.e. metal recovery is a function of chemical composition of the ore. Traditional approach is common for commodity types where grades are high. It is also a common method for the early stages of the mining projects, i.e. pre-feasibility study, feasibility study, mine commissioning. Often the development of geometallurgical program starts from traditional approach.
Proxies approach uses geometallurgical tests to characterize the metallurgical behaviour of ore in processing stages. Examples of geometallurgical tests are Davis tube (Niiranen and Böhm 2012) and Minnovex crusher index test (Kosick et al. 2002). Geometallurgical tests need to be applied early in the ore characterization in order to collect information on the ore variability (Mwangwa et al. 2015). Such tests are cheap and rapid, in comparison to laboratory scale metallurgical tests, and usually they do not require special equipment. They can be performed on samples of a small size and should reasonably well correlate with conventional tests and metallurgical results of the plant (Chauhan et al. 2013).

Mineralogical approach refers to program where geometallurgical model (i.e. deposit and process model) is built largely based on mineralogy. Often this means that accurate information on modal mineralogy is needed for the whole ore body (Lamberg et al. 2013). Thus, mineralogical data has to be quantitative and collection of information has to be continuous and systematic. Lund (2013) and Lamberg (2011) have demonstrated how geological model and process model can be linked using mineralogical information.

Referring to the approach as traditional, proxies or mineralogical depends on the traceable element (e.g., chemical element, mineral, grain, particle). And thus affects the sampling and analysis methods. Sampling frequency and types of tests used for defining metallurgical responses also vary between identified geometallurgical approaches.

### 3.2 Depth of application of geometallurgy

Depth of application is defined by how geometallurgical data is used in production management. Based on the survey eight levels were identified:

0. None - no geometallurgical data is collected and neither geometallurgical program nor geometallurgical model exists.

1. Collecting data - the geometallurgical data is collected systematically; however, it is not used for any production planning purposes or visualization of the information.

2. Visualization - the variability within the ore body is visualized based on the collected geometallurgical data.

3. Defining production constraints - geometallurgical data is used to define the feed quality constraints and production limitations for the process.

4. Forecasting production - geometallurgical data is used to forecast production.

5. Making changes in process based on feed quality - geometallurgy is used to plan changes to the process based on future variations in the feed.

6. Production planning - an accurate production plan is based on geometallurgical data.

7. Applying different production scenarios - decisions regarding investments, selection of alternative technologies, production interruptions (or production speeding up) are made based on application of geometallurgical data.

Levels from “zero” to “three” are considered to be passive and do not involve any production related actions. On the other hand, levels “four” to “seven” are considered to be active and may involve e.g., ore blending, selective mining, changing production flowsheet etc.

### 4 Selected examples

To clarify the classification few selected examples are described: Mikheevskoye (Russia), Kiirunavaara (Sweden) and Kemi (Finland) (Fig. 1).

#### 4.1 Traditional approach: Mikheevskoye porphyry copper mine

Mikheevskoye is a copper mine with reserves of approximately 400.0 million tonnes at 0.4% copper. The main ore mineral is chalcopyrite, but bornite is also present. Planned production is about 18.0 million tons of...
ore annually.

The mine applies traditional approach in their preliminary geometallurgical program. The domain geometallurgical model was established by Lishchuk (2014) in order to demonstrate the opportunities which exist within geometallurgy and create conditions for the reliable feed quality forecast. The model was developed during the ramp-up stage of the beneficiation plant. Thirteen geometallurgical ore types were identified by single copper cut-off of 0.2%, rock hardness, ore oxidation and magnetite content. The geological block model and assays of the samples collected from the freshly blasted blocks were the main sources for geometallurgical information.

Two alternative mining plan scenarios were developed and compared for the first five years of production. The first scenario was based solely on the head grade and the second one included ore domains. Scenario based on domains showed higher net present value than the head grade-based one. This is due to more accurate prediction of the production costs based on domains than on head grade.

The developed geometallurgical model would enable application even on scenario level, but at the moment the information is used only for visualization purposes. Although visualization level supports understanding of the feed variability for processing engineers, but additional laboratory tests would be required to define the metallurgical responses before applying the model on deeper application level. This will become both feasible and crucial at Mikheevskoye once molybdenum bearing ore is reached. This will bring up the question whether the concentrator plant should invest in a new production line for the production of molybdenum concentrate. This is clearly a decision where geometallurgy could lower the risk of unfeasible solution.

### Table 1. The minimum requirements for each application depth level

<table>
<thead>
<tr>
<th>Depth of application</th>
<th>Requirements</th>
<th>Data collected and used mainly by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collecting data</td>
<td>Geological data structure exists</td>
<td>Geologists</td>
</tr>
<tr>
<td>Visualization</td>
<td>Geological data model exists</td>
<td></td>
</tr>
<tr>
<td>Visualization / Defining production constraints</td>
<td>Ore properties stored in a numerical form (Software applied)</td>
<td>Geologists, processing engineers</td>
</tr>
<tr>
<td>Defining production constraints</td>
<td>Ore responses defined in a lab</td>
<td>Geologists, processing engineers</td>
</tr>
<tr>
<td>Defining production constraints / Forecasting production</td>
<td>Ore properties stored in a block model (possibility of domaining)</td>
<td></td>
</tr>
<tr>
<td>Make changes in process based on feed quality</td>
<td>Processing model exists for separate units/Liberation model known</td>
<td></td>
</tr>
<tr>
<td>Production planning</td>
<td>Production model exists</td>
<td>Geologists, processing engineers, mining and maintenance engineers</td>
</tr>
<tr>
<td>Applying different production scenarios</td>
<td>Production data stored in a block model</td>
<td>Geologists, processing engineers</td>
</tr>
<tr>
<td></td>
<td>Geometallurgical model is used as a part of real-time mining system</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Financial data stored in a block model</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Financial model exists and uses geometallurgical data as input</td>
<td>Geologists, processing engineers, mining and maintenance engineers, financial specialist</td>
</tr>
</tbody>
</table>

### 4.2 Proxy approach: Kuirunavaara iron mine

Kuirunavaara is an iron mine with estimated reserve of 666.0 million tons of ore and up to 69.0% iron grade (Niiranen and Böhm 2012). There are five ore types in Kuirunavaara, which are distinguished by iron and phosphorous content. Magnetite is practically the only ore mineral (Niiranen and Böhm 2012; Niiranen and Fredriksson 2012).

Kuirunavaara started to experience fluctuations of SiO$_2$ in the ore in 2007 and exploration drilling predicted increasing SiO$_2$ grade with the depth. This was forecasted to cause higher SiO$_2$ grade in the Fe concentrate, too. Therefore, a laboratory scale empirical method was developed by Niiranen and Böhm (2012) for predicting SiO$_2$ content of the Fe concentrate. The method was performed on drill core samples and included chemical assays, grindability and Davis tube tests. A predictive model was developed from the collected data. The model gives an estimate on the total energy demand of comminution and SiO$_2$ grade of the Fe concentrate for given ore, based on its chemical composition (Niiranen and Böhm 2012).

The Kuirunavaara mine currently applies a Proxies approach by reliance on Davis tube and grindability test; and geometallurgy is used for defining production constraints (SiO$_2$ grade).

### 4.3 Mineralogical approach: Kemi chromite mine

Kemi chromite mine in Northern Finland started production already in 1968 and current ore reserves include 33.0 million tons at 29.0% Cr$_2$O$_3$. Annual mill capacity is 2.7 million tons of ore. Kemi has two products. Upgraded lumpy ore with 35.5% Cr$_2$O$_3$ is produced by dense medium sink-float separation. Fine concentrate with 45.0% Cr$_2$O$_3$ is produced with gravity circuit applying spirals. Kemi sends both products to Tornio steel works for ferrochrome and finally stainless steel production. Mine and steel works production chain is integrated and mine needs to fulfil the requirements of
the Tornio works both in product quality and production amount of the two concentrates.

To answer the short and long term product requirements of the steel work, Kemi mine developed a geometallurgical program already in late 1990 (Leinonen 1998). The grain size of chromite varies in the deposit significantly and that has a large effect on processing. Therefore chromite grain size is measured in a systematic way from the drill core samples. Polished sections are prepared from drill core samples and the grain size distribution of chromite is determined with optical microscope image analysis. This information is fed into the ore block model. The grain size distribution of chromite is used to estimate how much lumpy ore and fine concentrate can be produced from the block and to forecast the expected recovery. Estimation is based on findings that the particle size after grinding follows the grain size of the original chromite in the ore. A nd that the recovery losses in the gravity separation are in the fine end (<80 microns) (Lamberg 2011).

In addition, an element to mineral conversion routine is used to convert elemental analysis by XRF to modal mineralogy. Modal mineralogy and texture information are used to create suitable blend for the plant to balance the production between two concentrates. Furthermore, certain processing parameters like specific gravity of dense medium used in the sink-float process get it setpoint values based on geometallurgical information.

Kemi uses mineralogical approach on a level where they adjust processing based on geometallurgical data (level 5 in Fig. 1).

5 Results and discussion

The data collected so far from geometallurgical programs is limited but some observations can be preliminary listed. There is a general trend in Fig. 1 that the deeper level geometallurgical programs use mineralogical approach. Traditional approach is used in shallow level and the proxy approach is applied in between. There is natural explanation for the observation. Development of geometallurgical program usually starts by using numerical data which is systematically collected with high data density; i.e. chemical assays on the drill core samples. This information in many cases is defective when developing metallurgical models since metallurgical response is related to mineralogy, not chemical composition of the ore. Therefore when geometallurgical programs go to higher level the use of mineralogical information increases.

The number of participants involved in the geometallurgical program would also change with the depth of the program (Table 1). The deeper level of geometallurgy corresponds to the deeper integration and cooperation between involved parts of the mineral production chain: i.e. processing plant, geology (exploration and production), mining, sales etc.

6 Conclusions

The classification system was developed in order to structure the data within a geometallurgical framework. The classification was based on geometallurgical approach and depth of application of the geometallurgy. Geometallurgical approach was defined by commodity, metallurgical tests and samples used. Depth of application was defined by purpose of the geometallurgy in a particular project.

This classification is a key element of the holistic vision of the geometallurgical program. It can be used to benchmark the geometallurgical projects.

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Determination of Chromite Composition from Multispectral Reflectance Measurements (400-1000 nm)

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Abstract. The relationship between the chemical composition and the multispectral reflectance values of chromite in the VNIR (Visible and Near-Infra-Red) realm is tested and mathematically analysed. Statistical tools as Pearson’s correlation coefficients, linear stepwise regression analysis and least-square adjustments are applied to two populations of data obtained from 14 selected samples of chromite: multi elemental microprobe analysis and multispectral reflectance values (400-1 000 nm). Results show that both data sets correlate, and suggest that the VNIR reflectance spectra can be used as a tool to determine the chemical composition of chromites.


1 Introduction

Reflectance measurements, unbiased by subjective color perceptions, assist the identification of ores with reflected light microscopy. Specular reflectances combined with Vickers microhardness determinations are keys to a widely known identification chart (McLeod and Chamberlain 1968). Further progress was achieved by the IMA / COM Quantitative Data File (Criddle and Stanley 1993). Recent developments expand the measured spectra to Near-IR wavelengths, aiming at the automated identification of ores by digital image analysis (§ 2.2, CAM EVA System).

However, rough mineral identification may coexist with a significant amount of uncertainty about the composition of the ore. Chromite is a typical example, as a member of the spinel family whose industrial use (and value) depends largely on its composition. The aim of this work is to test the possibility to determine chromite compositions optically. For this purpose, the VNIR spectra of selected ores with known compositions are compared, so that the relationships between specular reflectance values and composition can be analysed. Previous results on the spectral reflectance-compositional properties of spinels and chromites applied to remote sensing (Cloutis et al. 2004) suggest that this aim is reasonable.

2.12 Materials and Methods

Samples and Compositional Data

The ores were selected to cover an appropriate compositional range for natural chromites, from 14 samples described by Gervilla and Leblanc (1990) Proenza et al. (1999) Henares et al. (2010), González Jiménez et al. (2011) and Gervilla et al. (2012).

Analysed compositions cover a wide area in the Fe3+-free (or Fe3+-poor) base of the Haggerty (1976) spinel prism (Figure 1), thus allowing to check the role played by single major cations, or combinations of cations, in the reflectance of chromite. The scarcity of natural samples with Fe3+-free (or even Fe3+-poor) composition close to the FeCr2O4 and MgCr2O4 corners of the spinel prism hindered obtaining reflectance measures of these two Cr-rich regions. The only sample with Cr/(Cr+Al) > 0.8 (GK3A-1) contains significant amounts of Fe2O3 (9.36 wt.%). Although Fe2O3 can modify the reflectance of chromian spinel, the results obtained by Eales (1980) suggest that contents below 10 wt.% should not significantly alter the results expected in this study.

Chemical composition of chromite was determined by electron microprobe, using a CAMECA SX50 instrument in wavelength dispersive mode, at the Serveis Científico-Tècnics of the University of Barcelona (Spain). The analytical conditions were 20 kV excitation voltage, 20 nA sample current, and beam diameter of 3 µm. Counting times were 20 s on TAP/PET and 30 s on LiF crystals. ZAF corrections were corrected online. The following spectral lines were monitored: Mg Kα, Al Kα, Si Kα with the TAP diffraction crystal, Ti Kα and Cr Kα with the PET diffraction crystal, and V Kα, Mn Kα, Fe Kα, Ni Kα, and Zn Kα with the LiF diffraction crystal.

The calibration was performed using natural and synthetic standards: periclase (Mg), Al2O3 (Al), Cr2O3 (Cr), Fe2O3 (Fe), diopside (Si), rutile (Ti), pure metallic V, rhodonite (Mn), NiO (Ni), and sphalerite (Zn). Fe2O3 contents were calculated assuming stoichiometry. A total of 105 analysis of this type were performed over the fourteen above mentioned samples.
2.2 Measurement of VNIR Reflectances. The CAMEVA system

Multispectral reflectance measurements have been carried out with the CAMEVA System (Figure 2), jointly developed by UPM and AITEMIN (Castroviejo et al. 2009), and specifically designed for the acquisition of multispectral microscopic images in the visible and near infrared (VNIR: 400-1000 nm) range. It allows the capture of high-resolution multispectral images in units of absolute reflectance and the automated identification of ores (Castroviejo et al. 2010), based on their VNIR reflectances, which are compiled in the Data Base available at the IMA / COM web site (Castroviejo et al. 2014). Each ore is characterised by 13 reflectance values on 50 nm intervals from 400 to 1000 nm. Further information in Pirard (2004), Pirard et al. (2008) and Spanish patent no. 201130499, 2013.

![Figure 2. The CAMEVA System (School of Mines, UPM).](image)

2.3 Mathematical Analysis. Correlation of VNIR

Mathematical models have been designed to correlate multispectral chemical composition with multispectral reflectance values in each sample. The mathematical tools employed are classical statistical techniques like Pearson’s correlation coefficients, linear stepwise regression analysis and least-square adjustments. Statistical data processing was performed with the SPSS (v.20) package, developed by IBM Co. Theoretical treatment of this topic can be found in any classical textbook on statistical models (e.g. Freedman, 2009).

Figure 1. Samples plotted in the #Mg-#Cr plane.

The system has been conceived to perform automated image analysis and assess geometallurgical processes. It can also be used for multispectral characterisation of ores, as in the present case. A software application, specifically conceived to perform spectral analysis of minerals on acquired images, allows the operator to manually select rectangular regions of any size (≥ 1 pixel, i.e. 0.3 μm x 0.3 μm for a 20x objective) on grains appearing on the images. In each region the average multispectral reflectance is computed and stored as a line in a text file for subsequent statistical treatment. A total of 212 spectra (each comprising 13 measures at 50 nm intervals) were determined on the fourteen samples under consideration.

3 Results and Discussion.

3.1 Multispectral Reflectance Values as a Function of Composition

As a first step, a simple mathematical model was sought, able to predict the reflectance (R) measured at a wavelength λ. Of all models tested, the best results were obtained fitting by the least squares method curves of the type $R = a + b\lambda + c\lambda^2$, which in all cases gave coefficients of determination greater than 0.97 (Figure 3).

Following this path, the second step was to correlate the curve parameters a, b and c with the compositional elements of the analysed samples. After a multivariate linear regression analysis in stepwise modality, it was possible to correlate a with Al_2O_3, Fe_2O_3 and NiO, c with Cr_2O_3 and b as follows:

$$a = 23.018 - 0.169 \text{Al}_2\text{O}_3 - 0.372 \text{Fe}_2\text{O}_3 - 3.063 \text{NiO}$$

$$10^c = -0.739 - 690.608 b - 0.034 \text{Cr}_2\text{O}_3$$

where elemental contents are expressed in weight percent. For the parameter $a$ the relative error of this correlation is less than 2%, and 8% for c. So far, it is not possible to find a correlation of this type for the b coefficient. A rough approximation was to take the mean value of this parameter (-0.011) which has a standard deviation of 0.002. The reconstructed $R(\lambda)$ curves have relative errors regarding the experimental curves smaller than 6%.
Mathematical models have been designed to correlate VNIR under consideration.

Intervals) were determined on the fourteen samples of 212 spectra (each comprising 13 measures at 50 nm multispectral reflectance is computed and stored as a line pixel, i.e. 0.3 µm x 0.3 µm for a 20x objective) on grains manually select rectangular regions of any size (specifically conceived to perform spectral analysis of ores, as in the present case. A software application, can also be used for multispectral characterisation of image analysis and assess geometric processes. It tools employed are classical statistical techniques like reflectance values in each sample. The mathematical 2.2 Measurement of VNIR Reflectances. The Spanish patent no. 201130499, 2013. Information in Pirard (2004), Pirard et al. (2008) and available at the IMA / COM web site (Castroviejo et al. 2010), based on their VNIR of absolute reflectance and the automated identification capture of high-resolution multispectral images in units near infrared (VNIR: 400-1000 nm) range. It allows the of multispectral microscopic images in the visible and Multispectral reflectance measurements have been

## 3.2 Chromite Compositions Calculated from VNIR Values

Pearson’s correlations did not give any interesting values and only corroborated the well-known geochemical substitutions. From stepwise multivariate linear regression analysis some linear dependencies between Al2O3, Fe2O3 and NiO contents and reflectance were established:

\[
R_{400nm} = 17.824 - 0.120 \text{Al}_2\text{O}_3 - 0.180 \text{Fe}_2\text{O}_3 - 2.393 \text{NiO}
\]

\[
R_{700nm} = 15.522 - 0.097 \text{Al}_2\text{O}_3 - 0.084 \text{Fe}_2\text{O}_3 - 2.343 \text{NiO}
\]

\[
R_{1000nm} = 14.861 - 0.086 \text{Al}_2\text{O}_3 - 0.088 \text{Fe}_2\text{O}_3 - 2.498 \text{NiO}
\]

In all cases the coefficient of determination is greater than 0.9. Three samples (R-10, LG-21 and EN-8) were reserved as “control samples” and were not considered to build the models. In Figure 4 the calculated 400 nm reflectance values (based on compositions) are plotted against the measured values. The plot shows that the control samples (blue circles) are in accordance with the model, including sample R-10 (lowest left corner) which suggests that this correlation could also apply to a wider compositional field, approaching spinel (e.g. Cr poor, Al, Mg rich) compositions. For other wavelengths the plots obtained are very similar.

The behavior of FeO and MgO is quite different, and it does not fit any linear model. For these two elements it was necessary to use a quadratic model:

\[
R_{400nm} = 6.831 + 0.869 \text{FeO} - 0.022 (\text{FeO})^2
\]

with a determination coefficient of 0.500, and:

\[
R_{400nm} = 8.886 + 1.292 \text{MgO} - 0.062 (\text{MgO})^2
\]

with a determination coefficient of 0.760. These fits have been plotted in Figure 5.

## 4 Conclusions

VNIR spectra of chromite show significant variations. The major and minor element compositions of this ore mineral can also vary significantly in natural samples. Systematic analysis of both multispectral reflectance and multielement compositional values from 14 selected chromite samples covering a wide compositional area shows that both data sets can be mathematically correlated.

Although the limited sample size allows only preliminary conclusions and further data should be tested to fit a model of general validity, some significant trends have been disclosed, suggesting:
The correlation functions obtained allow the determination of compositional parameters from multispectral VNIR data, and vice versa.

The correlation between b parameter and chromite composition.

The differing relationships of reflectance with the contents of trivalent ions Al^{3+}/Fe^{3+} and of Fe^{2+}/Mg^{2+}.

The influence on reflectance of even small Ni^{2+} contents.

The possibility to build robust models of general validity correlating chromite composition with reflectance measures.

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1438 MINERAL RESOURCES IN A SUSTAINABLE WORLD • 13th SGA Biennial Meeting 2015. Proceedings, Volume 4
Mineralogical Controls on the Distribution of Antimony in a Base-Metal Flotation Test at the Rockliden Massive Sulphide Deposit, North-Central Sweden

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Abstract. The Rockliden Zn-Cu massive sulphide mineralisation shows elevated concentrations of critical elements. In particularly the presence of Sb in the Cu-Pb concentrate causes metallurgical challenges in the treatment of this flotation product. The Sb mineralogy at Rockliden is complex, comprising of four main Sb minerals. For this study one mafic dyke and three Sb-rich massive sulphide samples with different base-metal and Sb mineralogy were collected and subjected to a simplified flotation test. The Sb mineralogy of the flotation products was analysed using scanning electron microscope-based image analysis. The distribution of liberated and locked Sb minerals between the flotation products was studied using a particle tracking technique. A comparison of results from the different mineralisation types indicates systematic behaviour of specific particle types, pointing towards the predictability of distribution of the Sb minerals during base-metal flotation.

Keywords. Massive sulphides, antimony, mineral liberation, particle tracking.

1 Introduction

The Rockliden deposit is a Cu-Zn volcanogenic-hosted massive sulphide (VHMS-)type mineralisation located in north-central Sweden with an inferred mineral resource of 9.2 Mt with 4.0 wt% Zn, 1.8 wt% Cu, 0.4 wt% Pb and 48 g/t Ag (Minz et al. 2014; New Boliden 2014). Antimony (Sb) minerals form trace components in the VHMS-type deposit. The Sb mineralogy is complex and the main Sb minerals are tetrathedrite, boueinite, meneghinite-boulangerite, and gudmundite (Minz et al. 2013).

Although Sb is a minor to trace element at Rockliden, it is critical to the quality of products derived from processing of such ore. Typically, Sb grades of 0.1 to 0.3 wt% represent the lower limits for penalty charges on Cu concentrates sent to Cu smelters (Larouche 2001 and references therein). However, if Sb is extracted from the Cu concentrate, e.g. through alkaline sulphide leaching, it may be considered as a by-product that has technical applications such as alloy in lead (Pb) batteries (Anderson 2012; Awe 2013). Additionally, the Sb content of tailings ought to be considered as it has the potential to become an environmental hazard (Wilson et al. 2010).

Previous studies indicated that the complexity of the Sb mineralogy in massive sulphide, the mineral association and the degree of liberation influence the distribution of Sb between different flotation products (Lager and Forssberg 1990; Minz et al. 2013). The purpose of this study was to measure the distribution of Sb minerals into different flotation products by using SEM-based mineral liberation analysis as well as to evaluate mineralogical factors controlling the distribution by using a particle tracking technique. Results from the four tested feed samples are compared in order to demonstrate the systematic behaviour of the distribution of Sb minerals.

2 Methods

2.1 Drill core sampling and flotation test

Four sets of Sb-rich drill core samples were collected, representing two Zn-dominated massive sulphide ore types from the upper (UR-Zn) and lower (LR-Zn) part of the deposit, one Cu-dominated massive sulphide ore type (UR-Cu) and one mafic dyke sample (MD). Mafic dykes cross-cutting the massive sulphides were found to be rich in Sb (Minz et al. 2014). From each sample set, drill core intervals were selected based on similarities in the chemical composition and the Sb mineralogy. The selected drill core intervals belonging to a sample set were blended.

![Crushing, Assaying, SEM Analysis and Selection of Drill Core Samples](image)

**Figure 1.** Laboratory flotation test showing all sampled flotation products: Cu-Pb cleaner concentrate (Cu CC), Cu-Pb cleaner tailing (Cu CT), Zn cleaner concentrate (Zn CC), Zn cleaner tailing (Zn CT) and final tailing.
The blended composite samples (ca. 2kg) were ground with a laboratory rod mill to a P80 of about 50 µm (Fig. 1). The flotation test was conducted using a Magotteaux bottom driven flotation machine. Five flotation products were collected from each tested composite: a Cu-Pb cleaner concentrate (Cu CC), a Cu-Pb cleaner tailing (Cu CT), a Zn cleaner concentrate (Zn CC), a Zn cleaner tailing (Zn CT) and a final tailing (Fig. 1). All products were sieved into three size fractions (-20 µm, +20 to -45 µm, +45 µm) and chemical assays were obtained for each fraction by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at ALS Minerals Division, Piteå, Sweden. Further, about 10 g of each sample was separated from each size fraction for preparation of polished epoxy grain mounts by the Erzlabor, Helmholtz Institute Freiberg for Resource Technology, Germany.

2.2 MLA measurement and particle tracking

Analyses were carried out with a FEI Quanta 650F under the following analytical conditions: acceleration voltage of 25 keV and emission current of 10 nA. The grain X-ray mapping mode (GXMAP) was chosen for measurement with the Mineral Liberation Analyster (MLA) (Fandrich et al. 2007). MLA measurements were conducted at a pixel size of 0.75 µm/px, a minimum Quartz EDX-count of 2000 and a total particle count of >45000 (for samples of sieving fraction >20 µm) and >190000 (for samples of sieving fraction <20 µm). The MLA Suite 3.1.4 software was used for automated data acquisition and processing at the Geometallurgy Laboratory, Technische Universität Bergakademie Freiberg, Germany. The quality of the MLA analysis was checked against chemical assays.

The mineralogical composition of the feed was back calculated from the products of the four composites. Minerals distinguished by MLA were grouped to reduce the complexity in modal mineralogy. The distribution (recovery) of minerals and particles with different liberation classes was calculated with HSC Chemistry and mass balanced using a particle tracking technique (Lamberg and Vianna 2007).

3 Results

The modal mineralogy of the four composite samples is presented in Table 1. The main sulphide minerals are pyrite and sphalerite, followed by pyrrhotite in the Zn-dominated massive sulphide composites (UR-Zn and LR-Zn, Table 1), and by chalcopyrite with minor amounts of galena in the Cu-dominated massive sulphide (UR-Cu, Table 1). Non-sulphide gangue (NSG) comprises largely of silicates: quartz with minor amounts of plagioclase, muscovite, amphibole and chlorite group minerals. In the composite sample referred to as mafic dykes (MD, cf. Minz et al. 2014), the NSG is dominated by amphiboles.

The Zn-dominated massive sulphide composite samples are distinctly different in their Sb mineralogy. The UR-Zn composite is dominated by tetrahedrite and gudmundite and the LR-Zn composite is dominated by meneghinite and gudmundite (Table 1). The UR-Zn and UR-Cu composites have a similar Sb mineralogy. In the MD sample, Sb is dominantly hosted by meneghinite and bournonite.

### Table 1. Modal mineralogy of the composites (flotation feed).

<table>
<thead>
<tr>
<th>Composites</th>
<th>UR-Cu</th>
<th>UR-Zn</th>
<th>LR-Zn</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py</td>
<td>50.05</td>
<td>55.91</td>
<td>53.62</td>
<td>4.98</td>
</tr>
<tr>
<td>Sp</td>
<td>4.89</td>
<td>14.71</td>
<td>19.00</td>
<td>0.42</td>
</tr>
<tr>
<td>NSG</td>
<td>9.02</td>
<td>13.39</td>
<td>13.56</td>
<td>81.74</td>
</tr>
<tr>
<td>Po</td>
<td>14.30</td>
<td>7.88</td>
<td>9.05</td>
<td>0.44</td>
</tr>
<tr>
<td>Ccp</td>
<td>20.44</td>
<td>4.10</td>
<td>1.30</td>
<td>2.20</td>
</tr>
<tr>
<td>Gn</td>
<td>0.62</td>
<td>2.53</td>
<td>2.32</td>
<td>3.71</td>
</tr>
<tr>
<td>Tr</td>
<td>0.39</td>
<td>0.85</td>
<td>0.01</td>
<td>0.45</td>
</tr>
<tr>
<td>Bour</td>
<td>0.04</td>
<td>0.13</td>
<td>0.19</td>
<td>1.30</td>
</tr>
<tr>
<td>Mene</td>
<td>0.02</td>
<td>0.05</td>
<td>0.60</td>
<td>4.67</td>
</tr>
<tr>
<td>Gd</td>
<td>0.24</td>
<td>0.45</td>
<td>0.35</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Compared to the main sulphide minerals in UR-Cu, UR-Zn and LR-Zn, and the NSG in the MD composite, the Sb mineral grains are small (generally P80 < 30 µm) and show a relatively poor liberation in the flotation feed. The mode of occurrence of the two most abundant Sb minerals in the four feed samples is given in the left columns of the graphics in figure 2. Five to 10 wt% of gudmundite is locked with chalcopyrite and galena in binary particles of the massive sulphide composites (UR-Cu, UR-Zn and LR-Zn). The UR-Cu composite has a significantly higher chalcopyrite grade than UR-Zn composite (Table 1) and thus the amount of gudmundite locked with chalcopyrite was expected to be higher in the UR-Cu composite, but this was not observed comparing both composites (Fig. 2). It should be noted that the distribution (recovery) of gudmundite has a high standard deviation due to low grade of gudmundite (cf. Table 1). However, a lower amount of chalcopyrite is documented in the LR-Zn composite compared to the UR-Zn and the LR-Zn has a lower amount of binary gudmundite-chalcopyrite particle type.
Analyses were carried out with a FEI Quanta 650F under MLA measurement and particle tracking technology, Germany. Erzlabor, Helmholtz Institute Freiberg for Resource Preparation of polished epoxy grain mounts by the Minerals Division, Piteå, Sweden. Further, about 10 g of each sample was separated from each size fraction for atomic emission spectroscopy (ICP-AES) at ALS obtained for each fraction by inductively coupled plasma.

Flotation products were collected from each tested machine. Five composite: a Cu–Pb cleaner concentrate (Cu CC), a Cu–Pb cleaner tailing (Cu CT), a Zn cleaner concentrate (Zn CC), a Zn cleaner tailing (Zn CT) and a final tailing (Fig. 1). The flotation test was conducted using a Magotteaux bottom driven flotation machine. Five samples are distinctly different in their Sb mineralogy.

Table 1. Comparison of different particle types of the main Sb minerals in the flotation products. Number below the column shows the distribution (recovery) of main Sb minerals between the test products, feed = 100 %. The italic numbers next to the columns show the distribution (recovery) of specific particle types between the flotation products, italic number in parenthesis gives the standard deviation of the liberated Sb minerals. The standard deviation is based on the relative standard deviation = 100 / (NOP)^0.5 and estimated using bootstrap Monte Carlo simulation (NOP - number of particles of a specific particle type in a flotation feed and product). Abbreviations: B Ccp – binary with chalcopyrite, B Gn – binary with galena, B Sp – binary with sphalerite, B Py – binary with pyrite, B NSG – binary with non-sulphide gangue (silicates), for additional abbreviations see figure 1.
Although pyrite, sphalerite and silicates are major minerals in both composite samples, the amount of tetrahedrite, bournonite and meneghinite locked with pyrite and silicates is relatively low (Fig. 2). The only exception is the mafic dyke composite, where both meneghinite and bournonite are locked to a significant proportion with NSG, the main mineral group of this composite sample.

For the massive sulphide composites it was found that recovery for fully liberated chalcopyrite and galena is high in the Cu-Pb cleaner concentrate, generally above 90 w%. Similarly high recovery was documented for Cu- and Pb-bearing Sb sulphosalts, i.e. tetrahedrite, bournonite and meneghinite (Fig. 2). Only small amounts of the above mentioned minerals are found in the Zn cleaner concentrate and tailings, partly due to locking with sphalerite and silicates. The latter is particularly for material from the mafic dykes.

The distribution of gudmundite is different. For all massive sulphide composites only 33 to 37 w% of all gudmundite ends up in the tailings and a significant amount (14 to 28 w%) reports to the Cu-Pb cleaner concentrate (Fig. 2). Gudmundite locked with chalcopyrite or galena accounts for 5 to 10 w% of the gudmundite found in the feed, and more than 70 % of this particle type is recovered into the Cu-Pb cleaner concentrate (Fig. 2). Differing from other Sb minerals liberated gudmundite shows less selective behaviour during processing and its presence in Cu-Pb flotation can be partly attributed to slight hydrophobicity of the mineral.

4 Summary and Conclusion

The Cu- and Pb-bearing Sb sulphosalts, i.e. tetrahedrite, bournonite and meneghinite, are reporting largely to the Cu-Pb cleaner concentrate, as expected from previous studies on similar material (Lager and Forssberg 1990). The influence of locking with sphalerite, pyrite and silicates on the distribution into Zn cleaner concentrate and tailings was found negligible. Gudmundite shows preferred recovery into tailings but its behaviour is less selective than the Cu- and Pb-bearing Sb sulphosalts. The locking of gudmundite with chalcopyrite and galena was found to influence the distribution of gudmundite into the Cu-Pb cleaner concentrate.

This study indicates that there is systematic particle behaviour independent of the ore types from which the particles are derived. Using quantitative information on the particle behaviour, a metallurgical model for the distribution of Sb minerals in different associations and liberation classes can be built and implemented in a resource model. This would allow forecasting the Sb grade of the Cu-Pb cleaner concentrate, which in turn might help to evaluate an alternative treatment of this product, such as alkaline sulphide leaching (e.g. Awe 2013). However, this is cost intensive as the input of such a model would require the determination of modal composition of each geometallurgical domain, information on mineral associations and on the distribution of particle types.

An alternative model to the particle distribution model might be obtained through linking the behaviour of Sb minerals in the flotation test with the 3D distribution of rock and ore types in a process-adapted geological model. Rock- and ore-intrinsic parameters, i.e. proxies measuring, for example, the recovery, cannot be assumed to be additive and would need to be modelled using appropriate geostatistical tools (e.g. Dunham et al. 2007). Another challenge with such an approach would be the requirement of a reliable geological model, which has been found difficult to implement so far (Minz et al. 2014). However, a process-adapted geological model would allow evaluation of the abundance of mafic dykes within the mineralisation and their significance on the Sb distribution into tailings due to locking of Cu- and Pb-bearing Sb sulphosalts with NSG.

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Mineral Identification and Domain Characterisation using Two Automated Hyperspectral Core Logging Systems, Los Bronces Cu-Mo Porphyry Deposit

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Abstract. Acquiring adequate representivity of the mineralogical variability of an ore deposit is a recognised challenge for geometallurgical modelling. Automated hyperspectral core logging overcomes this through the rapid collection of contiguous infrared reflectance measurements for the objective and consistent logging of mineralogy in drill core or chips. This paper presents preliminary results from two automated hyperspectral core logging systems, the CSIRO-developed HyLogger-3 and Corescan's Hyperspectral Core Imager Mark III (HCI-3). Thirty-three metres of selected intervals sampled from multiple diamond drill holes across the Los Bronces Cu-Mo porphyry deposit, Chile, were assembled as a ‘composite virtual drill hole’ and scanned with both systems. Samples were selected to represent five alteration-related domains with predicted varying comminution/breakage attributes. Minerals identified from the shortwave-infrared (SWIR) data, collected by both core logging systems and confirmed by XRD analysis, include: muscovite (sericite), tourmaline, gypsum, chlorite, phlogopite/biotite and trace kaolinite and montmorillonite. Quartz and feldspar were also logged from the HyLogger-3 thermal-infrared (TIR) data. Domains were characterised based on the spatial distribution and intensity of one or more key minerals.

Future work will correlate the spectro-mineralogical results with breakage tests to investigate whether a fundamental relationship between rock hardness and drill core mineralogy can be established using hyperspectral core logging. Determining the hardness variability of a deposit reduces the risk and uncertainty of mill throughput and energy usage, leading to more efficient and profitable ore recovery.

Keywords. Hyperspectral, infrared, core logging, geometallurgy, HyLogger, Corescan, HCI-3, porphyry, domain, alteration.

1 Introduction

Drill core mineral characterisation is a key parameter required by geologists and geometallurgists for assessing the spatial distribution of an ore deposit’s mineral inventory. The drill core mineral information can be utilised to create ‘domains’ of similar mineral and rock characteristics with predicted processing behaviours. Incorporating the mineralogical domains in geometallurgical models can reduce the uncertainty and risk associated with ore processing and extraction.

Conventional logging of core or chips is critical for the recording of geological observations and typically involves the visual identification of the minerals present. This is a subjective procedure often yielding variable results amongst geologists. Established analytical techniques (e.g. petrography, MLA and XRD) provide very detailed, valuable mineral information but are expensive, can entail lengthy turn-around times and may require elaborate lab-based sample preparation and/or sample destruction.

Automated hyperspectral core logging is a tool that assists geologists by providing a rapid, non-destructive mineral analysis and imaging technique that scans the drill core or chips in their original trays. Sample preparation is minimal; the core needs only to be clean and dry. Based on infrared spectroscopy, the technique enables objective mineralogy to be logged ensuring consistency throughout a drill hole and across numerous drill holes within a deposit.

This paper presents preliminary results of the automated hyperspectral infrared logging of 33 m of diamond drill core from the Los Bronces porphyry Cu-Mo deposit for the purpose of mineral identification and domain characterisation. Data acquisition was undertaken using two commercially available, automated, infrared mineralogical core logging and imaging systems: the CSIRO-developed HyLogger-3 (Quigley et al, 2009) and Corescan’s Hyperspectral Core Imager Mark-III (HCI-3). The core logging systems and the mineralogical outputs are reviewed.

2 Los Bronces Cu-Mo Porphyry Mine

The Los Bronces mine is located 65 km north-east of Chile’s capital, Santiago at an altitude of 3,500m above sea level on the west side of the Andean Mountains. The mine is operated by Anglo American Chile.

Los Bronces is one of the world’s largest breccia-hosted copper-molybdenum porphyry related deposits and has been mined since 1864. Los Bronces produced 221,800t of copper and 948t of molybdenum concentrate in 2011. The existing ore reserve as of 31 December 2011, is 2.17 bt grading 0.62% Cu (11.5mt of contained copper) (Retrieved on 14 March 2015 from http://www.mining-technology.com/projects/los-bronces-copper-and-molybdenum-mine/).

New grinding, mineral transport and concentration facilities were implemented during a $2.8bn expansion project completed in 2011 increasing Los Bronces’ production capacity up to 400,000tpa.
3 Geology

The Los Bronces-Rio Blanco deposit is hosted by the late Miocene volcanic and volcaniclastic rocks of the moderately deformed Abanico Formation and weakly deformed Farellones Formation (Warnaars et al., 1985; Vergara et al., 1988; Serrano et al., 1996; Vargas et al., 1999; Hollings et al., 2005). This intrusion is strongly peraluminous, has a calc-alkaline composition with an alkali-calcic affinity and is largely composed of quartz monzonite and quartz monzodiorite (Warnaars et al., 1985).

Los Bronces has seven different coalescing breccias that formed after the main phase of the porphyry copper system. The nature of the breccia matrix is the most important distinguishing feature within the deposit and consists of varying amounts of quartz, tourmaline, specularite, pyrite, chalcopyrite, bornite, molybdenite, chlorite, anhydrite, sericite and rock flour (Warnaars et al. 1985).

Details of the geological setting and ore formation characteristics of the deposit are discussed in Warnaars et al. (1985), Serrano et al. (1996), Vargas et al. (1999), Frickkon (2005), Hollings et al. (2005), and Deckart et al. (2005).

4 “Composite Virtual Drill Hole” (CVDH)

A ‘composite virtual drill hole’ (CVDH) was physically created to combine drill core samples representative of the various Cu porphyry alteration zones/domains across the Los Bronces deposit into one dataset for testing and analysis (Figure 1). Drill core intervals were selected from pre-defined geological domains identified in the company database and further assessed on-site following inspection of the core and consultation with mine geologists. To maintain consistency, only samples from the dominant quartz monzonite lithology were selected for the CVDH.

The selected intervals represent five domains of the variable relationships between the quartz monzonite host-rock and hydrothermal alteration, including: weak, moderate and intense phyllic alteration, quartz vein and tourmaline breccia.

A 33 m long CVDH subset (42-85 m) was scanned by the HyLogger-3 and HCI-3 hyperspectral core logging systems.

5 Samples & Methodology

The collection of the HyLogger-3 data was undertaken by the Queensland Geological Survey in Brisbane, Queensland, Australia. The HyLogger-3 collects contiguous VNIR-SWIR (350-2500 nm) + TIR (6000-14,5000 nm) spectra within a ~14 mm x 10 mm field-of-view along a ‘profile’ line centred on the middle of the drill core, with a ~4 mm overlap between measurements. A total of 4276 spectra were collected from the 33 m long CVDH. For mineral identification and domain characterisation, this was reduced to 3456 spectra, following quality control pre-processing steps that involved the exclusion of non-geological spectra (e.g., wooden depth markers, tray ends and empty tray bases) from the HyLogger-3 dataset.

The HCI-3 data was acquired at a Corescan-hosting facility in Brisbane. The HCI-3 imaging spectrometer collects VNIR-SWIR (350-2500 nm) reflectance data in a 40 mm wide swath across the core at 500 um spatial resolution generating 150,000 spectra per metre, creating 2-3Gb/m. An estimated 4,950,000 spectra were collected from the CVDH.

![Figure 1. Composite Virtual Drill Hole log (QM: quartz monzonite, PHY: phyllic).](image)

Mineral interpretation of the HCI-3 data was carried out by Corescan using in-house proprietary software based on a Pearson’s Correlation type spectral matching routine of pure minerals found in the dataset, against every pixel. The HyLogger-3 data was analysed by the lead author using The Spectral Geologist-Core™ (version 7) software to create site-specific customised scalars to target each mineral’s diagnostic infrared absorption features based on polynomial-specific customised scalars and above minimum cut-offs.

To review the HCI-3 and HyLogger-3 results together, the Corescan HCI-3 relative abundance results were downsampl ed to 10 mm sample spacing and imported from an Excel spreadsheet into The Spectral Geologist-Core™ software.

6 Results and Discussion

The SWIR responsive hydroxyl-bearing minerals identified in the drill core from the HCI-3 and HyLogger-3 data were consistent and included: muscovite (sericite), chlorite, tourmaline, gypsum, phlogopite/biotite and trace kaolinite and montmorillonite (Table 1). The HyLogger-3 additionally acquired thermal infrared measurements from which anhydrous quartz/silica and feldspar were identified (Table 1). Results were confirmed by XRD.
Table 1. Minerals identified with the HCI-3 and HyLogger-3.

<table>
<thead>
<tr>
<th>Wavelength Range</th>
<th>Automated Infrared Mineralogical Core Logging System</th>
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<tbody>
<tr>
<td></td>
<td>HCI-3</td>
</tr>
<tr>
<td>SWIR</td>
<td>Major: sericite</td>
</tr>
<tr>
<td></td>
<td>Moderate: chlorite, gypsum</td>
</tr>
<tr>
<td></td>
<td>Minor: tourmaline, phlogopite</td>
</tr>
<tr>
<td></td>
<td>Trace: kaolinite and montmorillonite</td>
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<tr>
<td>TIR</td>
<td>NA</td>
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</table>

Domain boundaries as defined in the mine-site database were imported (Figure 2A) to compare with the spectro-mineralogical results and provide validation. Both hyperspectral core logging systems produced similar spatial distributions of muscovite/sericite (Figure 2B and C) and tourmaline (Figure 2D and E). A greater number of weak-tourmaline samples are presented in the HCI-3 data. However, after inspecting the linked HyLogger-3 spectra, many were identified as wood blocks and empty tray bases. Raising the lower limit of the cut-off in the algorithm would reduce the amount of false positives and improve the accuracy of the result. Some minor variations between the two sets of results can be accounted for by movement amongst the core pieces during transit between scanning facilities. Different value ranges for the colour coded intensity values are attributed to differences in the algorithms and do not impact the interpretation. Warm colours infer greater abundance, cool colours infer lower abundance.

A key observation between the results of the two core logging systems is the domain mineral characterisation and spatial extent is largely consistent, despite the significant difference in the number of spectra collected. Muscovite/sericite is ubiquitous in the dataset with the exception of a narrow tourmaline-rich interval at ~60-61 m. The mine-site logged weak, moderate-intense and intense phyllitic alteration domains were spectrally discriminated based on the relative changes in muscovite abundance/intensity, respectively increasing. Within-domain variations are also evident and may prove useful for further domain subdivision or boundary revision.

The tourmaline breccia domain 7 (61.1-64.6 m) also contained significant muscovite/sericite + quartz + minor tourmaline + biotite/phlogopite (not plotted). Quartz was identified throughout most of the CVDH in low-moderate abundance from the HyLogger-3 thermal infrared data. The highest abundance quartz-bearing samples define the quartz-vein domain (Figure 2F). The deeper part of the quartz-vein domain also contained highly abundant tourmaline, significantly more than the tourmaline-breccia domain, occurring as pervasive tourmaline intimately mixed with quartz.

The tourmaline-breccia in Domain 7 is dominated by the clast supported sericitised breccia, with significantly less tourmaline occurring as cement in the matrix.

Figure 2. All HyLogger-3 samples coloured by imported Domains 4-8 boundaries. B, HyLogger-3 muscovite/sericite spatial distribution, coloured by intensity. C, HCI-3 muscovite spatial distribution, coloured by intensity. D, HyLogger-3 tourmaline spatial distribution, coloured by intensity. E, HCI-3 tourmaline spatial distribution, coloured by intensity. F, HyLogger-3 quartz spatial distribution, coloured by intensity.

The muscovite and feldspar (not shown) interpreted results display an inverse spatial correlation to each other, with greater muscovite in the moderate to intense phyllitic alteration domains and greater feldspar in the weakly altered domains, where the primary mineralogy of the quartz monzonite prevailed. The inverse correlation of muscovite and feldspar could be used in future work for creating a metric related to alteration intensity based on mineral replacement that could potentially relate to rock hardness.
The textural context of the mineral results also needs to be taken into consideration when attempting to define geometallurgical domains. The depth registered high resolution imagery acquired by both systems, permits the spectro-mineralogical results to be viewed along with the drill core imagery. Information on the distribution of the mineralogy can therefore be observed and context provided answering questions such as - is the tourmaline in the matrix, veins or clasts? The HyLogger-3 imagery can be viewed in TSG-Core with the mineral results loaded as logs adjacent or below the core imagery. The imaging nature of the HCl-3 spectrometer enables the mineral results to be essentially viewed in situ, overlain on the core imagery where the inter-relationships between the mineral results can be observed. Algorithms to automate the extraction of textural information from the drill core imagery are a desired improvement and are currently being investigated by the developers of both the HyLogger-3 and HCl-3.

7 Conclusion

This preliminary review of Corescan’s HCl-3 and the CSIRO-developed HyLogger-3 has demonstrated the application and utility of both automated hyperspectral core logging systems applied to mineral identification and domain characterisation for the development of appropriate geometallurgical flow design.

Minerals identified from the SWIR data collected by both core logging systems and confirmed by XRD analysis include: muscovite (sericite), tourmaline, gypsum, chlorite, phlogopite/biotite and trace kaolinite and montmorillonite. Quartz and feldspar were also logged by the HyLogger-3 TIR data.

Domains were characterised based on the spatial distribution and intensity of one or more key minerals. Within-domain variations were also logged that may prove useful for further domain subdivision or boundary revision.

Three main differences between the automated hyperspectral core logging systems are:
1) Wavelength range. In addition to the VNIR-SWIR spectral range common to both systems, the HyLogger-3 also has a thermal-infrared (TIR) capability necessary for logging anhydrous minerals (e.g. feldspars, quartz) and thus provides a more comprehensive suite of drill core mineralogy.
2) The ‘imaging’ nature of the HCl-3 spectrometer enables the VNIR-SWIR mineral results to be viewed in situ overlain on the drill core imagery where inter-relationships between various minerals can be observed.
3) Data delivery. HCl-3 drill core data is retained by Corescan and interpreted results made available via a secure online web delivery service. HyLogger-3 data (spectra and drill core imagery) is owned and retained by the client for in-house or consultant-based analysis and interpretation within the commercially available TSG-Core software.

The spectro-mineralogical results are generated in preparation for more detailed studies on predictive comminution and geometallurgical modelling using automated hyperspectral core logging.

Acknowledgements

The authors would like to thank the staff at Anglo American Chile particularly Marcelo Rocha, Claudia Castillo and the Geometallurgy department at the Los Bronces mine. Also Lew Whitbourn and Peter Mason from CSIRO; Andy Green from OTBC Pty Ltd; Kathryn Conroy, Ronell Carey and Neil Goodey from Corescan Pty Limited; Sural Gopalakrishnan from the Queensland Geological Survey and Malcolm Powell and Cathy Evans from JKMRC, Sustainable Minerals Institute at The University of Queensland.

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1446 MINERAL RESOURCES IN A SUSTAINABLE WORLD • 13th SGA Biennial Meeting 2015. Proceedings, Volume 4
Ore Fragmentation Modelling for the Evaluation of the Liberation Mesh Size

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Abstract. For mineral processing, an ore can be defined as the assemblage of useful mineral grains and gangue mineral grains. The first step of ore mineral processing involves crushing the material in order to achieve required mineral liberation. When it is achieved, in the ideal case, resulting fragments are formed: 1) only by useful minerals or 2) only by gangue minerals. This work consists to develop a numerical tool to determine the liberation mesh size of a given ore. With this aim, 1) a sample of the considered ore is modelled by a binary 3D image segmentation. Then, 2) a grinding process is modelled by a digital approximation of a Voronoi tessellation of the image, with random seeds. Each Voronoi cell represents a fragment of the ground ore sample. Fragments must meet several conditions so that they reproduce the characteristics of the crushing products in the mineral industry (e.g. the particle size distribution must follow a Rosin-Rammler law and the shape of the fragments must be close to spheres). This modelling allows obtaining the characteristics of the liberation mesh size. This is an important parameter to evaluate the feasibility of a mining project because the grinding operations are very expensive. This study would: 1) to evaluate and predict grinding costs from the bulk ore texture and 2) to provide an assessment tool downstream of the means of current observations and conventional analysis.

Keywords. Liberation mesh size, modelling, Voronoi cell, grinding.

1 Introduction

For mineral processing, an ore can be defined as the assemblage of useful mineral grains and gangue mineral grains. The first step of ore mineral processing involves crushing this material in order to achieve required mineral liberation. The liberation mesh size of a mineral is the size below which a mineral particle is completely liberated, that is to say only constituted of mineral species to value (Fig. 1). In general, the mineral industry tolerates 20% of mixed particle (i.e. fragments compounded of useful minerals and gangue minerals) (Blazy 1970) but this depends on the commodities and cases. Obtaining the liberation mesh size is an important parameter to assess the feasibility of a mining project. The grinding operations are very costly in energy. Up to 70% of the expensed energy in a mine can be used for grinding. The evaluation of the minerals characteristics (size of each particle, average of particle size, particle shape, present minerals, modal mineralogy, chemical composition of minerals, distribution of valuable element between minerals, texture (grain size, mineral association), degree of liberation by size, associated minerals in particles, ...) is important to achieve the best possible treatment (Kelly and Spottiswood 1982; Gy 1967). But a rigorous description of such a product is time demanding and costly in evaluation and characterization of the resource.

The purpose of this work is to evaluate a liberation mesh size estimation to quantify the particle size of the ore in the early stages of mineral exploration, i.e. at the time when the samples of the studied mineralization have a volume at most some cubic decimeters.

Figure 1. Schematic ore fragmentation. The top image represents the bulk ore with useful minerals (in black) and gangue minerals (in white). The three other images correspond to successive stages of fragmentation. Down, the ideal liberation of the useful minerals is achieved.
2 An approach for the modelling of liberation mesh size

Theoretical studies on the particle size of fragmented ore have highlighted the role of some parameters: shape factor, particle size distribution parameter, and texture of the initial product (i.e. bulk ore). A model of mineral liberation must take into account these characteristics. In other words, we state that if these characteristics evaluated on a numerical model are the same as that of a real crushed sample, this grinding model can be considered as satisfactory.

2.1 Shape factor

The shape factor is defined using the opening d of the smallest square mesh of the sieve capable of passing the fragment (Gy 1967). For ground products of the mineral industry, the shape factor ($f = \frac{\text{volume of the particle}}{d^3}$) measures the deviation from a cubic shape (Gy 1967). The study of many crushed ores showed that for a fragment, f is usually close to 0.5 (Gy 1967), i.e. the shape of the fragments is close to sphere. In addition, the f parameter varies little from one mineral to another and for a given mineral, of a size to another (Gy 1967).

2.2 Particle size distribution parameter

It is useful to adjust the experimental data of the particle size measures to an analytical function. It consists in building a curve from mathematical functions and adjusting the parameters of this function to be closer to the experimental curve. These parameters will be handled so that the calculations with this function were easier than the calculations on experimental data. Different models are used for adjusting the particle size distributions (Allen 1981; Peleg 1996; Ouchterlony 2005). The most widely used model for the case of particle size data from the mineral industry is the Rosin-Rammler function. The model of Rosin-Rammler can be considered as a Weibull distribution (Patel 1976; Outal 2006).

The particle size distribution parameter was defined as $g = \frac{d_{95}}{d_5} > 4$ for many ores (Gy 1967).

2.3 Texture of the bulk ore

In this study, we developed a new approach to model ore grinding and determine the liberation mesh size. Ore images were obtained by X-ray microtomography which is a nondestructive imaging technique that provides 3D images of the interiors of materials (e.g. Rozenbaum and Rolland du Roscoat 2014). Each voxel in the 3D image was characterized by its grey level (ranging from 0 to 255 for an 8-byte image), which depended on the X-ray attenuation coefficient of the element. This attenuation coefficient depends on material density and on the atomic number of the components. In other words, at each space position of the 3D image, a grey value corresponds to a given phase (gangue and useful minerals).

Prior to model grinding, the different phases have to be distinguished that is known as the segmentation step.

Segmentation is the process of partitioning the grey level voxels of the 3D image into distinct phases. Due to noise inherent to image acquisition, a preprocessing step was firstly applied consisting in a noise reduction (filtering). This preprocessing step was followed by a thresholding step (see Le Trong et al. 2008 for more details). As a result, the segmented 3D image is transformed to a binarised image as shown in Fig. 2. The ore used for this study is hosted in Aptian carbonate formations of the northern Spain from Reocin (MVT deposit type). Therefore, in white is represented dolomite and marcasite (gangue phase) and sphalerite and galena in black (useful minerals).

2.4 Fragmentation model

Outal (2006) has observed that its processed image shows particles of a fragmented rock whose particular shape can be assimilated to a Voronoi diagram (Fig. 3). Therefore, for this study, we propose to model grinding results by 3D Voronoi cell paving. Voronoi diagrams represent distance relationships between objects. All Voronoi regions are in shape of polyhedra and convex (Fig. 3) that looks like fragments from grinding in mineral industries. The grindability of all the ore component phases is considered identical.

Figure 2. 2D images extracted from 3D binarised images. A. image rich in useful mineral; B. image poor in useful mineral. The gangue phase is in white (dolomite and marcasite) while the useful mineral is in black (sphalerite and galena).
2.2 Particle size distribution parameter for a given mineral, of a size to another (Gy 1967). The parameter varies little from one mineral to another and the shape of the fragments is close to a sphere. In addition, the study of many crushed ores showed that for a given phase (gangue and useful minerals), the shape factor, particle size distribution parameter, and texture of the ore depend on the material density and on the attenuation coefficient of the element. This attenuation coefficient depends on X-ray absorption coefficients for different elements (Rammler distribution).

2.1 Shape factor

The particle size distribution parameter was defined by Rosin-Rammler (Fig. 3) that looks like fragments from grinding in the real crushed sample, this grinding model can be handled so that the calculations with this function were easier than the calculations on experimental data. Different models are used for adjusting the particle size data from the mineral industry. The most widely used model for the case of liberation mesh size is the Rosin-Rammler distribution. The results are encouraging.

3. The proposed liberation model

To model the liberation mesh size, we numerically grind the 3D binary image of bulk ore with 3D Voronoi cells up to the liberation mesh size (Fig. 4). For this, we must take into account: 1) the texture of the ore; 2) grinding; 3) the edge effects.

To build the Voronoi cells, a set of random points is generated within the 3D binary image (Fig. 5). These points are called germs. Then, a computer code developed by authors allows Voronoi cell formation (cells expand until they touch other cells in each direction in space). This simulates the grinding as each dilated cell forms a fragment. For each fragment, we get its size, its useful mineral content and its shape factor. Note that the density of germs controls the shape of the granulometric curve. The edge effect is controlled by removing all the cells that are on the boundary of the image.

From a real bulk ore, we choose two binary 3D images: one rich in useful mineral and the other one poor in useful mineral (Fig. 2). For each image, we generate several quantities of germs (10000, 50000, 100000 and 200000) (Fig. 5). For each amount of germs, we study the size distribution of all fragments and the size distribution of fragments having at least 80% of useful mineral (obtaining practical liberation mesh size) (Fig. 6). These distributions are, in fact Rosin-Rammler distributions.

To validate our breakage ore model, we will compare the results of the modelling work with real measurements on mining product during grinding in the Reocin mine. This will validate the model or change it if it does not describe well enough the reality.

4. Conclusion

The purpose of this study is to make an estimate of the liberation mesh size with the data available in the early stages of mineral exploration. This is to allow estimating the energy cost of grinding to liberation mesh size and provide an assessment tool downstream current means of observation (HyChips, Qemsca, X-ray tomography) and conventional analysis. For this, we simulated a bulk ore grinding from Voronoi cells. The particle size distribution of these fragments is similar to a Rosin-Rammler distribution. The results are encouraging.

The ultimate goal of this study is to build a 3D diagram in which the particle size curve and for each size fraction, the liberation degree within the particle size fraction, are plotted.
An opportunity of improvement for this work is the introduction of preferential fragmentation i.e. the grindability of the different phases constituting the ore is no longer considered to be identical.

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QEMSCAN® Applied to Zn(Pb) Nonsulfide Ores: Advantages and Limitations

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Abstract. The mineralogy of supergene Zn(Pb) nonsulfides is difficult to characterize, due to the complex association of mineral species in these deposit types. Since these ores are commonly treated by hydrometallurgy, the lack of accurate mineralogical results can cause several problems in both processing and metallurgical stages. QEMSCAN® analyses have been carried out, in order to improve accuracy of nonsulfide ores characterization, in term of mineralogy, petrography, chemistry and quantitative amount. Three nonsulfide deposits with different grades of mineralogical complexity have been considered for this purpose: Hakkari Zn(Pb) in Turkey; Jabali Zn-Pb(Ag) in Yemen; Reef Ridge Zn in Alaska. Previous studies, which used traditional analytical methods were used as a basis to develop the QEMSCAN® analytical routine for the three deposits. The QEMSCAN® study, though confirming the main findings of previous research, has also added new information (i.e. the amount of trace elements, amorphous phases, impure phases etc.) that traditional technologies were not able to provide. SEM-EDS validation analysis was also necessary, in order to avoid misleading data. In conclusion, it was possible to understand the advantages and limitations of using the QEMSCAN® method for the choice of the best routine during feasibility study.

Keywords. Supergene nonsulfides Zn(Pb), Hakkari, Jabali, Reef Ridge, mineralogy, QEMSCAN®.

1 Introduction
Supergene Zn(Pb) nonsulfide deposits form from the oxidation of sulfide-bearing concentrations by meteoric waters (Hitzman et al. 2003). Their mineralogy, generally consisting of an association of many mineral species (i.e. Zn/Pb-carbonates, Zn-(hydr)oxides, Fe-(hydr)oxides, Fe/Pb-sulfates, Zn/Pb-phosphates and remnants of primary sulfides), is complex to characterize. For this reason, the economic value of nonsulfide zinc ores is strictly dependent not only on the geological knowledge of each deposit, but also in the specific characteristics of its mineralogical association (Bonì and Mondillo 2015). The mineralogical characterization of these deposits types, the definition of the mineral association, their textural parameters, and the element deportment, are all very important issues to predict the metal (Zn-Pb) recovery, and hence the sustainability of an orebody. Accurate and reliable information is needed to avoid misleading data that can cause several problems in the processing and metallurgical stages (recovery issues, penalties at the smelter, poor metal quality, and environmental damage).

The best methods known so far to characterize an orebody from the quantitative point of view, are “Automated Mineralogy" technologies such as QEMSCAN® (Quantitative Evaluation of Minerals by Electron Microscopy), which allow accurate information about several ore parameters to be obtained: modal mineralogy, element deportment, particle images, mineral association, theoretical grade recovery, shape and particle size and mineral liberation. This technique has been only sporadically used for the characterization of nonsulfide ores: the first published attempt was carried out on the Accha prospect (Peru) (Rollinson et al. 2011). Here we report the application of QEMSCAN® technology on three mineralogically different nonsulfide Zn(Pb) deposits: Hakkari Zn(Pb) in Turkey; Jabali Zn-Pb(Ag) in Yemen; Reef Ridge Zn in Alaska. These deposits were already subjected to mineralogical, petrographic and geochemical characterization by more traditional analytical techniques (OM, CL, XRD, SEM-EDS, WDS, ICP/MS). This study was carried out partly as a PhD Thesis by L. Santoro at the University of Napoli Federico II (Italy).

The Hakkari nonsulfide zinc deposit (estimated resources of about 10 Mt @ 15% Zn, MSA Group Ltd., 2013) is situated at the southeastern border of Turkey, ~60 km east of Hakkari and Sirnak Provincial boundary. The ore concentrations, mainly consisting of smithsonite and hemimorphite, mixed with Fe-Mn-(hydr)oxides and remnant sphalerite, are hosted in Jurassic carbonate rocks (Cudí Group) within the northern border of the Arabian Platform (Santoro et al. 2013). The Jabali Zn-Pb(Ag) nonsulfide deposit (resources of about 8.7 Mt @ 9.2% Zn, ZincOx resources plc. 2007) is located about 110 km east of Sana'a (Yemen). The rock hosting the ore is a dolomitized carbonate platform of the Jurassic Shuqr Formation (Al Ganad et al. 1994). Smithsonite is the most abundant economic mineral in the nonsulfide deposit, and is associated with minor hydrozincite, hemimorphite, acanthite and greenockite. Cerussite and anglesite also occur as main lead minerals. Goethite, hematite, and Mn-(hydr)oxides are common in the mining area; Ag-sulfide and native silver are also present locally (Mondillo et al. 2014). The small Reef Ridge prospect is located in the Yukon-Koyukuk region of west central Alaska (USA), hosted in Devonian carbonate rocks of the Farewell Terrane (Decker et al. 1994). The most abundant Zn mineral is smithsonite, replacing both sphalerite and the host carbonates, and also occurring as cement in vugs and fractures.
2. Materials and methods

Quantitative phase analysis (QPA) has been carried out on representative core samples of the three deposits, by using the QEMSCAN® technology. The samples (10 for Hakkarı, 20 for Jabali and 8 for Reef Ridge), each one corresponding to ~1 m long core interval, have been selected on the basis of their higher Zn content. About 1–2 g of sieved material from each sample was prepared into resin, to obtain ~3 cm² diameter blocks, which were polished and carbon-coated. QEMSCAN® fieldscan analytical mode (Gottlieb et al, 2000, Pirrie et al. 2004; Goodall and Scales 2007), produces distribution maps of the mineral phases, and allows the development of a customized database. This provides in turn statistical information on the particles, grain sizes, mineral association and quantitative analyses for each sample. The analyses were carried out using a QEMSCAN® 4300, with settings as described in Rollinson et al. (2011). The image resolution used for each sample was 10 µm. The modal mineralogy is expressed in mass %. The formulation of a Species Identification File (SIF), a list of mineral species identified for their distinct chemical composition (inferred mineralogy), was necessary to discriminate among the mineral species. Many entries were added to the SIF files on the basis of the chemistry: common minerals, nonsulfide minerals previously detected with more traditional techniques (Santoro et al. 2013, 2014; Mondillo et al. 2014; Santoro et al. 2015), as well as several ore compounds and other minerals detected by QEMSCAN® for the first time. Validation measurements were performed at the Camborne School of Mines, on a Zeiss EVO 50 SEM with Bruker 4010 EDS SDD detectors, and with Bruker Esprit software.

3. Results

QEMSCAN® analyses were carried out on several core samples of the three deposits (Fig. 1), whose mineralogical and petrographic characterization had been already carried out with traditional methods. The previous studies were used as basis to set the QEMSCAN® route, and SEM-EDS validation analyses were also used to confirm the QEMSCAN® main findings. QEMSCAN® analyses generally confirmed the previous results, but also added new accurate information on the mineralogy, element deportment, texture, mineral association and quantitative amount of each phase.

3.1. Hakkarı

QEMSCAN® analyses on the Hakkarı core samples confirmed in part the main findings of Santoro et al. (2013), and added some new information. Calcite host rock at Hakkarı is less abundant than the mineralized samples chosen for QEMSCAN® analysis. It occurs essentially as two main phases: as almost pure calcite (up to 12.96 wt.%), and as Cd-calcite (very rare), Dolomite is scarce in the whole deposit, but can reach locally up to 7.60 wt.%. Fe-dolomite and Zn-dolomite were also detected, but in very low percentages (maximum up to 1.56 wt.%). Smithsonite ranges from a few percent, up to 57.41 wt.% (Fig. 1).
3.2 Jabali

QEMSCAN® analyses confirmed the occurrence of the mineral phases already detected by Mondillo et al. (2014), but also added new data about mineral compounds not previously identified. The dolomite host rock occurs essentially as two main phases: as almost pure dolomite (from few wt.% up to 68 wt.%), and as Zn-dolomite (up to 20 wt.% ZnO), which appears to be a widespread phase (up to 44 wt.% throughout the deposit. Smithsonite, locally Mg-enriched, generally occurs in pores of the host rock, in major vugs, and/or at the border of weathered sphalerite. Galena is surrounded by secondary phases, whereas the Fe-Mn-(hydr)oxides are either scattered throughout the host rock, or concentrated in small veins. Minor Zn-Mn- and Fe-dolomite with an average concentration of ~5 wt.% was also detected. The main Zn-mineral at Jabali is smithsonite (up to 79 wt.%), (Fig. 1) followed by Zn-dolomite, Mg-smithsonite, Fe-(hydr)oxides and cerussite/anglesite. Mg-smithsonite (up to 15 wt.% Mg) occurs in variable amounts, generally from a few wt.% up to 16 wt.%. Sphalerite and galena are locally present (up to 12 wt.% and 8 wt.% respectively). Sphalerite is commonly rimmed by replacement smithsonite. Galena is locally surrounded by thin layers of acanthite and chloroaragrite. Cerussite/anglesite, Zn-clays, Fe-(hydr)oxides also containing Zn (up to 10-20 wt.% Zn) can be locally abundant. Minor amounts of haetaerolite, chalcopyrite and coronadite, calcite and quartz have also been detected. Smithsonite is mostly associated with Mg-smithsonite and Zn-dolomite and in minor amount with Fe-(hydr)oxides and Zn-enriched Fe-(hydr)oxides. Nevertheless, even though dolomite is the main host mineral, its association with smithsonite is quite low. Zn-clays, where present, commonly occur with smithsonite. Cerussite/anglesite, sphalerite, calcite, chalcopyrite, haetaerolite and coronadite, are also associated with smithsonite.

3.3 Reef Ridge

In the case of Reef Ridge, QEMSCAN® analyses allowed the calculation of modal mineralogy of the economic and gangue minerals, the definition of their distribution and mineral association and accurate information on Zn deportment. QEMSCAN® analyses showed that the most abundant Zn mineral is a rather pure smithsonite (up to ~62 wt.%). The main gangue mineral is dolomite (Fig. 1), which can be pure (up to ~58 wt.%), or contain Fe (~5 wt.%), and/or Zn (~10 wt.%); Fe-dolomite and Zn-dolomite were also quantitatively analyzed (up to a maximum value of ~3 wt.% and ~15 wt.% respectively). Fe-(hydr)oxides, and Zn-bearing Fe-(hydr)oxides (Zn=10 wt.%) are relatively abundant (up to a maximum of ~54 wt.%). Minor phases (muscovite, kaolinite, chlorite, jarosite/coquimite, K-feldspar, plagioclase) were also detected. Smithsonite is mostly associated with Zn-dolomite and Fe-(hydr)oxides, and with Zn-enriched Fe-(hydr)oxides as well. Minor kaolinite (up to ~5%) and muscovite (up to ~6%) are locally present together with smithsonite.

4 Discussion and conclusions

QEMSCAN® has been substantiated as a very useful analytical technique for nonsulfide ores, as it allows:

a) the definition and quantification of all the minerals present in the deposit (also those occurring in very low amounts or traces);

b) detection and quantification between "pure" and "impure" mineral phases, which is not possible with traditional methods (i.e., Fe-dolomite, Zn-dolomite);

c) to obtain the average abundance of the element deportment in the minerals;

d) to distinguish and quantify the amorphous phases on the basis of their chemical composition (i.e., Santoro et al. 2013, detected quite high percentages of not-well identified amorphous phases in the Hakkari samples. QEMSCAN® revealed that they are a mixture of jarosite/pyrite/Fe-hydroxides).

Moreover, QEMSCAN® is a valuable method of image analysis. In fact, one of its biggest advantages is the possibility to build, contemporaneously to the QPA analyses, several maps of the sample, in which each color corresponds to a mineral or to a mineral compound. In this way, it is easy to observe synoptically the occurrence and position of most minerals. Additional information that can be gained with QEMSCAN® is the mineral association, which is very useful to predict Zn(Pb) recovery, as it shows with which minerals, and how frequently the economic phases are related to the non-economic ones. From this information, hence, it is possible also to determine the processing options for the preliminary concentration of zinc/lead-bearing minerals, thus identifying potential processing problems. For example, in the Jabali ore, the QEMSCAN® analyses revealed that Zn-dolomite is strongly associated with smithsonite, hence it is impossible to recover the zinc trapped in the dolomite lattice, with current extractive technologies. However, despite QEMSCAN® being a valuable method to obtain an accurate characterization of nonsulfide ores, some limitation were identified during the analyses. These are briefly summed here:

a) QEMSCAN® is not able to discriminate between minerals with similar spectra (i.e., smithsonite/hydrozincite/zincite, hemimorphite/willemitie) because of its 1000 counts per spectra, which is inadequate to distinguish between minerals that differ only by their light element content (Rollinson et al. 2011). Moreover, the X-ray detection signals for C and O occurring in their crystal structure is limited, which is an issue when discriminating between the above minerals by their different concentrations of hydroxide (OH) and carbonate (CO2). SEM-EDS validation analyses or XRPD analyses can solve this issue;

b) in the lead-bearing nonsulfide deposits there is a problem in discriminating between cerussite (PbCO3) and anglesite (PbSO4), because of the X-ray interference of S-Ka and Pb Ma using EDS, which causes an overlap of the Pb and S peaks. Moreover, the C detection is not reliable, due to the carbon coating of the samples, and the typical weak response of C at 1000 counts. Hence, again, the only way to solve the carbon issue is to run SEM-EDS or XRPD analyses, to resolve the uncertainty.
detected by traditional methods (Santoro et al. 2013), contrary to Jabali, where anglesite was already detected by Mondillo et al. (2011, 2014).

c) misidentification of minerals: the mineral phases characterized by large chemical variability and/or smaller than the beam size excitation volume (i.e. clays), or also smaller than the used resolution (which is 10μm for routine analyses) may produce mixed X-ray spectra. In the case of Hakkari, a certain amount of sauconite, not previously detected by Santoro et al. (2013) was identified in a few samples. However, though not excluding a possible occurrence of Zn-smectite, it is also likely that the Hakkari “sauconite” may correspond instead to a mixture of kaolinite with tiny grains of smithsonite and/or hemimorphite. A high amount of jarosite was detected by QEMSCAN® in the Hakkari deposit. Since no jarosite was observed previously, new SEM-EDS validation analyses were carried out, and revealed the occurrence of minerals with mixed composition between pyrite/jarosite and Fe-(hydro)oxides. Moreover, QEMSCAN® analyses showed the occurrence of ankerite and Zn-ankerite, in the Hakkari, Jabali and Reef Ridge deposits. This determination was incorrect, because the “ankerite” was in reality dolomite mixed with Fe-dolomite and Zn-dolomite. In the Jabali deposit kaolinite is finely intergrown with sauconite (Zn-smectite), and as such it was impossible to distinguish between the two. Also the identification of sauconite, instead of a rough smithsonite-kaolinite mixture, was challenging, because of the fine size of these clay mineral particles. Other examples of this type of problem in the Jabali ore include the QEMSCAN® detection of Cd-sphalerite (that was later revealed to be greencornite mixed with sphalerite), Pb-achanthite (galena specks in acanthite), and Ag-smithsonite (small patches of achantite occurring in smithsonite) (Santoro et al. 2015). All these doubtful cases may be technically resolved by increasing the X-ray resolution from 10 to 5μm or less, but the very low amount of the above mentioned phases means that higher resolution (hence higher analytical cost) is not worthy for these projects. In most cases, the best option is to corroborate these data, solely for scientific purpose, with a scanning electron microscope.

The main conclusion of this study is that the characterization of nonsulfide Zn-deposit, and their quantitative evaluation (QPA) is quite tricky, because of their difficult mineralogy. However, a good definition of this type of ores is important to avoid several metallurgical issues. QEMSCAN® is a useful tool for ore characterization of less complex nonsulfides, because it allows improved detail of their texture, adding significant information about the major and trace mineral distribution and a good quantitative evaluation of the isomorphic phases that typically characterize many minerals occurring in this type of deposit. However, despite all these positive aspects, it is important to note that QEMSCAN® data cannot be used alone, because of possible ambiguity in minerals identification.

References


Geometallurgical Investigation of Ion Adsorption Clays

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Abstract. We performed a mineralogical, geochemical and geo-hydrometallurgical study on Rare Earth Element (REE) enriched lateritic Ion Adsorption Clays (IAC). IACs are formed by hydrolysis-driven lateritic weathering of parental rocks under humid tropical conditions. These parental rocks contain significant amounts of REE-bearing minerals, which are liable to weathering. As a result of acidic soil conditions – indicated by a pH < 4 – aluminosilicates (mainly feldspar) are altered to kaolinite. REE⁺ ions, released during the breakdown of REE minerals, migrate through the weathering system and are adsorbed onto the clay mineral surfaces. Parental rocks were identified as being composed of diorite and syenite. REE enriched pegmatites are formed in these rocks by hydrolysis-driven weathering of REE bearing pegmatitic minerals. The REE contents of the IACs analyzed are largely determined by the REE contents of the pegmatites from which they were derived. The REE contents of the IACs are only slightly enriched compared to the REE contents of the parental rocks, indicating that the REE in the IACs is not significantly enriched by the IACs themselves.

Keywords. Rare Earth Elements, Ion Adsorption Clays, Parental Rocks, REE Minerals, QEMSCAN, Sequential Extraction, Hydrometallurgy

1 Introduction

Rare earth elements (REE) are used in a variety of high technology devices, for instance hybrid cars, smartphones and permanent magnets. They are typically and historically extracted from the conventional minerals monazite (REEPO₄) and bastnäsite (REECO₃(F, OH)) which contain considerable amounts of radioactive elements and have relatively low concentrations of the more valuable heavy rare earth elements (HREE, Gadolinium – Lutetium). These are currently almost exclusively supplied by the Ion Adsorption Clay (IAC) deposits of southern China (Chi and Tian 2008). This study presents a geo- and hydrometallurgical investigation of a potential Ion Adsorption Clay material and its parental rocks from outside China.

2 Geometallurgical investigation of ion adsorption clays and parental rocks

2.1 Geochemistry and mineralogy

Based on geochemical analyses, the investigated parental rocks can be discriminated into SiO₂ undersaturated (diopside-bearing diorite and syenite) and SiO₂ rich pegmatitic specimens. Whereas the former have a relatively low average REE concentration (~300 ppm), the latter are highly enriched in REE (average ~11000 ppm) and radioactive components Th (~1700 ppm) and U (~170 ppm). Additional valuable elements are Nb (~2600 ppm) and Zr (~10000 ppm). Both rock types show differing C1 normalization patterns (Fig. 1) after McDonough and Sun (1995). The pegmatitic rocks have distinctive negative Eu anomalies, whereas the other rock groups show no explicit anomaly at all.

![Figure 1. C1 normalized REE pattern.](image)

REE minerals are relatively abundant in pegmatitic rocks comprising of monazite (Ce, La), bastnaesite (Ce, La), pyrochlore, fergusonite (Y), zircon and thorite (Fig. 2, A-D). The majority of REE in SiO₂ undersaturated rocks is probably bound to zircon and apatite. The primary minerals of the pegmatitic rocks are quartz (~40 vol. %), K-feldspar (~25 vol. %) and aegirine (20 vol. %), with minor amounts of plagioclase (~4 vol. %) and Fe-hydroxides (~4 vol. %). The SiO₂ undersaturated rocks mainly consist of plagioclase (~35 vol. %), K-feldspar and nepheline (~30 vol. %), Ca-amphibole (~25 vol. %) and augite (~5 vol. %).

Geometallurgy 1455
During the weathering process, alumosilicates (mainly feldspar) are altered into clay minerals. The REE ions are released by the breakdown of REE minerals and migrate through the weathering system whereby HREE are preferentially adsorbed onto clay mineral surfaces, because of the increase in surface complexation constant related to the increasing atomic number within the REE series (Aagaard 1974).

The results show that the LREE are preferentially adsorbed onto clay mineral and Fe (hydr-) oxide surfaces where the CIA range reported for Chinese IAC (~66-92 %; Wu et al. 1990, Murakami and Ishihara 2008). XRD analysis and Rietveld quantification revealed consequentially a high abundance of clay minerals with predominantly kaolinite (~22-80 wt.%). Quartz contents (~4-40 wt.%) are highly variable depending on the sample origin. Minor proportions of zircon were identified (<1 wt.%; Fig. 4). Iron (hydr-) oxides occur in terms of goethite (~0-19 wt.%) and hematite (~0-3 wt.%). Minor amounts of gibbsite indicate a weak bauxitization (~0-7 wt.% with one exception of ~28 wt.%).

Elemental change calculations after Nesbitt (1979), using Al₂O₃ as an immobile reference element (Murakami and Ishihara 2008), indicate a strong depletion of REE in laterites derived from pegmatites. In contrast, the laterites formed over SiO₂-undersaturated rocks are moderately REE enriched. This is because of the assumed relatively small volume of REE rich pegmatitic dykes within the alkaline complex that is involved in weathering and therefore provides less of its characteristics to the IAC. However, the proportion is significant as related to the ore body formation and REE enrichment.

2.2 Sequential extraction and hydrometallurgy

A sequential extraction using the method of Galan et al. (2003) was applied for the investigation of the bonding character of REE species in the lateritic samples. The process included four extraction stages suitable for the analysis of Fe-rich sediments (exchangeable fraction and carbonates, oxides, organic material and sulphides, residual fraction). Each fraction is obtained with a specific solvent leading to the extraction of individual components and their subsequent identification (Tessier et al. 1979). The results show that the LREE are preferentially...
The industrial recovery of REE-bearing IACs is usually done by leaching the ore with electrolytic solutions of sodium- or ammonium-sulfates, chlorides or nitrates to liberate the adsorptive ligated REE. To keep the solute REE in solution, an acidic pH is adjusted with mineral acids like HCl, HNO₃, or H₂SO₄. High pH-values lead to less REE extraction yields because of hydrolysis. In comparison, a decreasing pH increases the solubility of impurities like the matrix elements of IACs (e.g., Fe, Al and Si). The general leaching mechanism complies with an ion exchange of cations of the used electrolytic solutions, shown in formula 1, to liberate the adsorptive ligated REE (Zhang and Edwards 2013; Moldoveanu and Papangelakis 2013; Coppin et al. 2002).

\[
[AI,SiO₅(OH)₃]_m \text{n REE} + 3n \text{Me}^{+} \\
[AI,SiO₅(OH)₃]_m 3n \text{Me} + n \text{REE}^{3+} \quad 1
\]

According (Zhang and Edwards 2013):
\( x = 2, y = 5 \) and \( z = 4 \) (other ratios possible)

To verify the direct implementation of the studied IAC in state of the art process routes, leaching tests with mineral acids (HCl, HNO₃, H₂SO₄) with different concentrations (0.1 and 0.5 mol/L), pure salt solutions (Na⁺ and NH₄⁺ based, \( c = 0.5 \text{ mol/L} \)) and composites are investigated. Constant parameters are the leaching time of 1 h at 30 °C with a solid:liquid-ratio of 1:5. After leaching, the suspension is filtrated. The metal concentration of the filtrate is analyzed with ICP-OES and the solids with XRF. Based on the elemental analysis, the REE extraction yield (R) and the selectivity (S) to major matrix elements serve as evaluation criteria.

The evaluation of sulfate, nitrate and chloride based leaching systems indicates an increased REE extraction yield of sulfate based systems. The experiments with single mineral acids as well as with single salt solutions point out the sulfate based reagents as the most favorable leaching system to extract REE from IACs. An increasing mineral acid concentration from 0.1 to 0.5 mol/L does not liberate a significant additional amount of REE but leads to a higher dissolution of impurities e.g. Fe and effects less selectivity as mentioned in the literature.

Sodium- and ammonium-sulfate-based reagents show similar leach results but a mixture of mineral acid (0.1 mol/L) and salt solution (0.5 mol/L) increases the REE metal yield by about 10 to 20 %.

As a result, the most efficient leaching system is presented in Figure 6. The graph is downscaled from sixteen to four selected REE with high contents in the initial material to minimize the effect of analytical errors. 

La, Ce, Nd representing the LREE and Y representing the HREE. The extraction yields indicate high REE recovery rates of 50 to 95 %. The increasing recovery from La to Y is related to the sequential extraction results and confirms a decreasing adsorption behavior with increasing atomic number. It is supposed that fraction 1 (adsorbed REE) can be liberated at elevated process parameters. The anomaly of the reduced recovery rate of Ce can probably be explained with the +IV oxidation state which requires a more aggressive leaching environment for liberation. The kinetic evaluation of the extraction yields from 0 to 60 minutes indicates a direct liberation of REE with marginal increasing over time. This is a typical behavior of IACs because of the easy liberation of adsorptive ligated REE or oxides on the surface. To extract the remaining REE the crystal structure has to be destructed.
This can be realized e.g. by time, but leads to an excessive liberation of matrix elements illustrated in Figure 7, which points out the quotient of the extraction yield of Nd to major matrix elements (Fe, Al, Ti, Si) depending on time (formula 2).

\[
S(M_1:M_2) = \frac{R(M_1)}{R(M_2)}
\]

\[
R(M) = \text{e.g. metal yield of Nd}
\]

\[
R(M) = \text{e.g. metal yield of Fe, Al, Ti or Si}
\]

Figure 7. Selectivity of Neodymium and major matrix elements of direct leaching experiments (logarithmic approximation) (0.1 mol/L H_2SO_4 and 0.5 mol/L (NH_4)_2SO_4, 30 °C, solid:liquid-ratio 1:5).

3 Conclusion

Ion Adsorption Clays are formed under lateritic weathering in tropical to semitropical climates from parental rocks with high abundances of labile REE minerals. Investigated lateritic samples were derived from SiO_2 undersaturated and REE poor rocks as well as pegmatitic rocks with high REE concentrations due to the presence of REE minerals such as monazite (Ce, La), bastnaesite (Ce, La), pyrochlore and fergusonite (Y). During the breakdown of these minerals, REE^3+ ions are released and attached onto clay mineral surfaces. The lateritic samples show a consistent mature weathering status and high abundances of clay minerals, mainly kaolinite. For laterites to form an Ion Adsorption Clay ore body it is a prerequisite to carry a high abundance of clay minerals and they must have been derived from a parental rock with a substantial REE-enrichment. REE variations within the ore body (~150 – ~1200 ppm) should have no distinct economic impact on mining due to a relatively easy and cost-efficient excavation process of lateritic material in general. In terms of beneficiation, low and high grade material can be mixed. However, matter with low non clay mineral content (e.g. quartz) is preferred.

The results of sequential extraction analyses indicate that the majority of LREE are present in the exchangeable fraction, thus adsorbed onto clay mineral and Fe/Al (hydr-) oxide surfaces. With increasing atomic number, REE are progressively located within the residual fraction (silicates).

Performed leaching experiments with the investigated IACs demonstrate an economic advantage based on increased REE recovery rates with minor addition of mineral acids to state of the art salt solutions. In comparison to chloride and nitrate based systems, the best leaching efficiencies could be achieved with sulfate based systems, particularly using a mixture of H_2SO_4 and (NH_4)_2SO_4. Short leaching times are favorable to prevent an excessive liberation of matrix elements especially Fe and Si. Further investigations will be focused on these impurities in the following purifying steps, implemented in the state of the art, with respect on the REE product quality.

In order to achieve a better understanding of the geometallurgy of the ore body in terms of the leaching process, high resolution QEMSCAN analyses of the leach residues may provide useful data for further evaluation of the process efficiency and on possibly remaining REE phases/compounds.

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Based on increased REE recovery rates with minor investigated IACs demonstrate an economic advantage from SiO2 undersaturated and REE poor rocks as well as parental rocks with high abundances of labile REE residual fraction (silicates).

That the majority of LREE are present in the preferred. Matter with low non clay mineral content (e.g. quartz) is low and high grade material can be mixed. However, of lateritic material in general. In terms of beneficiation, and Fe/Al (hydr-) oxide surfaces. With increasing atomic weight of these minerals, REE3+ ions are released and attached onto clay mineral surfaces. The during the breakdown of these minerals, REE minerals such as monazite (Ce, La), bastnaesite (Ce, La), pyrochlore and fergusonite (Y).

Performed leaching experiments with the approximation (0.1 mol/L H2SO4 and 0.5 mol/L (NH4)2SO4, elements of direct leaching experiments logarithmic Figure 7. Which points out the quotient of the extraction yield of Nd to major matrix elements (Fe, Al, Ti, Si) depending on time (formula 2).

This can be realized e.g. by time, but leads to an excessive liberation of matrix elements especially Fe and Si. Further investigations will be focused on these impurities in the following purifying steps, implemented and Si. Further investigations will be focused on these.

In comparison to chloride and nitrate based systems, the quality.

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associated with PGPR extraction, with the hypothesis that multi-species association of different plants to the efficiency of metal uptake was evaluated. Few studies attempted to relate the diversity of plants (Wardle et al. 2004; Benizri and Amiaud 2005) to functional groups closely related to the community and the diversity of soil bacterial communities and microbial rhizodeposits (Benizri and Amiaud 2005), rendering thus the concept of plant diversity and composition induce a variety of opportunities for the use of plants in bioremediation techniques based on plants and biodegradable (Garbisu and Alkorta 2001) and environmentally friendly methods for cleaning-up metal-contaminated soils and for extracting valuable metals associated rhizosphere microorganisms offer an important perspective. A 120-d mesocosm study was carried out with soil collected from the top layer (10-40 cm) of a natural forest ultramafic Hypermagnesic Hypereutric Cambisol (i.e. forest serpentine natural association of B. tymphaea – N. tymphaea). Sixty eight nickel resistant strains of A. murale or B. tymphaea, on co-cropping with selected rhizobacterial strains, isolated from the rhizosphere of a Ni-rich ultramafic soil. Also, the effects on soil physicochemical properties and on microbial communities’ changes colonizing the rhizosphere were evaluated. Secondly, this study aimed at evaluating the effect of bacterial isolate screened for its PGP capacities (IAA, siderophores, ACCd production). The effects of bacterial association was inoculated with one selected bacterial strain NB24, seemed to be a good choice for an efficient phytoextraction when plants were inoculated with this PGPR strain. The genetic characterization of all four species on the efficiency of Ni extraction from a Ni-rich ultramafic soil. Also, the effects on soil physicochemical properties and on microbial communities’ changes colonizing the rhizosphere were evaluated. The effect of all treatments on the efficiency of Ni extraction were evaluated. Moreover, a few studies dealt mainly concerned crop associations (Murakami and Ae 2007; Jiang et al. 2010). Most of these experiments showed that co-cropping with non-hyperaccumulator hyperaccumulator plants with other species (Wu et al. 2009; Liu et al. 2011). Therefore, the objective of the present work was first to compare the cropping of single hyperaccumulator plant species (either Alyssum murale, Noccaea-Bornmuellera or Noccaea tymphaea, Leptoplax emarginata) with co-cropping of hyperaccumulator plants.
Enhanced Phytoextraction of Nickel from Contaminated Soil by Hyperaccumulator Plant Co-Cropping Associated with PGPR

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Abstract. The objective of this work was first to compare the cropping of single hyperaccumulator plant species (either Alyssum murale, Noccaea tymphaea, Leptoplax emarginata or Bornmuellera tymphaea) with co-cropping of all four species on the efficiency of Ni extraction from a Ni-rich ultramafic soil. Also, the effects on soil physicochemical properties and on microbial communities’ changes colonizing the rhizosphere were evaluated. Secondly, this study aimed at evaluating the effect of selected rhizobacterial strains, isolated from the rhizosphere of one of the different natural plant associations (B. tymphaea, N. tymphaea), on plant biomass production and nickel phytoextraction by these two hyperaccumulator plants. The screening of isolates from this plant association for their PGPR traits revealed one PGPR strain (NB24). The genetic characterization showed that it was similar to Variovorax paradoxus. After 6 months of culture, biomass and quantities of nickel in the plants were assessed. The results showed significant improvement of root growth and an increase of Ni uptake when plants were inoculated with this PGPR strain. The combination Noccaea-Bornmuellera inoculated by the PGPR strain Variovorax NB24, seemed to be a good choice for an efficient phytoextraction in situ.

Keywords. Nickel, phytomining, hyperaccumulator plants, rhizobacteria, rhizosphere, PGPR.

1 Introduction

Heavy metals, such as nickel (Ni), are non-biodegradable (Garbisu and Alkorta 2001) and bioremediation techniques based on plants and associated rhizodeposits offer an environmental friendly method for cleaning-up metal-contaminated soils and for extracting valuable metals (Chaney 1983; Baker et al. 1994; Lucisine et al. 2014). Plant diversity and composition induce a variety of rhizodeposits (Benizri and Amiaud 2005), rendering thus the diversity of soil bacterial communities and microbial functional groups closely related to the community and diversity of plants (Wardle et al. 2004; Benizri and Amiaud 2005). Few studies attempted to relate the association of different plants to the efficiency of metal extraction, with the hypothesis that multi-species vegetation covers promote the development and activity of rhizosphere microorganisms. Studies up to now mainly concerned crop associations (Murakami and Ae 2009; Liu et al. 2011). Moreover, a few studies dealt with the effect of the combination of metal hyperaccumulator plants with other species (Wu et al. 2007; Jiang et al. 2010). Most of these experiments showed that co-cropping with non-hyperaccumulator plants enhanced the growth of the hyperaccumulator and increased the metal extraction and often improve the living condition of less metal-tolerant plants.

Therefore, the objective of the present work was first to compare the cropping of single hyperaccumulator plant species (either A. murale, N. tymphaea, L. emarginata or B. tymphaea) with co-cropping of all four species. The effect of all treatments on the efficiency of Ni extraction from a serpentine soil (i.e. naturally nickel-rich) and on the rhizosphere microbial community changes was studied.

Secondly, this study aimed at evaluating the effect on plant biomass production and nickel phytoextraction, of selected rhizobacterial strains, isolated from the rhizosphere of one of this natural plant association (B. tymphaea, N. tymphaea). Sixty-eight nickel resistant bacterial strains were isolated from the rhizosphere of a serpentine natural association of B. tymphaea, N. tymphaea. Then, bacterial isolates were screened for their PGP capacities. This hyperaccumulator plant association was inoculated with one selected bacterial isolate screened for its PGP capacities (IAA, siderophores, ACCd production). The effects of bacterial inoculants on soil metal availability, plant growth and Ni extraction were evaluated.

2 Materials and methods

2.1 Soil characteristics and experimental design

A 120-d mesocosm study was carried out with soil collected from the top layer (10-40 cm) of a natural forest ultramafic Hypermagnesic Hypereutric Cambisol...
5.49 and an organic matter content of 10.3%. The main chamber for four months.

1480 mg·kg−1. The mesocosms (3 kg of soil per naturally rich in nickel (Ni) and the total Ni content was 1480 mg·kg−1. The mesocosms (3 kg of soil per mesocosm) were planted with plant species considered separately (monospecific cover: Leptopla (Bois) O.E. Schulz, Noccaea tymphaea (Hausk.) F.K. Mey. Bornmueller tymphaea Hausskn or Alyssum murale Waldst. & Kit) and combined (multispecies cover). Total plant density was 8 per mesocosm. Control mesocosms were not planted. The experiment had a completely randomized block design with seven replications that had the following treatments: L: Leptopla; N: Noccaea; A: Alyssum; B: Bornmueller; LNA:B: a mixture of the four species; SWP: soil without plant. M esoscosms were transferred to an environmental growth chamber (photoperiod 16 h, temperature 15°C night and 20°C day, relative humidity 70%, PPF: 350 mmol m−2 s−1) and adjusted to 75% of soil water holding capacity. M esoscosms were kept in the growth chamber for four months.

2.2 Biotic parameters

Ni concentrations in plant parts. After four months of culture, plant parts were collected, and respective dry weights were recorded. Ni concentration in shoots and roots was measured by ICP-AES (Liberty II, Varian) after acid digestion. A Bioaccumulation Coefficient (BAC) was employed to qualify heavy metal accumulation efficiency in plants (BAC = Cp/Cs, where, Cp and Cs are heavy metal concentrations in plant parts and in soil at the beginning of the experiment; ie.1480 mg·kg−1) (Zayed et al. 1998). Heavy metal root-to-shoot translocation factor was calculated (TF = Cs/Cr, where, Cs and Cr are metal concentrations in the shoot and root) (Tappero et al. 2007).

Soil microbial activity. At the end of the experiment, the number of culturable bacteria as colony forming units (CFU) was determined by spread-plating soil suspensions onto TSA 10% (Tryptone Soy Agar, Difco). The soil microbial biomass carbon (MB-C) was estimated using the fumigation extraction technique previously described by Vance et al. (1987). The determination of auxin-like compounds from the soil samples was adapted from the method described by Small et al. (2010). 1-aminoacyclopropane-1-carboxylate deaminase (ACCd) activity was determined based on the method described by Honma and Shimomura (1978) for measuring ACC deaminase in cell extracts. β-glucosidase (EC 3.2.1.21), arylsulphatase (EC 3.1.6.1), acid phosphatase (EC 3.1.3.2) and urease (EC 3.5.1.5) activities were determined according to Tabatabai (1982). Spectrophotometric determination of the hydrolysis of fluorescein diacetate (FDA) was also used to determine microbial activity in soil.

2.3 Abiotic parameters

Moisture content of the soil samples was determined at 105°C until a constant weight was achieved. Ni in soil samples from each mesocosm was extracted with the DTPA-TEA solution (0.005 M DTPA, 0.01 M CaCl2, 0.1 M triethanolamine, pH 7.3) (Lindsay and Norvell, 1978) and Ni concentration in solution was measured by ICP-AES. Soil pH was measured using a pH meter in a soil/water solution mixture (soil water ratio 1:5).

2.4 Genetic and functional (ie. PGP capacities) characterization of nickel resistant rhizobacteria isolated from rhizosphere soil

Bacteria strains were isolated from the rhizosphere soil of the natural hyperaccumulator plant association: B. tymphaea - N. tymphaea (NB). This natural association was found at Katar Pass (1700 m) in Greece (39° 47'765" N, 21° 13'739" E). A sample (3 g) of the rhizosphere soil was used for the determination of the number of culturable bacteria as colony forming units (CFU) by spread-plating them onto TSA supplemented with various concentrations of Ni from a filter sterilized stock solution. Nickel was added as NiSO4, 6H2O at concentrations of 0.5, 5, 7.5 and 10 mM. Agar plates were then incubated in the dark at 27°C for 12 days. From the plates containing Ni concentration of 7.5 mM, we carried a collection of strains. Then, each isolate was cultured in 6 ml of NB medium for 15 hours on shaker table (120 rpm) at 30°C and finally stored individually in 20% sterile glycerol and kept in the freezer (-20 °C). Then, each isolate was cultured in 8 ml of NB medium for 48 hours on shaker table (120 rpm) at 27°C. After centrifugation, DNA was extracted from the pellet with the FastDNA®SPIN Kit (MP Biomedicals) in accordance with the manufacturer’s instructions. The 16S rDNA sequences were amplified with universal primers (Oligonucleotides) for 30 cycles. The 16S rDNA sequences were edited and screened against those in the GenBank database using BLASTn (http://www.ncbi.nlm.nih.gov/). Each isolate was then screened for various plant growth promoting (PGP) characteristics: siderophore production, IAA and ACCd production.

2.5 Influence of Ni resistant PGPR on plant growth and Ni uptake

A after 4 months of culture of the hyperaccumulator plant association B. tymphaea-N. tymphaea (inoculated ‘NBI’) or not inoculated ‘NBni’), plant parts were collected and their dry weights were recorded. Ni concentration was measured by ICP-AES after acid digestion.
Bioaccumulation Coefficient (BAC), Bioconcentration factor (BCF) and heavy metal translocation (TF) were estimated (Tappero et al. 2007).

2.6 Statistical analysis

Variance analysis was carried out on all data (one-way ANOVA). All data were submitted to principal component analysis (PCA). Mean coordinates of individuals were calculated for the first two principal components (PC1, PC2) and compared by variance analysis (one-way ANOVA). The software used for all statistical analyses was StatBow software (Grimmersoft, Paris, France, [http://www.statbox.com](http://www.statbox.com)).

3 Results

3.1 Effect of mono- and multispecies covers on physicochemical and microbiological parameters

To consider all parameters together, we carried out another Principal Component Analysis (PCA) based on physicochemical and biological variables (Figure 1). Axis 1, which explained 24% of total variability, strongly discriminated unplanted soils (SWP), (negative abscissa), from planted mesocosms (positive abscissa) (Figure 1a). Thus, SWP were clearly opposed to the different cover types and in particular those of B and N. Axis 2, which represented 14% of the total variability, clearly discriminated monospecific cover of N from the other covers (A, L, B, LNAB). If we focus on the explanatory variables (Figure 1b), it appears that the presence of a cover, either single or multi-species, caused a decrease in the concentration of extractable soil Ni (PC1). Correspondingly, we noted that the concentrations of Ni in shoots ('CNiS') were significantly inversely correlated (R = -0.70, p < 0.05) to the quantities of Ni present in soil, B, which had accumulated the highest amount of Ni in shoot, was the species for which the rate of Ni in soil was the lowest. In addition, it is clear from our analysis that the more important the plant biomass, the greater the concentrations of Ni in shoots (R = 0.56, p < 0.05). This was especially marked in order of importance for B > N > L and LNAB > A. PC2 seems to discriminate vegetation cover according to the pH values of the different soils. The N rhizosphere showed the lowest pH values unlike all the other covers. We noted, however, a significant inverse correlation between the concentration of Ni in the roots (C Ni R) and translocation factor TF (R = -0.42, p < 0.05). We also observed a positive correlation between pH and CFU (R = 0.32, p < 0.05) and a significant correlation between CFU and most measured microbial activities (Ure, Pho, Gluc, R = 0.28, p < 0.10). Among the microbial activities measured, ACCd activity was significantly correlated to the concentration of Ni in the roots (R = 0.29, p < 0.10). Finally, the size of cultivable bacterial communities appeared to be favored by the presence of a vegetation cover and positively correlated with root biomass (R Bio, R = 0.35, p < 0.05).

![Figure 1. (a) Ordination plot of soil samples, generated by Principal Component Analysis of the physicochemical and microbiological parameters. Points represent means of seven replicate samples (L: Leptoplast; N: Noccaea; A: Alysum; B: Bornmueller; LNAB: mixture of the four species; SWP: soil without plant). (b) Physicochemical and microbiological parameters involved in the discrimination of soil samples. (Ni soil: DTPA-extractable nickel from soil (mg.kg⁻¹); CEC: cation exchange capacity (cmol.kg⁻¹); ACCd: 1-Aminocyclopropane-1-Carboxylic Acid Deaminase (nM.g⁻¹h⁻¹); Ure: urease (µg NH₃-N.g⁻¹dry soil.h⁻¹); Gluc: β-glucosidase (µg p-nitrophenol.g⁻¹dry soil.h⁻¹); FDA: fluorescein di-acetate (µg FDA.g⁻¹dry soil.h⁻¹); Pho: phosphatase acid (µg p-nitrophenol.g⁻¹dry soil.h⁻¹); Arey: arylsulfatase (µg p-nitrophenol sulfate.g⁻¹dry soil.h⁻¹); Hum: soil humidity (%); CNiR et CNiS: root and shoot nickel concentrations (mg.kg⁻¹); RBiom et SBiom: root and shoot biomass (g); MB-C: microbial biomass carbon (mg C.g⁻¹dry soil); CFU: Unity forming colony (log10 cfu.g⁻¹dry soil); TF: Translocation factor; BCF: Bioconcentration factor).](image)
Moreover, it appeared that the inoculation promoted following inoculation (NBi: 6.5 g; NBni 5.1 g). It appeared that the amount of Ni in the aerial parts, it appeared that the amount of Ni in the root (Figure 3). In the case of particular by B. Bornmuellera phytoextracted Ni.

The amount of Ni in NBi root was significantly higher than that in NBni root (Figure 3). In the case of aerial parts, it appeared that the amount of Ni in the shoots of the inoculated plant association was also significantly higher than that in non-inoculated cover. Moreover, the inoculation increased Ni phytoextraction in particular by B.

Figure 2. Root (black bar) and shoot (grey and white bars) biomass (g) per cover. Mean values followed by different lowercase (root), italic (shoot) or capital letters (total biomass) are significantly different at p<0.05 (Newman-Keuls test), (n = 4).

Figure 3. Amounts of Ni phytoextracted in shoots (grey and white bars) and roots (black bar) per pot (mg). Mean values followed by different lowercase (root), lower italic (Noccaea shoot), upper italic (Bornmuellera shoot) or uppercase (total shoot biomass) are significantly different at p<0.05 (Kruskal test), (n = 4).

4 Conclusion

This study identified an efficient candidate strain which could be useful for future field-based trials. Indeed, we have seen that plant growth-promoting effects by associated bacteria, mainly the PGPR Variorovax NB24 isolated from a natural nickel-rich soil, can significantly improve plant association performance (e.g. Noccaea and Bornmuellera) and result in higher amounts of phytoextracted Ni.
Agromining for Nickel: a Complete Chain that Optimizes Ecosystem Services Rendered by Ultramafic Landscapes

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Abstract. Serpentine (i.e. ultramafic) outcrops in Europe cover >10,000 km² and have a low fertility and low productivity, making them unattractive for traditional agriculture. Many of these areas are slowly abandoned by local farmers, with a rural exodus and landscape closure. However, ultramafic landscapes have the potential to provide multiple ecosystem services and can contribute to Europe’s goals towards ensuring food security, production of renewable raw materials and renewable energy. Phytomining (Agromining) cultivates plants that are able to accumulate trace metals from metal-rich soils and transport them to the shoots (>1%), which can then be harvested as a bio-ore to recover highly valuable metals such as nickel (Ni). Nickel agromining can offer an eco-efficient alternative to classical pyro- or hydrometallurgical processes, as well as providing biomass for local energy production. Phytomining agroecosystems can lead to better soil resource efficiency and can offer a fully integrated, new agromining agriculture that could cover thousands of km² in Europe and benefit local communities with a sustainable rural development.

Keywords. Phytomining, Life Cycle Assessment, Hyperaccumulator plants, Fuel crops, Hydrometallurgy, Agroecology

1 Introduction

Serpentine (i.e. ultramafic) outcrops are biodiversity hotspots, especially the larger ultramafic areas. Serpentine soils can be stressful environments for plant growth and the plant communities in these areas often present a high number of endemic species, which have evolved both morphological and physiological adaptations differentiating them from the flora of adjacent geological substrates. Serpentine agricultural soils are generally characterised by low fertility and productivity, making them unattractive for agriculture (Bani et al. 2015). As a consequence, many of these areas are slowly abandoned by local farmers. The adjacent steep or rocky slopes have never been cultivated and usually host the highest number of endemic species. Ultramafic flora includes unusual plant groups (hyperaccumulators), which are able to accumulate extremely high concentrations of Ni in their aerial biomass.

2 Nickel phytomining

The worldwide demand for Ni is experiencing an unprecedented growth under current industrial and economic pressures. However, technologies are lacking to exploit unweathered primary sources (ultramafic soils) in which Ni is present at significant contents (1,500-4,000 mg kg⁻¹), but where its extraction by conventional mining processes is economically non-viable. Hyperaccumulator plants are cultivated to accumulate trace metals from soils and transport them to shoots, which can then be harvested (Chaney et al. 2007; van der Ent et al. 2015). Yields have been optimised, and up to 120 kg Ni ha⁻¹ is currently produced in field plots in Europe (Bani et al. 2015a, 2015b). Hydrometallurgy from hyperaccumulator ash (after combustion and energy production) can produce Ni-based chemicals (e.g. hydrated ammonium nickel sulphate with a purity of >99%) worth up to $20 000 per ton in a purified form (Barbaroux et al. 2012; Zhang et al. 2014). Therefore, the production of high value-added Ni products, around a thousand tons per year from combined phytomining and hydrometallurgy offers a high potential of profitability. Phytomining has been developed and optimised from field agronomy to full metallurgical process and brought to pilot scale in both North America and Albania.

3 A new concept: agromining for metals

Agromining is a more integrated concept than phytomining (van der Ent et al. 2015) with the aim of optimising ecosystem services of ultramafic regions at landscape level. Agromining is a complete design of new agroecological cropping systems and associated metallurgical chain (including recycling of process by-products in crops). Carrying out a complete Life Cycle Assessment of the agromining chain is designed to optimise i) Provisioning services (green Ni products, fuel
biomass for local communities), ii) supporting and regulating services (amelioration of soil quality and productivity for agriculture, ensuring the conservation of rare and endangered species, stimulating populations of pollinating insects, enhancing carbon storage in ultramafic landscapes and iii) cultural services (maintaining agricultural communities in ultramafic landscapes, improving landscape quality, stimulating tourism).

3 How to design agromining in Europe with the objective of optimising ecosystem services

Europe host large ultramafic outcrops (Figure 1), mainly situated in the Iberian and Italian peninsulas, Corsica and the Balkan region (van der Ent et al. 2015). These regions are also home for a large plant hyperaccumulator diversity which can be utilised in agromining projects (Figure 1).

Figure 1. Ultramafic outcrops and Ni-hyperaccumulator taxa occurrence in Europe and western Anatolian peninsula.

Global & Social issues

<table>
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<tr>
<th>Global Climate Change</th>
<th>Local Food System</th>
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Local stakeholders

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<th>Phytomining companies</th>
<th>Metal industry</th>
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<tr>
<td>Provides employment</td>
<td>Rural development</td>
</tr>
<tr>
<td>Economic attractiveness</td>
<td>Provides raw material for activity</td>
</tr>
</tbody>
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Local communities

| Provides biomass for local energy needs | Positive impact on landscape (e.g. tourism) | Needs lack of negative impact on local food |

Farmers – Farmer associations

| Provides additional income | Better soil fertility & productivity over long term | Supports existing crop and cattle production |

Enhanced farming activity supports economy & local quality of life

Regulators

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<tr>
<th>Local Governments – State institutions – EU – Regulators</th>
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Need for specific regulations:
- Economic frame
- Environmental issues

Figure 2. Interactions of agromining activities in ultramafic regions of Europe with local and state stakeholders in the frame of global issues.
Phytomining strategic metals and other elements from naturally mineralized soils and mineral wastes

Agromining for Ni in Europe should provide adapted cropping systems combining phytomining, food, medicinal or forage crops in such a way so as to restrict the entry of trace metals into the food chain and protect human and animal health. It should at the same time optimise all ecosystem services towards populations, territories and nature (Figure 2). Phytomining systems will be developed throughout the project with the goal of optimising their ecosystem services. Therefore, the Life Cycle Assessment of phytomining will serve as a guideline to organise all research objectives.

The implementation of Ni agromining in Europe should rely on the three following steps in order to optimise ecosystem services rendered by this new agricultural activity:

- Assessment of phytomining at landscape level after complete design of new agroecological cropping systems.
- Establishment of a complete Life Cycle Assessment of the phytomining chain.
- Specific description and optimisation of the following ecosystem services:
  1. Amelioration of soil quality and productivity for agriculture
  2. Supplying industry with a green Ni resource and tailored Pure Ni salts
  3. Producing fuel biomass for local communities
  4. Ensuring the conservation of rare and endangered species by introducing them in new cropping systems
  5. Stimulating and increasing the population of pollinating insects through cropping large surfaces of hyperaccumulator crops
  6. Limiting Ni contents in food products (honey, etc)
  7. Enhancing carbon storage in ultramafic landscapes.

4 Conclusions and perspectives

These technologies are about to be launched at a territory scale thanks to several private initiatives, which are looking for areas to implement phytomining. Phytomining agroecosystems will benefit local communities in terms of rural development and sustainability. Trade-off between provisioning services (food and non-food) will be a key to the success of its implementation in many areas of Europe (e.g. Albania).

Setting up agromining research stations in representative ultramafic areas (i.e. northwestern Spain and Albania) will help to build a generic approach that will be applicable to all ultramafic regions of Europe and the Mediterranean basin. These research centres will act as field demonstrations for farmers but also for public stakeholders, local communities and private stakeholders (capacitation and structuring of the activity). It will also be a basis for future adapted agricultural policies for the economic development of ultramafic regions of Europe.

Acknowledgements

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References

Cadmium Recovery from Hyperaccumulator Plants
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Abstract. Cadmium in soils is generally present at very low concentrations but it is a very toxic heavy metal. It is considered fairly mobile and easily bioavailable, so it can enter into the food chain through plant uptake or migrate deep into the soil and contaminate groundwater. Soil remediation is therefore a major concern. Cadmium can be phytoextracted by different hyperaccumulator plants. The present contribution focuses on cadmium recovery from those plants, in order to recycle this metal and avoid the dumping of contaminated biomass.

Keywords. Cadmium, phytomining, recovery, hydrometallurgy

1 Cadmium in soils
Cadmium is a relatively rare metal. Its quantity is estimated at 15 mg kg⁻¹ in the lithosphere. There are no cadmium ores in metallurgically exploitable quantities. The ore containing the most cadmium is greenockite (CdS 77.8 wt %). Greenockite is present in the Zn ores. The presence of cadmium in soils is also due to human activities such as:
- spreading and agricultural amendments. Cadmium can be quite abundant in the phosphate fertilizers (variable content by geographical origin).
- industrial sources. Cadmium is a byproduct of zinc refining; it can be released into the atmosphere in the metallurgy of iron, steel or in lead refining.
- many urban activities and road traffic release cadmium into the environment (domestic waste incineration, combustion of fossil fuels, sewage sludge etc.).

There is no reliable technique to remove cadmium from soil except phytoextraction with cadmium hyperaccumulator plants. The aim of the present contribution is to assess the relevance of recycling cadmium from hyperaccumulator biomass. This research is conducted in the context of the LORVER project (www.lorver.org) which aims to create a feedstock chain to produce biomass on wastelands for industrial purposes, to produce energy, fibre and metal products.

2 Cadmium hyperaccumulator plants
High metal concentrations of heavy metals are often toxic to plants. Some, however, have developed a number of strategies to resist heavy metal toxicity. Plants such as Noccaea caerulescens have the capability to extract metals from soil and accumulate them in their tissues. Noccaea caerulescens is presented in Figure 1.

Metals are sequestered in cells or intracellular compartments, preferentially in the shoot. When the plant contains a large amount of metal without being affected, it is considered as a hyperaccumulator plant. For Cd >100 mg kg⁻¹ in shoot dry matter is exceptional when growing in the natural habitat. A number of cadmium hyperaccumulator plants have been identified, e.g. Sorghum (Zancheta et al. 2015), Sedum spp. (Li et al. 2014, Luo et al. 2014, Yang et al. 2014, Arnamwong et al. 2015), Noccaea caerulescens (Nedelkoska ans Doran 2000, Boominathan and Doran 2003, Kupper et al. 2004, Ma et al. 2005, Vogel-Mikus et al. 2008, Regvar et al. 2008, Likar et al. 2010, Milner et al. 2012, Lovy et al. 2013, Seregin et al. 2014, Ubugunov et al. 2014, Broadhurst et al. 2015, Dinh et al. 2015, Simmons et al. 2015). The shoots of Noccaea caerulescens can contain up to 2000 mg kg⁻¹ Cd when growing on naturally mineralised soil and up to 20,000 mg kg⁻¹ when grown to maturity hydroponically (Abouhamed et al. 2007). This plant could be appropriate plant for Cd phytoextraction and soil remediation. In this context, the objective of this study is the recovery of cadmium from the Noccaea caerulescens plants by hydrometallurgical process.

Figure 1. Noccaea caerulescens plant.

3 Cadmium recovery from Noccaea caerulescens
Noccaea caerulescens plants were provided by Dr Rees, Pr Morel, Dr Sirguey and Dr Sterckeman from the Laboratory Soils and Environment. The dry biomass was analysed by ICP-AES. It contained between 3000 to 4000 mg of Cd kg⁻¹ dry matter. The plant also contains other metals like Zn, Al, Cu, Fe, K, Mg and also P and S. Our first objective has been to separate Cd from the other metallic elements. The plant can be ashed at a certain temperature (620 °C) to avoid volatilisation of Cd and/or Zn.

Plant calcination enables us to concentrate the metals in the ash. Conventional techniques used in hydrometallurgy to separate metals are then possible: - ion exchange,
Phytomining strategic metals and other elements from naturally mineralized soils and mineral wastes

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Plant calcination enables us to concentrate the metals in the ash. Conventional techniques used in hydrometallurgy to separate metals are then possible:
- ion exchange,
- cementation,
- liquid-liquid separation,
- precipitation,
- electro-deposition.

The aim is to obtain pure Cd salts that are mainly used in accumulators and batteries. The manufacture of Ni-Cd batteries represents 80% of the consumption of cadmium.

Cadmium is also used in various applications such as:
- the development of pigments based on cadmium sulphide (CdS) to the plastic, ceramics, glasses, enamels coloring,
- stabilizers to retard the degradation processes in polyvinylchloride (PVC). Cadmium is present under carboxylates, laurate or stearate forms,
- electrolytic coating, utilised on steel, aluminium.

Cadmium is used particularly in aeronautics against atmospheric corrosion. Cadmium coatings exhibit excellent plating characteristics on a wide variety of substrates.

- manufacture of welding or brazing sticks,
- development of photovoltaic cells containing cadmium sulphide (CdS) and cadmium telluride (CdTe),
- optronics with the development of photodetectors (HgCdTe).

Figure 1. Patterns of cadmium consumption (International Cadmium Association)

Presently, work is in progress at the bench scale in order to identify possible synthesis routes. These routes will then be assessed from an economic standpoint and from an environmental perspective using life cycle analysis. Depending on the outcomes, the process will be upscaled to the pilot scale.

Acknowledgements

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Improving the Nickel Phytomining Capacity of Hyperaccumulating Subspecies of Alyssum serpillifolium

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Abstract. The extreme ability of nickel-hyperaccumulators (such as members of the genera Alyssum or Noccaea) to accumulate Ni in their harvestable tissues makes these plants particularly useful in phytomining strategies. Phytomining offers the opportunity to recover valuable metals, such as Ni, from hyperaccumulator biomass. However, to be economically viable it is necessary to maximise the Ni uptake efficiency of hyperaccumulators and the nickel yield. Plant breeding of improved accumulating plant cultivars, the use of agronomic practices or biotechnological approaches can all significantly enhance plant productivity and nickel removal. Here we present the results of a series of bench-scale studies in which different strategies were implemented to enhance the biomass production or the Ni concentration in the harvested biomass of such hyperaccumulating plant species.

Keywords. Alyssum pintodasilvae, Alyssum malacitanum, serpentine, ultramafic

1 Introduction

Studies were carried out to (1) improve plant productivity and Ni yield using soil amendments (compost or manure), plant growth regulators or various cropping patterns, and (2) to modify soil Ni availability and plant Ni uptake using bioaugmentation. The main aims of these studies were to optimise the phytoextraction efficiency of distinct Alyssum and Noccaea species, with particular emphasis on the two Ni-hyperaccumulating subspecies of Alyssum serpillifolium which are endemic to the Iberian Peninsula (Alyssum malacitanum and Alyssum pintodasilvae).

2 Materials and methods

Distinct populations of A. malacitanum and A. pintodasilvae growing across the main ultramafic outcrops of the Iberian Peninsula were evaluated for differences in biomass production and Ni accumulation capacity. The influence of this plant type on soil physicochemical properties and soil Ni bioavailability was also studied. Biomass production and Ni yield of different Ni hyperaccumulators (A. pintodasilvae, A. malacitanum, A. bertoloni) grown in serpentine soils was tested after amendment with either mineral fertilizers or organic mixtures. The influence of co-cropping leguminous plants with the hyperaccumulating Alyssum pintodasilvae on plant growth and productivity, Ni accumulation and soil quality were assessed. The hyperaccumulator was co-cropped with native legumes growing in ultramafic soils (Anthyllis vulneraria subsp. iberica, Lotus corniculatus) or a commercial cultivar (Vicia sativa cv. Prontivesa). Four different commercially available Plant Growth Regulators (PGRs) (based on cytokinins, gibberellins and auxins) were applied to the plant aerial parts at three different concentrations to promote biomass production and/or shoot Ni accumulation. Finally, rhizobacterial strains associated with the Ni-hyperaccumulators A. pintodasilvae and A. malacitanum were evaluated for their effects on soil Ni availability and for plant growth-promoting traits, and selected strains were used as inoculants to improve the growth and Ni uptake of A. pintodasilvae in natural serpentine soils and in Ni-contaminated agricultural soils.

3 Results and discussion

Inter- and intra-population variability in Ni tolerance and accumulation patterns were evaluated in five populations of A. pintodasilvae and A. malacitanum when grown in three different conditions: in situ plants growing in the field, plants cultivated in hydroponic culture solutions enriched with Ni and plants cultivated in a pot experiment using serpentine soil. Population-specific effects on the physicochemical properties of the rhizosphere soil were observed. However, in general, rhizosphere soils presented a higher pH, organic C and total N content, cation exchange capacity and Ca/Mg quotient. In addition, root activity generally led to an increase in plant-available soil Ni fractions and modifications in the soil Ni fractionation. In the field-collected plants the inter-population variance in Ni accumulation patterns was more pronounced than when the progeny were grown in controlled conditions. In both the hydroponic and pot experiments a high variability in the measured parameters was found within populations rather than between populations. Nonetheless, the significant differences revealed under controlled conditions in aspects such as biomass production and root-shoot Ni transfer could be further explored as a means of increasing the Ni yield of Alyssum serpillifolium subspecies.

The phytoextraction efficiency of different Ni hyperaccumulators (Alyssum pintodasilvae, A.
A. malacitanum, A. bertolonii and Noccaea goesingense) grown in serpentine soils was tested after amendment with either mineral fertilizers or organic composts (based on municipal solid wastes). Soils were non-amended, amended with NPK fertilisers or with compost at increasing doses (2.5%, 5% and 10% w/w). The highest biomass producers were N. goesingense, followed by A. bertolonii and the two populations of A. malacitanum. Plants grown in compost-amended soils always produced a higher biomass than NPK soils or controls. A 5% addition of compost generally led to an optimum biomass production and Ni yield. The application of compost could provide plants with essential nutrients and improve soil structure.

The effect of PGRs on biomass production was dependent on the plant species, the PGR type and the concentration at which it was applied. Indoleacetic acid (IAA)-based products (K and P) consistently increased biomass production compared to untreated control plants in all four plant species tested (Figure 1). As a consequence of the increase observed in biomass after the application of phytohormones, a significant increase in the Ni phytoextraction efficiency was also observed (but this was species- and PGR type-dependent). More in-depth studies are planned using different IAA-based PGRs so as to fully optimize the beneficial effects that they can have on Ni phytoextraction efficiency of hyperaccumulating plant species.

**Figure 1.** Effect of different PGR treatments (Control (K0 and P0); K1 (0.01 mg L⁻¹); K2 (0.05 mg L⁻¹); K3 (0.1 mg L⁻¹); P1 (5 mg L⁻¹); P2 (30 mg L⁻¹); P3 (50 mg L⁻¹)) on shoot dry weight (g) of Alyssum corsicum, Alyssum malacitanum, Alyssum murale and Noccaea goesingense. Mean shoot biomass (± standard error) of six replicates are shown. Differences between treatments within species are shown by a different letter (P<0.05).

Rhizobacterial inoculants influenced plant growth and Ni uptake and accumulation, but the effect of the strains was dependent upon soil type and the plant physiological status. The increase in plant biomass and/or Ni accumulation significantly promoted shoot Ni removal. One strain (identified as Arthrobacter nicotinovorans SA40) was able to promote plant growth and phytoextraction of Ni in contrasting soil types and could be a useful candidate for future field-based trials.

Overall the results show that many of these strategies can be successfully implemented to increase plant biomass and soil Ni removal. The next step will be to test these strategies on a field scale.

**Acknowledgements**

The financial support of the Spanish Ministerio de Economía e Competitividad and FEDER (project CTM 2012-39904-C02-01) is greatly appreciated.
Recovering Metals from Sewage Sludge, Waste Incineration Residues and Similar Substances with Metal Accumulating Plants

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Abstract. Sewage sludges and ashes from waste incineration plants are known sinks of many elements that are either important nutrients for biological organisms (phosphorus, potassium, magnesium, etc.) or valuable metals (nickel, chrome, zinc, etc.). Often these end-of-stream-residues end up in landfills. On the other hand, Austria and many other industrial countries have to import up to 90% of the material inputs of metals from abroad. Some plants have a notable capacity to accumulate high concentrations of various metals in their tissues while growing on soils with high metal loads, hence called metal hyperaccumulators. This project examined the capacity to concentrate valuable target metals in harvestable plant tissue. Five different plant species were grown under laboratory conditions on substrates containing sewage sludge, ashes from waste incineration plants and industrial residues. The evaluated results are promising: Plant species with natural fast growth and large biomass production are very suitable to the sewage-sludge substrate. Other metal accumulators with slower growth and smaller habitus have less affinity with this substrate rich in organic nutrients. Higher levels of waste incineration ashes and metal loads in the substrate are acceptable for plants, if soluble salts (chlorides, sulphates, etc.) are partly eluded first.

Keywords. hyperaccumulation; metalophytes; sewage sludge; waste incineration residues; metal recovery

1 Introduction

Sewage sludges as well as ashes from waste incineration plants are known accumulation sinks of many elements that are either important nutrients for biological organisms (phosphorus, potassium, magnesium, etc.) or valuable metals when considered on their own in pure form (nickel, chrome, zinc, etc.); they can also be serious pollutants when they occur in wild mixtures at localized anthropogenic end- of-stream points. Recovering these metal and mineral resources requires high-energy input and sophisticated equipment, making it an uneconomic process.

Austria and many other countries have to import up to 90% of the material inputs of metals from abroad (Eisenmenger et al. 2011; Krutzler et al. 2012). These primary resources are becoming more expensive and their availability more uncertain as easily mineable reserves are becoming scarce. On the other hand agriculture uses large volumes of mineral fertilizers, which are often sourced from mines as well. These converted biological nutrients are taken up by crops and through the food chain and human consumption end up in sewage systems and in wastewater treatment plants in great quantities. The metabolized nutrients mostly do not return to agriculture, but due to contamination with heavy metals are diverted to be used as construction aggregates or are thermally treated and end up rather uselessly in landfills (BAWP 2011).

Some plants are naturally adapted to grow on soils with high metal loads, with concentrations that would be toxic to most other plants. And some of these metal tolerant plants have the notable capacity to accumulate and store high quantities of some metals in their tissue, they are known as metal hyperaccumulators (Verbruggen et al. 2009; Hassan and Aarts 2011). The project Bio-Ore aims to explore new pathways to concentrate metals from diluted sources such as sewage sludge and wastewater by using highly efficient biological absorption and transport mechanisms. These enzymatic systems from plants work with very little energy input. The process is called bioaccumulation and can be most effectively observed in so-called hyperaccumulating metalophytes, which are studied for its suitability to be incorporated in metal recovery processes.

2 Methods

2.1 Substrate

A mixture of sewage sludge and waste incineration ashes (fluidized bed furnace) was to be used as a basis for the growth substrate for the metal accumulating plants. The selected plants are mentioned in various publications to be adapted to high metal concentrations in substrates and to accumulate certain metals of economic interest, they are members of the Brassicaceae, Asteraceae, Pontederiaceae, Pteridaceae and Gleicheniaceae families.

A series of preliminary tests were carried out to find out the best substrate mixture, in order to optimize the concentration of heavy metals without resulting in fatal acute toxicity for the selected plants. It was found that the high concentration of soluble salts (chloride, sulphate, sodium) in both sewage sludge and the waste incineration ashes where a limiting factor for plant growth. These salts can be washed out with water with only very minimal losses of heavy metals. Only about 2% to 3% or less of the metals are washed out this way.

In the end, a mixture of 50% (w/w) sewage sludge, 5% waste incineration ashes and the rest common sand, some compost and straw clippings was found to be an...
acceptable substrate for all the plants involved. In this mixture the presence of chromates probably plays a key role in setting a limit regarding toxicity for higher plants. Citric acid was used to lower the slight alkaline pH to a level between 5.5 and 6, and to aid in the mobilisation of metals. The exception was Eichornia crassipes, which was cultivated floating in 7 litres of water mixed with 1 kg of sewage sludge and 0.5 kg of waste incineration ashes.

2.2 Planting

It was found that planting seeds directly into the sewage sludge substrate led to very poor germination results. It turned out best to pre-germinate plants in normal seedling substrates and then transplant the young plants into the target substrates after they had some centimetres of height and a basic root-ball developed. Plants where potted into 13 litre planting-pots where each pot received 10 kg of substrate. All plant species are grown with three repetitions (three pots) and each 13 l pot holds at least three plants. The planted pots where placed under artificial lighting by using LED-lights that are optimized for the photoactive light spectrum for plant photosynthesis (PAR) (see Figure 1). All plants receive between 3500 and 5000 Lux at the topmost set of leaves. Artificial light is kept on for 15 hours per day. Temperatures were kept above 15°C at all times. An automatic irrigation system is used, where a sensor based on soil electric resistance automatically initiates an irrigation process when a certain threshold is reached. Irrigation is delivered through low flow drippers. The water used is deionized in order to avoid having any metals added to the substrate through tap water, particularly calcium and magnesium cations, which can be antagonists for the uptake of some target metals.

![Figure 1. Trial set-up under laboratory conditions](image)

3 Results and discussion

Metal accumulation occurred in all used plants under certain conditions. Nitrogen seems to play an important role for the plants and their decision, which metals to (hyper)accumulate. Unfortunately Pteris cretica showed the worst metal accumulation in comparison to the other plants. Alyssum murale showed interesting accumulations for molybdenum in nutrient rich conditions of sewage sludge and good accumulation for nickel, rubidium and manganese under poor nutrient conditions. The accumulator plant Dryopteris filix-mas could be interesting for further investigation about vanadium and molybdenum. Two varieties of sunflower were tested, where rubidium and manganese showed promising results. Eichornia crassipes was grown on watered industrial sludge and showed high accumulation for cadmium, nickel, rubidium and zinc. Phytolacca...
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Figure 1. Trial set-up under laboratory conditions

Dryopteris filix-mas, which showed interesting promising results. Two varieties of sunflower were tested, where rubidium and manganese showed vanadium and molybdenum. Two varieties of sunflower conditions. The accumulator plant nickel, rubidium and manganese under poor nutrient conditions of sewage sludge and good accumulation for the plants and their decision, which metals to

The results of this project provide the groundwork for further research and development steps that may bring to practical implementation a technological option with potentially huge benefits:

- The recovery of valuable metal resources from sewage sludge, incineration ashes and metal rich waste waters by environmentally friendly and low energy means.
- Simultaneous decontamination of the input substrates from heavy metals, opening the possibility for these nutrient streams to be redirected to biological regeneration processes (for example use as fertilizers in agriculture) without fear of polluting soils with heavy metal loads.
- Simultaneous generation of biomass on contaminated substrates, which can yield usable energy surplus through incineration during processing.

4 Conclusions

All in all, the results look very promising to keep up the work and stretch it to other waste streams as well. Therefore a national follow-up research project started in March 2014, where two years of field trials with hyperaccumulative plants and further phytomining strategies (recovering of metals) are developed.

Figure 2. A accumulation rates of certain metals.

Acknowledgements

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Phytomining strategic metals and other elements from naturally mineralized soils and mineral wastes
Heavy Metal Uptake by Species from Metalliferous Sites in Northern Greece

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Abstract. Plant samples collected from 65 populations of 35 taxa from 20 metalliferous sites of northern Greece together with surface soil samples from their growth area were analysed for their total concentrations of Cu, Pb, Zn, Cd, Ni, Cr, Mn, Fe, Ca, Mg, K, Na. pH was also determined in the soil samples. Metal accumulation varied considerably within the populations of the same taxa. However, it was obvious in many cases that the amount of metals in the soil affected their uptake by the plants. Zinc indicated a stronger tendency to be accumulated in plant tissues than Cu and Pb. Increased K uptake was noticed in relation to the soil content. The Ca/Mg quotient, which was in almost all cases < 1 in the soil, was much increased in the plants.

Alyssum chalcidicum and Alyssum heldreichii were distinguished by their ability to accumulate Ni. The following species indicated abnormally high concentrations of one or more of the metals Cu, Pb, Zn and Cd: Cistus incanus ssp. creticus (Pb, Cd), Thlaspi ochroleucum (Pb, Zn), Minuartia greuteriana (Pb), Viola arvensis (Cd), Centaurea grisebachii (Zn), Silene conica (Zn) and Scleranthus perennis (Cu).

Keywords. Heavy metals, accumulation, northern Greece, Alyssum heldreichii, Alyssum murale, Rumex acetosella, Minuartia, Thlaspi, Cistus, Centaurea, Viola

1  Introduction
There is an extensive literature worldwide dealing with heavy metal tolerance of plants, as well as plant species which are hyperaccumulators of heavy metals and their role as indicators of geochemical anomalies (Brooks et al. 1979; Baker 1981; Brooks 1983; Reeves 1988). Although Greece is rich in ore deposits, until recently few papers were published, related to the subject. The majority of them concern metal rich areas in northern Greece in the decade commencing 1980 (Karataglis et al. 1982; Babalonas 1984a, b, 1988, 1989; Babalonas et al. 1984; Kelepertsis et al. 1985; Reeves et al. 1986; Babalonas and Reeves 1988; Babalonas et al. 1997).

The present paper is a part of a more extensive research program on the vegetation of metalliferous sites in northern Greece (Konstantinou 1992; Konstantinou and Babalonas 1992; Bergmeier et al. 2009). It aims to gain further information on the metal uptake by populations of various plant species growing on substrates with different mineralisation in relation to the soil content. The majority of the taxa studied are different, constant or abundant in the vegetation types growing on twenty metalliferous sites of northern Greece.

2  Materials and methods
Plant samples (aerial parts) were collected from 65 populations of 35 taxa from 20 metalliferous sites in northern Greece (Fig. 1). Surface (0-10 cm) soil samples from their growth area were analysed for their total concentrations in Cu, Pb, Zn, Cd, Ni, Cr, Mn, Fe, Ca, Mg, K, Na. Soil acidity was determined electrometrically in a 1:2.5 (weight:volume) soil-water slurry.

Plant samples were washed thoroughly in tap-water, air-dried, pulverised and oven-dried at 105°C for 2 h. The soil samples were air-dried and sifted with a 2 mm sieve. Before analysis soils were ground gently with an agate pestle and mortar, sifted with a 0.2 mm sieve and oven-dried at 105°C for several hours (Allen et al. 1974; Brooks 1983). Total metal concentrations were measured by Atomic Absorption Spectrophotometry (AAS) after wet digestion of samples with a 4:1 (v:v) mixture of nitric and perchloric acids (Allen et al. 1974).

Figure 1. Map of the study area with the localities of the collection sites. Four sites are not shown to avoid overlapping labels (Akropotamia is adjacent to Lipsidrio and Laodikino, Antigonia to Akritas, Gerakario to Vathi and Kokkinolakos to Stagira and Skuries). For information about the geological substrate and the altitude of the sites see Bergmeier et al. (2009).

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The analyses (Table 1) showed that the geochemical anomalies in the substrate were reflected more or less by the plants. Metal uptake varied considerably within the populations of the same taxa. However, it was obvious in many cases that the amount of metals in the soil affected their uptake by the plants. Among the metals Cu, Pb and...
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Zn, the latter indicated a stronger tendency to be accumulated in the plant tissues.

**Cu.** A nomalous to highly anomalous Cu concentrations (23-205 μg/g) were reported for most plant species from copper-rich substrates. Scleranthus perennis from Skouries showed the highest concentration (205 μg/g) (Table 1). Copper concentrations in the soil must exceed ca. 1000 μg/g in order that the plants contain Cu concentrations considerably higher than 8 μg/g. As Cu is an essential element for plant nutrition, the Cu content of most plants tends to be internally than externally regulated, so that concentrations in plants remain low and relatively constant irrespective of soil content up to a critical level (Konstantinou and Babalonas 1996).

**Pb.** Lead concentrations in the plants did not exceed 20 μg/g, when total Pb concentrations in the soil ranged between 31-692 μg/g. Lead concentrations in the soil must exceed ca. 700 μg/g, so that the Pb concentrations in the aerial part of plants be ranged between 29-2300 μg/g. Cistus incanus ssp. creticus showed the highest Pb concentration (2300 μg/g), whereas normally high concentrations, exceeding 1000 μg/g, were also found in Minuartia greuteriana (1175 μg/g, Kirki) and Thlaspi ochroleucum (Vouves, 1345 μg/g) (Table 1).

**Zn.** Zinc concentrations exceeding 1000 μg/g were reported for the populations of 5 species, Centauraea grisebachii (1760 μg/g, Kokkinolakos), Minuartia hirsuta ssp. falcata (1200 μg/g, Stagira and 990 μg/g Kokkinolakos), Rumex acetosella (1000 μg/g, Kokkinolakos), Silene conica (1360 μg/g, Sotiras and 860 μg/g, Vouves) and Thlaspi ochroleucum (1820 μg/g, Vouves and 2100 μg/g, Sotiras) (Table 1). The populations of the former three species grew on soils with total Zn concentrations ranging between 1500-4400 μg/g, whereas the rest of them grew on soils with mean total concentrations 35735 μg/g and 71700 μg/g. Even though there was a great difference between the total Zn content of the soils among the sites, this was not reflected within the plants. This may be attributed to the reduced availability of Zn due to the high pH of the soil at some sites. In the majority of the plant populations studied, Zn content ranged between 128-780 μg/g, whereas in the soil it was between 1500-71700 μg/g. In only a few cases, the Zn content of the plants was < 100 μg/g.

**Cd.** Cadmium concentrations in the plants were within normal levels (i.e. 0.001-0.3 μg/g, Allen et al. 1974), except for Viola arvensis (40 μg/g, Sotiras), Cistus incanus ssp. creticus (37 μg/g, Vouves), Thlaspi ochroleucum (22 μg/g, Vouves) and Aethionema saxatile (17 μg/g, Sotiras) (Table 1).

**Ni, Cr.** Nickel and chromium are abundant in the serpentine soils. Alyssum chalcidicum and Al. heldreichii were distinguished by their ability to accumulate Ni in extremely high quantities (3000-6900 μg/g) (Table 1). Alyssum chalcidicum is one of the six species, included in A. murale s.l. (Ball and Dudley 1964). It is known that the genus Alyssum contains the largest number of Ni hyperaccumulators, especially species in the Section Odontarrhena (Brooks et al. 1979; Reeves et al. 1983). Nickel concentrations in all other plants analysed were lower than 63 μg/g.

**Fe, Mn.** Concentrations of Fe and Mn in plant tissues showed a greater independence from their concentrations in the soil.

**Ca, Mg.** Most noteworthy is the behaviour of the populations studied concerning the ratio of Ca to Mg uptake. The Ca/Mg quotient, which was in almost all cases < 1 in the soil, was much higher in the plants (Table 1). Similar observations were made for various Silene species from serpentine soils by Babalonas and Reeves (1988), as well as for other species from metalliferous (other than serpentine) soils (Babalonas et al. 1987; Konstantinou and Babalonas 1996). The presence of increased levels of Ca in plants may well be related to the involvement of Ca in resistance against heavy metal toxicity and also against Mg toxicity at high Mg concentrations (Heikal et al. 1989).

**K, Na.** An increased K uptake by the plants in quantities much higher than those in the soil was noticed (Table 1). This may well be related to an ameliorative effect of K on unfavorable soil conditions due to the presence of heavy metals (Sieghardt 1987).

**Sodium concentrations within the plants were not of particular interest.**

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species from North Greece in relation to the serpentine problem. Phytomining strategic metals and other elements from naturally mineralized soils and mineral wastes


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Table 1. Examples of relationships between metal total concentrations in the aerial part of plant species (μg/g dry weight) and soil (μg/g). (fl.: flowering, fr.: fruiting, fol.: in foliage).

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Phytomining strategic metals and other elements from naturally mineralized soils and mineral wastes 1479
Diversity and Evolution of the Molecular Mechanisms Involved in Nickel Hyperaccumulation in Plants

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Claude Grison
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Abstract.
Worldwide, more than 450 plant species scattered through 40+ families are known to accumulate > 0.1% nickel in their leaf dry matter. These hyperaccumulator plant species can be used to restore nickel mining sites and their biomass valorised to produce nickel with a limited impact on the environment. However, the development of these sustainable phytotechnologies is limited by our knowledge of the molecular mechanisms involved in nickel tolerance and hyperaccumulation. Using RNA-Seq-based comparative transcriptomics and functional studies, we aim to identify the molecular mechanisms involved in nickel tolerance and accumulation in a wide diversity of plant species. Using this original information, we will be able to study the diversity and the evolution of the mechanisms involved in nickel accumulation in plants. These studies will reveal important genes that could be used to support the development of sustainable phytotechnologies such as nickel phytomining and green chemistry.

Keywords.
Hyperaccumulators, Nickel, Metal transporters, Chelators, Green Chemistry.

1 Diversity and access to nickel hyperaccumulator species

More than 450 plant species are known to accumulate > 0.1% (dry weight) of nickel in their leaves and are so called nickel hyperaccumulators. These hyperaccumulators are found in more than 40 plant families scattered in several orders of dicotyledonous plants (Figure 1). These peculiar plants are found in several hotspots around the globe including, Cuba, New Caledonia, Europe and Indonesia (Reeves et al. 1999, Jaffré et al. 2013, van der Ent et al. 2015). This evolutionary and geographical dispersion suggests that nickel hyperaccumulation appeared independently several times during evolution of plants. These plant species receive an increasing interest because they can be used to restore mining sites and the biomass can be valorised as a bio-ore (Losfeld et al. 2012; van der Ent et al. 2015). In this project, we have established a network of collaboration in Europe, New Caledonia and Cuba to access several hyperaccumulator species from Noccaea (Brassicaceae), Psychotria (Rubiaceae), Geissois (Cunoniaceae) and Leucocroton (Euphorbiaceae) genera.

2 Identification of genes linked to nickel hyperaccumulation using RNA-Seq based comparative transcriptomics.

Nickel hyperaccumulation is a complex trait involving several steps from the absorption of nickel from the soil by the roots to the accumulation of the metal in leaves (Hanikenne and Nouet 2011). Our general strategy to identify genes linked to nickel hyperaccumulation is to compare the transcriptome of a nickel hyperaccumulator with the one of a closely related non-accumulator species (e.g. Noccaea caerulescens vs. Microthlaspi perfoliatum; Psychotria gabriellae vs. Psychotria semperflorens). We extract RNA from roots and leaves of both hyperaccumulator and non-accumulator species and compare gene expression between species using an RNA-Seq approach. Genes showing a statistically significant difference of expression between the two species are considered as candidate genes for nickel hyperaccumulation (Figure 2). The identification of gene networks linked to nickel hyperaccumulation in distant plant families will allow us to identify the mechanisms of nickel accumulation that have been conserved through evolution of plants or that are more specific to a plant family.
Diversity and Evolution of the Molecular Mechanisms Involved in Nickel Hyperaccumulation in Plants

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Figure 1. Phylogenetic distribution of nickel hyperaccumulators. The number of Ni hyperaccumulators in each order is presented as a bar (logarithmic scale). The red bar indicates that the observed number of hyperaccumulators significantly exceeds the theoretical number. H indicates species accumulating >10,000 mg kg⁻¹ nickel. * indicates the presence of hyperaccumulators from New Caledonia (From Jaffré et al. 2013).

Figure 2. Transcriptomic comparison between the nickel hyperaccumulator *N. caerulescens* and *M. perfoliatum*. RNA from each species was extracted from shoots of plants grown in presence of nickel and sequenced using Illumina 100 bp paired-end. Reads were aligned against the *N. caerulescens* transcriptome (Lin et al. 2014) and quantified using CLC Genomic Workbench. Data are presented using a logarithmic scale.

Functional characterisation of genes linked to nickel hyperaccumulation

Candidate genes identified by the RNA-Seq approach are studied at the functional level to understand their role in nickel tolerance and accumulation. More specifically, we focus on gene coding for metal transporters and genes involved in the biosynthesis of metal chelators because they are likely to play an important role in nickel accumulation.

We express these genes in a heterologous system such as yeast and transgenic plants to test their effect on nickel sensitivity and accumulation (Figure 3).

The identification of genes involved in nickel hyperaccumulation will help us to better understand the key steps involved in nickel hyperaccumulation and to better understand the evolution of this complex trait in plants.

Acknowledgements

We would like to thank all the members of our teams that are involved in the presented work. We also thank local authorities for plant collection authorisations. This project receives support from ANR (ANR-13-ADAP-0004 EvoMetonicks), CNRS (Défi ENVIROMICS GENE-4-CHEM), the French Ministry of Foreign Affairs (SCAC French Embassy in Cuba) and the Labex SPS.

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Phytomining strategic metals and other elements from naturally mineralized soils and mineral wastes

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References

The Ability of Wetland Plants to Extract Metals from Drainage Water at Forested Peatlands on Acid Sulphate Soils

Tiina Maileena Nieminen
Natural Resources Institute Finland, Luke, Box 18, 01301 Vantaa, Finland - tiina.m.nieminen@luke.fi

Abstract:
Finland has the largest known occurrence of acid sulphate soils in Europe. The knowledge of their distribution in forested lands is inaccurate, but c. 1000 km² of forests are located in areas where the presence of acid sulphate soils has been predicted to be highly probable by Geological Survey of Finland. The effects of forest management on the quality of drainage water should be under special control especially in peatlands underlain by sulphide-bearing sediments. The efficiency of natural and constructed wetlands in removing dissolved metals from the drainage water is evaluated with special emphasis on the role of wetland plants in water purification.

Keywords: acidification, heavy metals, sulphides, silviculture, water protection

1 Introduction

Finland has the largest known occurrence of acid sulphate soils in Europe, c. 1000 km² of agricultural land using Soil Taxonomy Criteria. The knowledge of their distribution in forested lands is more inaccurate, but c. 1000 km² of forests are located in areas where the presence of acid sulphate soils has been predicted to be highly probable by Geological Survey of Finland. Acid sulphate soils are soils which contain or have contained metal sulphides. These sulphides are susceptible to oxidation when subjected to aerobic conditions. Soils containing sediments dominated by metal sulphides cause high acidity and release of heavy metals when excavated or drained as the sulphides within the soil react gradually with the oxygen in the air and form sulphuric acid. Consequently, leaching of acidity and heavy metals can kill plants and animals such as fish, contaminate food crops and drinking water, and corrode concrete and steel structures. In Finland, the discharge of several metals (e.g. Cd, Ni, Zn) to water courses from acid sulphate soils is much greater than the corresponding discharge from the entire Finnish industry.

2 Scope of this study

2.1 Distribution of acid sulphate soils

The global coverage of sulphide-bearing sediments has been estimated to be over 170 000 km². Acid sulphate soils cover extensive areas particularly on the tropical coasts, Southeast Asia, the Caribbean and West Africa, and they are widespread on the coasts of Australia. In Europe the acid sulphate soils are found around the Baltic Sea. Until the recent decades, the main focus in treatment of these soils has been to prevent acidification and toxicity to crop plants, and only limited attention has been paid to the environmental threat caused by the release of acidity and heavy metals to the surrounding watersheds. Even less concern has been paid to semi-natural ecosystems, such as managed forests. Development of preventive methods for acidity and metal release for soils already under crop cultivation, timber production or construction, as well as for undisturbed pristine soils under a pressure of land use change, is a great challenge for the future.

2.2 Forested peatlands on acid sulphate soils

In Finland, 49 500 km² of peatlands have been drained for forestry, and most of these peatland forests will be at the regeneration stage within 10 to 30 years. Ditch network maintenance is often a prerequisite for a successful establishment of the following tree generation. In these areas, forestry practices such as final harvesting, ditch network maintenance and site mounding at the regeneration phase, have to be adjusted to inhibit deleterious effects to watersheds. This study describes the best available techniques to be used in peatland forestry on acid sulphate soils in order to minimize exposing sulphides to oxidation. The efficiency of natural and constructed wetlands in removing dissolved metals from the drainage water is evaluated with special emphasis on the role of wetland plants in water purification.

3 Mitigation of metal release from forested peatlands

In terms of forest management activities, ditch network maintenance poses the highest risk of acidification and metal release into surface waters. The general national recommendation for the drainage depth is 80-100 cm and 40 m for the distance between the ditches to target the removal of excess water in order to ensure sufficient aeration of the root zone of the tree stands. However, if sulphide-bearing sediments are found at depths close to 80 cm depth, a better solution would be to create a dense ditch network by installing new shallow ditches between the original ones. The most important precaution is to avoid reaching the depths of sulphide containing sediments in soil.
Phytomining of Valuable Metals from Waste Incineration bottom Ash using Hyperaccumulator Plants

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Abstract. Phytomining could be an alternative technology for the recovery of valuable metals from secondary sources, such as waste incineration bottom ash. The aim of this work is to recover strategic metals from waste incineration bottom ash using metal-accumulating and hyperaccumulating plants. Our work is targeting critical raw materials defined by the European Commission in 2014. The target metal species in our project are amongst others gallium, antimony, cobalt, molybdenum, manganese, copper, zinc, vanadium, chromium, nickel and selected rare earth elements. Five plant species (Brassica napus, B. juncea, two different clones of Nicotiana tabacum, Sedum plumbeizincicola, and Alyssum pintodasilvae) are currently being tested for potential accumulation of these metals from a mixture of waste incineration bottom ash, residues from mechanical biological waste treatment and biochar.

Keywords. Waste incineration bottom ash, phytomining, valuable metals

1 Introduction

Worldwide, the availability and accessibility of primary sources of certain economically important metals is under pressure resulting in supply risks and increasing prices for these materials. Securing the availability of strategic metals is especially important for the vitality and competitiveness of the European economy (EC 2014). An alternative way of retrieving these valuable metals is the recycling and use of anthropogenic secondary sources, such as waste incineration residues. Around 580,000 tons of waste incineration residues were produced in 2012 in Austria, with 455,000 tons of that material being landfilled (FMA 2014). In that way, a great resource potential is lost every year. Phytomining could offer an environmentally sound and cheap technology to recover valuable metals from waste incineration residues.

The aim of our research is to investigate the potential of phytomining from waste incineration bottom ash by growing metal-accumulating and hyperaccumulating plants on these substrates and treat the metal enriched biomass to obtain a bio-ore. Waste incineration bottom ash was characterised and conditioned to obtain a suitable substrate for plant growth. A pot experiment with different substrate mixtures and plants is currently under investigation in the greenhouse.

2 Materials and methods

2.1 Characterisation of waste incineration bottom ash

As a first step, material from Vienna’s (Austria) municipal solid waste incineration, as well as residues from hazardous waste incineration and sewage sludge incineration were analysed. Samples were sieved to < 5 mm for further analyses. Pseudo-total metal contents were determined after aqua regia extraction. The plant-available metal fraction was determined after extraction with 1M NH₄NO₃ solution. These extracts were screened for trace elements using ICP-MS (Elan 9000 DRCe, Perkin Elmer). Further characterisation of the material included pH, electrical conductivity, total carbon and nitrogen content, TOC and cation exchange capacity.

Different amendments, mainly from the waste industry, as well as different acidifying agents were tested for optimising the substrate for plant growth.

2.2 Pot experiment

A pot experiment was set up in an experimental greenhouse in December 2014. The experimental set-up consisted of a full factorial design involving five plant species (Brassica napus, B. juncea, two different clones of Nicotiana tabacum, Sedum plumbeizincicola and Alyssum pintodasilvae) with two different substrates and an unplanted control. The substrates consisted of a mixture of waste incineration bottom ash (70%), residues from mechanical biological treatment (MBT) of municipal solid waste (20%) and biochar (10%). Two different mixtures were used, including either bottom ash from hazardous waste incineration (HWI) or municipal solid waste incineration (MSWI). Fast-growing species (B. napus and B. juncea) were harvested after two months of growth and the plant tissue was analysed for accumulation of the target metals. The influence of plants on substrate characteristics and labile metal pools will also be evaluated.

3 Preliminary results

3.1 Characterisation of waste incineration bottom ash

In general, the bottom ash can be characterised by a very high pH (up to 12.5), high salinity (2-8 mS cm⁻¹) and high heavy metal concentrations. Washing the bottom ash with diluted HNO₃ showed to be effective for
lowering the pH of the material. The acid treated substrate in combination with material from MBT of municipal solid waste and biochar proved to be a promising substrate for plant growth.

Our work is targeting critical raw materials defined by the European Commission in 2014. The target metal species in our project are amongst others gallium, antimony, cobalt, molybdenum, manganese, copper, zinc, vanadium, chromium, nickel and selected rare earth elements. These elements are present at low to moderate concentrations in the bottom ash (see Figs. 1 and 2).

3.2 Pot experiment

Pots with B. napus and B. juncea were harvested in January 2015 after 8 weeks of growth. Preliminary results of the plant uptake of some trace elements with regards to the different treatments are shown in Figs. 3 and 4. The two hyperaccumulator species S. plumbizincicola and A. pintodasilvae grew slowly and seem to have problems to cope with the difficult substrate. Half of the tobacco plants showed moderate growth, whereas the other half died off, independent of the substrate mixture and clone. These plants, currently still remaining in the experiment, will be harvested after four months of growth and will be analysed for accumulation of the target metals.

![Figure 1. Pseudo-total concentrations of selected trace elements in bottom ash from municipal solid waste incineration (MSWI) and hazardous waste incineration (HWI).](image1)

![Figure 2. Pseudo-total concentrations of selected rare earth elements in bottom ash from municipal solid waste incineration (MSWI) and hazardous waste incineration (HWI).](image2)

![Figure 3. Concentrations of selected trace elements in plant tissue of B. napus (BN) and B. juncea (BJ) grown on bottom ash from municipal solid waste incineration (MSWI) or hazardous waste incineration (HWI).](image3)

![Figure 4. Concentrations of selected trace elements in plant tissue of B. napus (BN) and B. juncea (BJ) grown on bottom ash from municipal solid waste incineration (MSWI) or hazardous waste incineration (HWI).](image4)

Acknowledgements

This project is financially supported by the Austrian Research Promotion Agency (FFG, No. 843643).

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FMA, Federal Ministry of Agriculture and Forestry, Environment and Water Management (2014) Inventory of Waste Management in Austria, Status Report 2013 (Die Bestandsaufnahme der Abfallwirtschaft in Österreich, Statusbericht 2013) (in German)
Nickel Phytoextraction by Seven Populations of Hyperaccumulating Brassicaceae

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*Laboratoire Réactions et Génie des Procédés, UMR 7274 - Université de Lorraine - CNRS, BP 20451, 54001 Nancy  
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Abstract. Population samples of four species of nickel hyperaccumulators, Leptopax emarginata, Alyssum murale, Noccaea tymphaea and Bornmullera tymphaea were grown to assess and compare their extraction potential for metallic elements and observe their leaf elemental composition (major and minor). A cropping trial was conducted for 70 days under controlled conditions in an ultramafic soil (1400 mg.kg⁻¹ total Ni and 83 mg.kg⁻¹ DTPA-extractable Ni). After harvesting, the shoots were analysed by ICP to assay the concentrations of trace and major elements present. Seven populations gave different results depending on the elements studied. However, the correlations of elements between populations were close. We noted different abilities for Ni hyperaccumulation between the 4 populations of A. murale. After 70 days growth, B. tymphaea and L. emarginata were the most effective species for phytoextraction of Ni under our conditions. N. tymphaea also showed a particular ability to concentrate Cd.

Keywords. Nickel, hyperaccumulator plants, hytomining, intraspecific variability, element concentrations

1 Introduction

Hyperaccumulator plants are able to accumulate one or more metals to very high concentrations. In the case of nickel, the threshold for hyperaccumulation is set at 1000 mg.kg⁻¹ of Ni in the dry matter (Brooks et al. 1997). The majority of Ni hyperaccumulators in the Northern Hemisphere, belong to the Brassicaceae family (Krämer et al. 2010). Alyssum murale is one of the most studied species (Bani et al. 2007), the genera Bornmullera, Noccaea and Leptopax also contain Ni hyperaccumulating species that have strong potential for phytoextraction of Ni (Chardot et al. 2007, Rue et al. 2015). In the wild, these plants are found on serpentine soils (Proctor and Woodell 1971). Total concentrations of Ni in serpentine soils vary between 1000 and 7000 mg kg⁻¹ (Sheoran et al. 2009), of which only a small proportion is available for plants. These soils are soils of choice to study the behaviour and development of Ni hyperaccumulators. On the other hand, these soils have an acidic pH which promotes the passage of Ni from the solid phase from the soil to the soil solution and thus its entry into the plant (Chardot 2007).

Ni sequestered in plants can then be recovered by various hydrometallurgical processes for the revaluation of the metal (Barbaroux et al. 2012, Zhang et al. 2014).

The economic feasibility of phytomining metalliferous land is controlled primarily by the cost of the metal, the plant biomass and the metal concentration in plants (Brooks et al. 1998, Chaney et al. 2007). Thus, the optimisation of agronomic practices for growing these plants is one of the current challenges. It involves the selection of efficient plants, i.e. plants with high biomass production and a high concentration of metals in their shoots (Zhang et al. 2014).

The aim of this research is to evaluate the phytoextraction potential of various Ni hyperaccumulators across species, populations and the individuals.

2 Materials and methods

Four species of hyperaccumulators, Leptopax emarginata (LEPT), Alyssum murale (AS2, AS10, AS15, ALB), Noccaea tymphaea (NOC), Bornmullera tymphaea (BORN) from the Balkans were chosen. For each, one population was tested except for Alyssum murale where 4 populations from different geographic origins were tested. Seventy individuals from each population were grown. Thus, seven populations of 70 individuals were grown for 70 days on an ultramafic soil (composition Table 1; 70 g of soil/pot) under controlled conditions. The pH of the soil is 6.14 and the capacity cationic exchange is 31.3 cmol⁺ kg⁻¹.

Table 1. Concentration in trace elements in soil (mg kg⁻¹)

<table>
<thead>
<tr>
<th>Element</th>
<th>Total</th>
<th>Extractable (DTPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>161.06 ± 4.27</td>
<td>0.47 ± 0.02</td>
</tr>
<tr>
<td>Ni</td>
<td>1241 ± 12.5</td>
<td>83.1 ± 0.02</td>
</tr>
<tr>
<td>Mo</td>
<td>1873 ± 50.8</td>
<td>6.5 ± 0.37</td>
</tr>
<tr>
<td>Cr</td>
<td>1670 ± 31.9</td>
<td>0.044 ± 0.22</td>
</tr>
<tr>
<td>Zn</td>
<td>113.53 ± 0.43</td>
<td>2.12 ± 0.03</td>
</tr>
</tbody>
</table>

3 Results and discussion

All individuals tested from all populations had Ni concentrations ranging between 2500 and 4000 mg kg⁻¹ in their shoots, exceeding the threshold of hyperaccumulation (1000 mg kg⁻¹ dry matter).

L. emarginata was significantly the species with the highest biomass (Figure 1) whilst B. tymphaea had the highest concentration in Ni.

Figure 1. Biomass of shoots of the seven populations (n=70). Alyssum murale (ALB, AS10, AS2, AS15), Bornmullera tymphaea (BORN), Leptopax emarginata (LEPT), Noccaea tymphaea (NOC).
The four populations of *A. murale* showed significant differences in terms of biomass production and metal concentrations. *N. tymphaea* is distinguished from the other species by its elemental composition, it has concentrations of Cd, Zn and Fe well above those of the other species but had a lower biomass (Figure 3).

Further detailed analysis of the metal elements and cations of accumulated by the various populations of these four species will allow us to focus efforts on certain populations where individuals can then lead to optimisation of the extraction of nickel by hydrometallurgical processes.

**Figure 2.** Ordination plot of shoot samples, generated by Principal Components Analysis of the parameters. AS2, AS10, AS15 and ALB: four populations of *A. murale*, NOC: *N. tymphaea*; BORN: *B. tymbphaeae*; LEPT: *L. emarginata*; Bio: biomass. **b**. Parameters involved in the discrimination of shoot samples.

4 Conclusion and perspectives

Both the intra- and inter-population variability of Ni accumulation in the four species are very high. *L. emarginata* and *B. tymphaea* offer good potential for Ni phytoextraction under our experimental conditions. However, the measured metal concentrations are lower than for individuals collected in the field at the flowering stage.

The selection of ideal individuals is one of the agromining improvement objectives. These selected individuals will be best able to integrate nickel recovery processes by hydrometallurgical processes, taking into account the constraints related to the purification of the product.

Applications of this work are being considered for multi-contaminated matrices, paying special attention to tolerance of high concentrations of metals and co-contamination.

**Acknowledgements**

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**References**


Nickel Agromining for ANSH Production

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Abstract. This contribution is an overview of the results we have obtained for several years in our Ni phytomining research. Crops of the Ni-hyperaccumulator plant, Alyssum murale are being grown in the Balkans (Albania) and high Ni yields have been achieved – 100 kg Ni per ha. Once harvested and dried, A. murale biomass is incinerated and the ashes are treated by a hydrometallurgical process that we have designed and patented to produce a high value added salt, sulphate and ammonium nickel double salt hexahydrate, which is used for electrolytic surface treatment. The process steps are described and the main results presented. We have demonstrated the feasibility of the synthesis of this nickel double salt after phytoextraction. This process is currently being up-scaled to the pilot scale. A start-up project has been launched to develop this activity with two directions, the production of Ni salt and consulting activity for phytoextraction.

Keywords. phytoextraction, nickel, hyperaccumulator plant, hydrometallurgy, secondary resources

1 Introduction

Soils and wastes with high metal content are a source of compounds of industrial interest. However, metal concentrations are generally too low for conventional mining and metallurgical recovery. In these conditions, phytomining offers a great interest. Phytomining is based on the properties of some plants, hyperaccumulator plants, able not only to tolerate but also to accumulate metals contained in soils and transfer them from their roots to their aerial parts. Metals are then extracted from soils and concentrated in the biomass. Biomass can be treated by pyro- or hydrometallurgical processes to recover metals, or to produce high-added value metal salts.

Nickel is the most hyperaccumulated metal, ca 400 Ni hyperaccumulators have been reported worldwide (Verbruggen et al. 2009). These plants easily contain up to 10 g Ni kg⁻¹ (1 wt %) in their tissues (Zhang et al. 2014) provided they are grown on soils having a high enough content of available Ni (M’assoura et al. 2004, Chardot et al. 2005). Among them, 45 belong to the genus Alyssum (e.g. Alyssum murale, A. bertolonii, etc.). Vast areas of ultramafic rocks, naturally rich in metals such as Ni, are present in numerous places around the world (e.g. Mediterranean countries, New Caledonia, Canada, Brazil, Cuba, The United States) (Proctor et al. 1971; Cailléau et al. 2009; Bani et al. 2009; Tang et al. 2009). These serpentine soils contain 1 to 7 g Ni kg⁻¹; they have a low fertility and are generally abandoned by agriculture. For these lands, ‘freezing’ has been so far the most economically viable management solution, although it is unsatisfactory from health and environmental perspectives. An agronomic approach aimed at growing Ni hyperaccumulators has a great interest for such regions, since it gives a value to these abandoned soils, and gradually decreases their toxicity and increases their fertility. The feasibility of growing Ni hyperaccumulators to reach high yields of Ni has already been demonstrated (Chaney et al. 2007; Bani et al. 2007). Field trials that we have performed in Albania have shown that it was possible to produce 1 t dry biomass per ha, corresponding to more than 110 kg Ni (Bani et al. 2007; Bani et al. 2015).

Once harvested and dried, biomass can be incinerated at moderate temperature, around 600 °C, and the produced ashes can be considered as a bio-ore, containing 20 wt % Ni. Ashes can be treated by pyrometallurgical or hydrometallurgical processes to produce metal or high added value products such as catalysts or nickel salts (Li et al. 2003; Barbaroux et al. 2012; Losfeld et al. 2012; van der Ent et al. 2015). Ni recycling has an economic interest since Ni has a relatively high value, despite it has recently dropped (ca 14 000 US$ t⁻¹, London Metal Exchange); the value of Ni salts drastically increases with their purity.

This contribution presents an overview of the research we have been performing in this area for a few years, concerning plant production and the process we have designed to obtain a high purity Ni salt, sulphate and ammonium Ni double salt hexahydrate. This salt is used in electrolytic surface treatment and chemical synthesis.

2 Materials and methods

Ultramafic outcrops are widespread in the Balkans. Our work has focused on Alyssum murale (Bani et al. 2007; Bani et al. 2009; Zhang et al. 2014; Bani et al. 2015) but we have also investigated other species from the Brassicaceae, collected in Albania and Greece (Zhang et al. 2014) They are able to accumulate on average more than 10 g Ni per kg of dry biomass in their aerial parts. The highest concentrations were recorded in the leaves of Leptoplax emarginata (ca 34 g Ni per kg of dry biomass).
Our work is mainly based on Alyssum murale grown in Albania (1 t of biomass per year) in Pojskë (Pogradec, East of Albania), in the region of Pogradec, latitude 40°59'55.28"N; longitude 20°38'0.92"E. Plants were harvested at the mid-flowering stage, when the Ni content in the aerial part is at its highest. These harvests were possible after a plant cultivation following the pioneering work on phytoextraction agronomy (Bani et al. 2009; Bani et al. 2015).

Plants were collected by hand, sun-dried, sent from Pogradec to Nancy and kept at ambient temperature (20°C). Flowers, stems, seeds and leaves were separated and oven-dried at 70°C for 24 h; the dry plant parts were weighed, crushed and finely ground. The Ni concentration was measured in each part of the plants separately and as a composite (Zhang et al. 2014).

Ground plants were incinerated in a furnace (model 1400 furnace, Barnstead Thermolyne). The best conditions have been determined by using two temperatures. A temperature of 550 °C (and more generally up to 700 °C) is well suited, since it allows the destruction of organic matter but Ni is not volatilized.

Solid matrices were first mineralized: subsamples (0.1 - 0.2 g) were pre-digested with 8.5 mL MnO2 (≥ 69%) and 1.5 mL H2O2 (50%) before microwave digestion (Milestone StartD Digestion System). Then all the digests were analysed by plasma emission spectroscopy (ICP-AES, Thermo iCAP 6000 Series ICP Scientific Emission Spectrometer), a multi-element solution (SCP sciences) being used for standardisation. Ashes and salts were characterised by X.R.D.

The initial hydrometallurgical process (Barbaroux et al. 2010, Barbaroux et al. 2012) has been improved (Zhang 2014). After incineration, ashes are washed with water. Then Ni is solubilised with 2 M sulphuric acid at 95 °C for 2 h (150 g ashes L−1). The filtered leachate is neutralised with 5 M calcium hydroxide to produce a pH of 5. Sodium fluoride is then added to remove Mg by magnesium fluoride precipitation. The suspension is filtered and water is evaporated at 100 °C to reduce the volume by a factor of 3. Ni is recovered by crystallisation with ammonium sulphate at 0 °C. This recovery is based on the low solubility of ammonium disulphate salt Ni(NH4)2(SO4)2·6H2O (ANSH) at 0 °C, 1.4 g salt per 100 g of water. The salt is dissolved in water re-crystallised. All the details concerning the process are given in (Zhang 2014).

3 Results

The overall Ni concentration in the plants used for the process was about 10 g Ni per kg of dry biomass. The other major elements were Ca, K and Mg at respective concentrations of 8.4, 7.6 and 3.9 g kg−1. Trace elements were present at very low concentrations (Barbaroux et al. 2010; Zhang et al. 2014; Zhang 2014). Incineration at 550 °C reduced the mass by a factor of 6.6 and concentrated all the elements. Metal mass balance between dry plants and ashes were met, showing there was no metal loss in the ashing process (Zhang et al. 2014).

ANSH production: the ash washing step with water enabled us to significantly reduce the concentration of potassium in the ashes. The acid leaching has been tested in different conditions of acid concentrations, temperatures and duration. With the concentration given here, all the Ni was transferred from the ashes to the solution.

Neutralisation with calcium hydroxide enabled us to increase the pH and remove Fe by precipitating Fe(OH)3. Mg was removed in the form of MgF2. These steps have been improved.

The two crystallisation steps enabled us to obtain crystals with a purity of 99.1%, as assessed by ICP-AES, XRD and gravimetric analysis.

4 Discussion

Our results have shown the feasibility of ANSH production from the biomass of the hyperaccumulating plant Alyssum murale. With these conditions, we have performed a detailed economic study and it was shown that the process can lead to a high level of return.

Since the patent deposition, further work has been done on the hydrometallurgical process in two main directions. The first one was to optimise the process and increase the salt purity. As was shown in the results, the most difficult steps are the removal of K, Ca and above all, Mg. We have found new pathways to increase the removal of these elements. For example, a greater amount of K can be eliminated during ash washing. In the same way, progress has been made in Mg removal, avoiding the use of sodium fluoride. We are also working on the minimisation of effluent and solid waste release, with the idea of recycling at each step. The process is currently optimised under these conditions, and the results are currently in acquisition and finalisation.

The second direction was upscaling. A pilot has been designed and built to prove the feasibility of the process at a higher scale with the objective of scaling-up to enable industrialisation. Experiments are in progress and the first results are as currently expected. Additionally, the economic study is being refined to take into account the changes in the process. A life cycle assessment is beginning to quantify the impact of the process on the environment.

This presentation mostly focuses on the hydrometallurgical process but in all our studies, we consider the global chain, which combines the phytoextraction and the hydrometallurgical steps. The cultivation of hyperaccumulating plants in regions covered by serpentine soils offers many advantages. It gives a new value to these lands characterised by a low fertility and provides a new income to the farmers. Since it is non-destructive, metal removal will improve soil quality and make it useful for further crop production usage. Also, it would preserve and develop other ecosystem services from low value lands (e.g. regulation services: soil quality; carbon storage; cultural services: aesthetic, social stability). A part from natural soils, phytoextraction can also be applied to the decontamination of soils that have been contaminated by metals after industrial or mining activities. It should be able to be successfully applied in the revegetation of sterile mine heaps.
5 Conclusions and perspectives

In this contribution, we give an example of the potentialities of phytomining through the example of the production of the nickel double salt from the biomass of Alyssum murale, a native species of the Balkans. However, many other perspectives can be considered. Many plants of other regions of the world, e.g. under tropical climates (Cuba, Brazil, South China, etc.) should give very interesting results regarding phytomining. Plants can be selected to attain very high Ni extraction rates.

We can also envisage other nickel products. The production of Ni metal has been shown feasible but other Ni salts of high added value could also be produced. Furthermore, elements other than Ni could be of interest for phytomining, provided that: (1) hyperaccumulating plants exist, (2) they can be grown to attain sufficient raw material, i.e. a high concentration of the element in the biomass and high biomass production, and (3) the synthesis of high added-value products is feasible. For example, hyperaccumulator plants are known for Zn, Cd, As, Cu and some other trace metals; the challenge would be the extraction of other elements. This method would enable us to extract valuable elements from secondary resources in which they are dispersed.

In 2013, we launched a start-up project, accompanied by the ‘Incubateur Lorrain’ of Nancy University. We are examining the possibility of creating a company, with two activities: (1) the production of Ni salts by phytomining, and (2) consulting services for phytorextraction. A market analysis is being conducted to evaluate the interest in this creation.

Acknowledgements

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References

phosphorus, nitrogen or other nutrients), (ii) costs associated
with farmers and landowners to manage crop production
with agromining companies, whereas agromining works via arrangements
Ent et al. 2015a). In the tropical context, phytomining
(iv) price of the target metal on world markets (Van der
operating costs; (iii) land ownership or lease costs; and
feasibility assessments include: (i) total development
costs through trial stages to full operation; (ii) predicted
returns to farmers.

However, economic feasibility ultimately depends on the
availability of surface areas enriched in the target
element market price, the annual yield per unit area and
hyperaccumulators are known for these trace elements.
Agromining or phytomining may be undertaken to
produce As, Se, Cd, Co, Mn, Ni, Tl or Zn, as suitable
valuable trace elements (Chaney et al. 1998). This
technology may be termed either ‘agromining’ or
'phytomining' depending on the type of application (Van
dependent on the type of application (Van
to seek industry adoption, a large-scale demonstration is
commercial application of the technology has not yet
happened however, and to build the case for investors or
regarding agronomic and plant-based systems (agromining
an alternative type of agriculture by farmers (agromining),
bio-accumulation system in agricultural soils to generate economic
rehabilitation strategy, agromining is appropriate on low-
developed sites. Agromining and phytomining are being developed
(or ‘metal crops’) may be implemented either as
biomass (or ‘metal crops’) may be either as
metal-contaminated soils makes a compelling case for
the phenomenon of abnormal accumulation of Cu-Co in
crop regions, and these plants accumulate extraordinarily high
concentrations (up to 2%) of Cu and Co metal in their
living tissues (Reeves and Baker 2000).

Co hyperaccumulator plants is a special feature of this
Copper-Cobalt Belt. The existence of more than 30 Cu-
Co hyperaccumulator species that occur nowhere else (Brooks et al. 1985;
many species that occur nowhere else (Brooks et al. 1985;
described from the Copper-Cobalt Belt, including many

3 Suitable soils for implementation

3.1 Copper-Cobalt Belt

Copper-Cobalt Belt. The existence of more than 30 Cu-

4 Current developments

4.1 DR Congo and Zambia (Cu, Co)

The concomitant occurrence of Cu-Co hyperac-
Phytomining strategic metals and other elements from naturally mineralized soils and mineral wastes

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Abstract. Harvesting metals from hyperaccumulator biomass (or ‘metal crops’) may be implemented either as an alternative type of agriculture by farmers (agromining), or implemented on mined-out or degraded land (phytomining). Scientific experiments and field trials relating to agromining/phytomining are being developed at various locations around the world. Large-scale commercial application of the technology has not yet happened however, and to build the case for investors or to seek industry adoption, a large-scale demonstration is urgently needed. We outline current developments in the agromining/phytomining field on the basis of research undertaken by our team.

Keywords. bio-ore, hyperaccumulator, nickel, trials

1 Agromining and Phytomining

Growing and harvesting selected hyperaccumulator plants on agronomical scale followed by metallurgical processing of the bio-ore may produce economically valuable trace elements (Chaney et al. 1998). This technology may be termed either ‘agromining’ or ‘phytomining’ depending on the type of application (Van der Ent et al. 2015a). Whereas phytomining is implemented on degraded or mined land as part of a rehabilitation strategy, agromining is appropriate on low-productivity agricultural soils to generate economic returns to farmers.

2 Feasibility

Agromining or phytomining may be undertaken to produce As, Se, Cd, Co, Mn, Ni, Tl or Zn, as suitable hyperaccumulators are known for these trace elements. However, economic feasibility ultimately depends on the element market price, the annual yield per unit area and the availability of surface areas enriched in the target element (Van der Ent et al. 2015a). Considering these factors, the technology will be especially feasible for Ni, Se and Tl but large surface areas with enrichment exist only for Ni and Se. Other factors to be considered in feasibility assessments include: (i) total development costs through trial stages to full operation; (ii) predicted operating costs; (iii) land ownership or lease costs; and (iv) price of the target metal on world markets (Van der Ent et al. 2015a). In the tropical context, phytomining will take place in mining leases funded by mining companies, whereas agromining works via arrangements with farmers and landowners to manage crop production and harvest, with payment on the basis of the Ni contained in the harvested crop.

3 Suitable soils for implementation

Recent research in Malaysia demonstrates that not all ultramafic soils are suitable for agromining/phytomining as the potential Ni yield depends on the soil available Ni pools (Van der Ent et al. 2013). Tropical Ni hyperaccumulator plants in Sabah (Malaysia) are distributed on circum-neutral serpentinitic and saprolite soils with high Ni plant-availability (Van der Ent et al. 2015b). The landscapes after conventional Ni strip-mining appear promising for phytomining because the chemical characteristics match this natural habitat. The potential lifetime of a phytomining operation may be estimated by considering the Ni concentration in 1 ha (total Ni concentration of 2000 mg kg⁻¹ over 1 m of which 10% is plant-available) and with a metal crop producing an annual yield of 100 kg Ni ha⁻¹. Given this scenario the agromining operation could last for 30 years.

4 Current developments

The development of agromining/phytomining is currently progressing in several areas around the world, specifically with extensive field trials undertaken over a number of years in Albania, the future trials planned in Spain and Greece, and recent reconnaissance and experimental work in Malaysia, Indonesia and Zambia. Below we outline the present status of some of these developments:

4.1 DR Congo and Zambia (Cu, Co)

The Copper-Cobalt Belt of the DR Congo and Zambia is one of the most important metallogenic regions and, without doubt, the richest metallophyte location in the world. To date, over 600 metallophytes have been described from the Copper-Cobalt Belt, including many species that occur nowhere else (Brooks et al. 1985; Baker et al. 2010). These metallophytes occur on isolated copper-mineralised hills spread throughout the Copper-Cobalt Belt. The existence of more than 30 Cu-Co hyperaccumulator plants is a special feature of this region, and these plants accumulate extraordinarily high concentrations (up to 2%) of Cu and Co metal in their living tissues (Reeves and Baker 2000).

The concomitant occurrence of Cu-Co hyperaccumulator plants and large areas with metal-enriched and metal-contaminated soils makes a compelling case for developing these phytotechnologies in Zambia. Although the phenomenon of abnormal accumulation of Cu-Co in certain plants from the Copper-Cobalt Belt has been
known since the 1950s, no study to date has elucidated metal speciation and distribution in these Cu-Co hyperaccumulator plants. Funded by the International Mining for Development Centre (IM 4 DC) in Australia a fieldwork campaign was successfully completed in Zambia in November 2014. During the fieldwork a range of active and abandoned mines and tailings storage facilities were visited in the Copperbelt Region of Zambia. Three Cu-Co hyperaccumulator plants were sampled for ongoing micro-PIXE and synchrotron XAS studies in South Africa and Australia respectively.

4.2 Experimental studies in Malaysia (Ni)

Tropical Ni phytomining trials are currently established in Sabah (Malaysia) near Kinabalu Park. Using two native Ni hyperaccumulator species, Rinorea bengalensis and Phyllanthus securinegoides, experimental studies are being undertaken to establish optimal agronomic practises to stimulate biomass production and Ni yield. This work aims to identify operational agronomics and provide ‘real-life’ evidence for attainable yields. In a parallel strategy, handheld X-ray Fluorescence (XRF) technology is being applied to screen tens of thousands of herbarium specimens held at major tropical herbaria for hyperaccumulators of Ni and other elements to increase the number of possible species for application in agromining/phytomining. Adding greater numbers of hyperaccumulators to the knowledge base increases the options for selection of species with optimal characteristics to match local conditions. These characteristics include the ability to re-spout after pruning, inherent growth rate, irrigation requirements, nutrient needs and Ni allocation in different fractions of the above-ground biomass.

4.3 Exploration in Indonesia (Ni)

In partnership with Eramet/PT Weda Bay Nickel, tropical Ni phytomining is currently being developed in Halmahera Island in the Maluku Province of Indonesia. The extremely high plant diversity of the rainforest on Halmahera Island, in combination with over 5000 km² of ultramafic soils, offers both high potential for the discovery of Ni hyperaccumulator plants, but also a great challenge as information on the occurrence such plants is virtually non-existent at present. Therefore the first stage of the current project is to identify native Ni hyperaccumulator plants in Halmahera Island. In order to be considered suitable or application as ‘metal crops’ in future phytomining operations, attention focuses on finding plants with at least 1% foliar Ni (so-called ‘hypernickelophores’). One such plant has already been recorded on the basis of herbarium collections, Rinorea bengalensis, the same species that is the subject of ongoing experimental work in Sabah (Malaysia).

Rapidly re-establishing plant growth on ultramafic soils after Ni mining is necessary to reduce soil run-off. However, establishing vegetation on mined soils is challenging due to the extreme physical and chemical characteristics of the saprolite materials. Therefore, appropriate matching of native Ni hyperaccumulator species to local soil and climatic conditions is critical. This process must be repeated in different bioclimatic regions and on different soils.

4.4 Other elements and possible opportunities

Phytomining may also be a possibility for a number of other valuable trace elements present in some types of minerals wastes such as tailings. Current research activities with collaborators include experimental work with Berkheya coddi for extraction of Platinum Group Elements (PGEs) from mineral wastes in South Africa, the possibility of extraction of Tl from Zn-Pb-Cu tailings in Australia, and rare earth elements (REE) from mineral wastes in China.

5 Conclusions and outlook

Although agromining/phytomining technology has been successfully demonstrated in academia, no large-scale implementation has yet been seen. This may result from a lack of awareness of the technology in the minerals industry. However, the expected expiry of the patents this year may stimulate renewed interest from commercial entities and investors. Current research activities are centred on parallel strategies in the Mediterranean Region and in Australia. The combined efforts are now gaining momentum and significantly advance our knowledge on the success factors critical to agromining/phytomining.

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SESSION 16
Social and environmental issues in sustainable mining practices

Convenors
Alain Cheilletz, Michel Deshaies, Laure Giamberini, Bruno Goffé, Yann Gunzburger, Jean Louis Morel, Jorge Relvas
the role of bacterial activity in seasonal and spatial variations have been attributed to hydrology, pH and/or redox conditions giving rise to strong seasonal variations of arsenic concentrations in surface waters. These can act as arsenic source and/or sink, according to redox processes of these wastes. Mine drainage sediments reveal seasonal variations. Partial Least Square analysis show that arsenite, (which is the more mobile arsenic form) concentration in water coming from waters and sediments sampled between 1995 and 1999, 2002 and 2004, and 2006 and 2007. From these variations data, it can be noted that arsenic solid speciation and mobility at the interface of mine drainage sediments. The Gabe-Gottes arsenic mine (France) is the more mobile arsenic form. 

Mine drainage sediments concentrate toxic elements such as arsenic or antimony. Sediments are part of a creek upstream and downstream mining area, and characterized. Physical, chemical and biological processes of these wastes participate to environmental contaminations with trace metallic elements and metalloids such as arsenic or antimony. Sediments are considered as a sink and also a source since according to redox, temperature and pH conditions soluble forms of these metallic elements and metalloids in sediments. The Gabe-Gottes arsenic mine (France) can be generated contributing to water pollution. Here we address the question of factors affecting arsenic speciation and mobility at the interface of mine drainage sediments. The Gabe-Gottes arsenic mine (France) is the more mobile arsenic form. 

Arsenic, prokaryotes, biogeochemistry, microbial communities, and 907r (5'CCGTCAATTCMTTTGAGTTT3') for bacterial and archaeal 16S RNA genes were amplified for DGGE. Primers were 341f (5'AGAGTTTGATCTTACGA7'3') and 1386r (5'CCGCCGCGCGGCGGGCGGGGCGGGGGCACGG3') for bacterial communities, and for archaea 934f (5'CGCCCGCCGCGCGCGGCGGGCGGGGCGG3') and 1064r (5'GGGAATTGGCGGGGAGCAC 3') and 1386r (5'CCGCCGCGCGGCGGGCGGGGCGGGGGCACGG3') for bacterial and archaeal 16S RNA genes were amplified for DGGE. Primers were 341f (5'AGAGTTTGATCTTACGA7'3') and 1386r (5'CCGCCGCGCGGCGGGCGGGGCGGGGGCACGG3') for bacterial communities, and for archaea 934f (5'CGCCCGCCGCGCGCGGCGGGCGGGGCGG3') and 1064r (5'GGGAATTGGCGGGGAGCAC 3').


determined by HPLC ICP-MS. Precipitations and flow rate data were considered to describe hydrologic conditions. Arsenic solid speciation data obtained on mine water phases was determined by HPLC ICP-MS. Precipitations and flow rate data were considered to describe hydrologic conditions. Arsenic solid speciation data obtained on mine water phases was determined by HPLC ICP-MS.
Abstract. Mine drainage sediments concentrate toxic elements issued from minerals alteration processes. For metalloids such as arsenic or antimony, sediments are considered as a sink and also a source since according to redox, temperature and pH conditions soluble forms can be generated contributing to water pollution. Here we address the question of factors affecting arsenic speciation and mobility at the interface of mine drainage sediments. The Gabe-Gottes arsenic mine (France) drainage sediments were chosen to address this question. Arsenic solid speciation data obtained on mine drainage sediments reveal seasonal variations. Chemical, physical, climatic and biological variables coming from waters and sediments sampled between 2010 and 2012 on five stations located upstream and downstream the Gabe-Gottes arsenic mine were analysed together. Principal Component Analysis and Partial Least Square analysis show that arsenite, (which is the more mobile arsenic form) concentration in water correlates with water parameters such as nitrogen sources, phosphates, sulphates, pH, conductivity, hydrology parameters and sediment parameters such as bacterial abundance and arsenic detoxification genes (aioA, ACR3-1) abundance in sediments. Multivariate regression trees reveal that bacterial and archaeal community structures in sediments are respectively explained by sediment iron and arsenic concentrations.

Keywords. Arsenic, prokaryotes, biogeochemistry, speciation, mobility, sediments

1 Introduction

Past and actual mining activities often cause on site deposits of mineral wastes. Subsequent alteration processes of these wastes participates to environmental contaminations with trace metallic elements and metalloids particularly in soils, water, sediments, and even in the biota. Mine drainage collect and concentrate these metallic elements and metalloids in sediments.

In arsenic contaminated mine drainage, sediments can act as arsenic source and/or sink, according to redox conditions giving rise to strong seasonal variations of arsenic concentrations in surface waters. These variations have been attributed to hydrology, pH and/or bacterial activity. In France, mining of silver-bearing mineralization in hercynian Vosges Mountains (Gabe-Gottes, N 48°12'863, E 007°09'569, Sainte Marie aux Mines, France) have generated punctual high arsenic concentrations in river system downstream. To evaluate the role of bacterial activity in seasonal and space variations of arsenic concentrations and redox status in water phase, water and sediment samples were collected and characterized. Physical, chemical and biological variables were statistically analyzed.

2 Methods/experimental

2.1 Sampling and analysis

Sampling was realized on five stations, from a 2km long part of a creek upstream and downstream mining area, (December 2010, March 2011, June 2011, September 2011). Sediment samples (2 Kg mean samples) were rapidly frozen. Water samples (2 L) and sediment interstitial water were filtered on 0.45µm after centrifugation at 10000g for 15min. For solid speciation determination, sediments were dried under vacuum, grinded and sieved on 100µm. Arsenic solid speciation has been determined by X ray absorption spectroscopy (XANES, EXAFS). Sediments were stored at -80°C for DNA extraction. Water pH and conductivity were measured on site. Mineralization of sediments was performed with the French standard AFNOR NF X 31-151. Organic content was determined from mass loss after 4 hours at 550°C. Metal and metalloid concentrations were determined after acidification by atomic absorption spectrophotometry, and ions concentrations by ion chromatography. The total phosphorus, total nitrogen (TKN), chemical oxygen demand, biological oxygen demand of wastewater during decomposition occurring over a 5-day period, and total suspended solids were determined according to French standards (AFNOR, 1994). Arsenic speciation in the water phases was determined by HPLC ICP-MS. Precipitations and flow rate data were considered to describe hydrologic conditions.

2.2 Microbial community analysis

PowerMax soil DNA isolation kit (MoBio) was used for sediment DNA extraction. Bacterial and archaeal 16S RNA genes were amplified for DGGE. Primers were 341fGC2(5'CCGCGCCCGCGGCCGCGGCCGCGGCGGGCGGGCGGGCGGGCGGGCGGGCCGCCGGCCTACGGAGGCAGCACG3') and 907r (5'CCGTCAATTCMTTTGAGTTT3') for bacterial communities, and for archaea 934f (5'CCGCGCCGCGCCGCGGCCGCGCCGCGGCGGGCAGC3') and 1386r (5'GGTCTTCACGGCAAGGCGAC3').
3 Results and discussion

3.1 Solid speciation monitoring

Solid speciation was determined in the mine exhaure sediments at different seasons. XANES spectra obtained show an evolution of arsenic solid speciation. $\text{As}(0)$ was only detected as a minor form in December and March, $\text{As}^{(III)}$ was the dominant form in September, $\text{As}^{(V)}$ was the dominant form in December, March and June.

3.2 Spatio-temporal monitoring analysis

We constituted a database informing 69 physical, chemical and biological variables concerning a neutral arsenic mine drainage. PCA were realized on data concerning water and sediment solid phases to identify and eliminate redundant variables. Remaining variables were used in a partial list square with Tanagra software. Arsenic speciation in water was chosen as explained variable. 4 axes explaining 84% of variance were retained. Following the general consensus on PLS interpretation, we focus on variable with VIP values above 1 over the 4 axes. Correlations between those important variables were evaluated through similar trends in model effect loadings. Results indicate that the most important variables to explain arsenic speciation in water are in water phase: nitrogen sources, phosphates, sulfates, pH, conductivity, hydrology parameters, and in sediment bacterial abundance and arsenic oxidation (aioA) and detoxification genes (ACR3) abundance. Factorial plane resulting from the PLS analysis shows a strong correlation between arsenite concentration in water and aioA and ACR3 bacterial genes. Correlation is also observed between arsenate concentration in the water column and bacterial abundance in the sediment. Results suggest the implication of sediment bacteria in arsenic speciation in water.

3.3 Environmental factors explaining the prokaryote community dynamics

Multivariate regression trees were performed to compare microbial fingerprint with environmental factors. Operational taxonomic units obtained by DGGE analysis performed on sediment DNA were exported to R software (Development Core Team, 2011) and compared to the following environmental data: pH, conductivity, arsenite, arsenate, nitrogen sources, sulfates, phosphates, abundance of functional genes, $\text{As}$, $\text{Fe}$ and $\text{Mn}$ concentrations in sediments. $\text{As}^{(III)}$ was the dominant form in September, $\text{As}^{(V)}$ was the dominant form in December, March and June.

![Figure 1. Result of the multivariate regression tree analysis performed on bacteria.](image)

![Figure 2. Result of the multivariate regression tree analysis performed on archaea.](image)
sediments. Indeed arsenic detoxification systems influence arsenic speciation. Moreover both bacterial and archaeal community structures of the sediment are influenced by arsenic concentration in the sediment. Iron concentration in the sediment is the major factor structuring bacterial community in Gabe-Gottes mine drainage sediment.

Acknowledgements

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References

Social Acceptability during the Exploration Stage

A Social Risk Index for Mining Projects: Evaluating the Likelihood of Better Social Acceptability for a Project

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The Fraser Institute annually surveys mining companies to determine their level of social license to operate. Based on the survey results, the "social licence to operate" is lower in the majority of countries and regions worldwide, with the highest roads of social license to operate seen in the United States, the United Kingdom, and Canada. Delays in the permitting process are one of the reasons for low social license to operate. In 2013, a survey of 38 countries revealed that the process could take up to 2 years, with the most common time frame being 2 to 4 years. Delays in the permitting process are a major factor in the low social license to operate in many countries.

The concept of "social license to operate" is widely recognized in the mining sector, but it is not yet well-established. It is a term used to describe the consent of stakeholders for a project to proceed. The approval process is critical to gaining social license to operate, and it can be a source of delay. The process of obtaining permits can be lengthy, and it can take up to 2 years. Delays in the permitting process are a major factor in the low social license to operate in many countries.

The perception of the project by the community is also a crucial factor in the success of a mining project. Over 80% of the respondents in the Fraser Institute survey stated that the most important factor in gaining social license to operate was the perception of the project by the community. The project must be perceived as beneficial to the community, and the company must communicate effectively with the community to ensure that it is perceived as beneficial.

The social risk index developed in this study is a tool that can be used to evaluate the likelihood of better social acceptability for a project. It can be used to evaluate the social acceptability of a project at the beginning of the exploration stage. The index is based on the following variables: the characteristics of the nearest community, the nature of the deposit, the social and economic conditions of the region, the impact of the project on the environment, and the attitudes of the community towards mining.

The index can be used to identify the most important factors that influence social acceptability and to develop strategies to improve social acceptability. The index can also be used to compare the social acceptability of different projects and to identify areas of improvement. The index can be used by investors, mining companies, and communities to ensure that mining projects are socially acceptable and to improve social acceptability.

Keywords: social acceptability, communities, risk, mining
A Social Risk Index for Mining Projects: Evaluating Social Acceptability during the Exploration Stage

1 Context

Recent developments in the international sphere clearly show that companies will have to be more transparent and accountable to the general public to be able to continue operating in the coming years. Examples that come to mind are the Bangladesh Safety Accord for the garment industry, which was adopted following the Rana Plaza tragedy, and the Guiding Principles on Business and Human Rights, unanimously endorsed by the United Nations Human Rights Council in 2011.

The mining industry is no stranger to this type of commitments. The Extractive Industries Transparency Initiative and the Kimberly Process are among the best known among the initiatives taken by the industry. Yet, it is worth noting that many of the toolkits and guidelines developed for the mining industry are to be applied during the exploration phase. However, we know that many projects encounter hurdles before that phase, during exploration and the approval process. A recent study (Franks et al. 2014) calculates the amounts lost by mining companies when operations are interrupted, which can be as high as $20 million per week. During early exploration, the costs can reach $10,000 per day. For advanced exploration, it can be up to $50,000 per day.

The Fraser Institute annually surveys mining companies around the world. In its 2013 report, questions on delays in permitting or for approval caused by public opposition were included. The answers show that “[o]ver 36 per cent of companies agreed that public opposition to mining had affected the permitting and/or approval process”. The most common cause for opposition were “environmental or water usage” (in more than 59% of the cases) and “Indigenous or Aboriginal rights or title” (in nearly 32% of the cases). Delays were from 6 months to 4 years, the most common answer being from 2 to 4 years (Wilson et al. 2014: 77-78). Even if one can be critical vis-à-vis these data – a better project can come out of these delays and the discussions causing them – they still mean that current processes to assess and manage social risks are not optimal.

Costs and delays are important reasons explaining the growing amount of scholarly work done on the issue of the “social licence to operate” (for example: Moffat and Zhang 2014; Prno and Slocombe 2014; Owen and Kemp 2013), to use the expression currently in favour in the extractive domain.

2 Developing a new tool

A multidisciplinary team based in Université du Québec à Montréal (Canada) has been working on a social risk index to better understand the conditions influencing the social licence to operate during the exploration phase. We wanted to develop a tool that would be valuable for all stakeholders (investors, mining company, community, and government) at the beginning of a mining project, while it is still possible to change some aspects of it. The tool is useful before comprehensive studies for environmental impacts are to be done, studies that are needed to obtain the permits and certificates necessary for the construction of the mining site, when the project is more difficult to change.

Starting with the idea that some aspects of a mining projects are given, such as the localisation of the site, the characteristics of the nearest community, and the particularities of the company promoting the project, our endeavour was firstly to identify the most important such aspects in relation with social acceptability. To put it another way, which aspects can condition the most the reception of a project by a community?

In addition, we shared the view expressed by many specialists that community relations have to start as early as possible in a project. This implies that some communication has taken place between the company and the community, and that it would be possible to find
criteria to evaluate the quality of this communication and its early results.

A theoretical model was thus created to structure the project. It is built on two triangles: the first is the space of characterisation, and the second, of communication (Figure 1).

- In the three angles of the first triangle, we find the project and its natural environment, the community where it will be located, and the company proposing it.
- In the second triangle, the space of communications, the aspects considered are: the distance between actors' positions; the flexibility in actors' positions; and the fluidity of communications between the actors.

Figure 1. The model shows how the relevant information for the index is organized in different spaces: characterisation and communication.

For each of these angles, key factors influencing social risk were identified.

The second triangle is much more subject to interpretation than the first one, but perceptions are not excluded from the space of characterisation because we realized that in some cases, they were more relevant than the objective aspect of the characteristic.

Models trying to explain relationships and power as they touch the mining world in a country or in the global arena almost inevitably include the State or governments. The model used for this research project is not. It does not exclude it completely, because mayor and councillors are included in our conception of the community, but the State as a separate actor is not represented. The reason is the following: because we are considering mining projects in only one province for now, the State is the same for all of these projects, and will not be a discriminating factor influencing social risk in relation with these projects. It would be more accurate to say that the State has been circumvented, put aside because its influence on the different projects can be considered a constant.

To develop the social risk index, the methodology adopted included a few phases. The first was the realisation of literature reviews in different disciplines to help the team select the most significant variables for each angle of the triangles. Many discussions were also necessary to obtain a limited number of variables, since our objective was to do a relatively simple tool, which would not necessitate much time or resources to use. For each variable, the different values it could take and their relation with social risk were assessed by the team.

This work was done for the two triangles, but for the second one on communication, the team agreed that its contribution to the index would be to qualify the results of the first triangle with a perspective for the future. The results' format after an analysis is thus composed of three elements: A, B, C, or D for the first triangle, +, −, or = for the second one, and a percentage reflecting the proportion of variables where information was provided.

To be able to evaluate the validity of the results obtained through the index, two separate tests were undertaken. The first is a press analysis of the same mining projects that were used for the index. According to this analysis, the projects were classified from the least socially risky to the most socially risky. The second test had a similar objective, i.e. obtaining a classification of the same mining projects, according to the opinion of key informers, people with a very good knowledge of mining...
projects in Québec, and representing the four groups of potential users for the index (companies, investors, communities, and governments). The three classifications were then compared. The results show differences, but acceptable ones.

The questionnaire for the communication part was probed by a few communication specialists. A thorough test was not feasible in the timeframe we had to complete the project.

3 Results

For the first triangle, the variables selected by the team are presented in Table 1.

Table 1. Selected variables for the space of characterisation

<table>
<thead>
<tr>
<th>Angles</th>
<th>Groupings</th>
<th>Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Company</td>
<td>Organization</td>
<td>Dedicated person for community relations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Presence of sustainable development</td>
</tr>
<tr>
<td>History</td>
<td>Age</td>
<td>Environmental infractions</td>
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<td></td>
<td></td>
<td>Difficulties with communities</td>
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<td></td>
<td></td>
<td>Headquarters localisation</td>
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<td></td>
<td></td>
<td>Local project office</td>
</tr>
<tr>
<td>Leadership</td>
<td>Years of experience</td>
<td>In a major company or a mining association</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Financial infraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Disciplines represented in the board of directors</td>
</tr>
<tr>
<td>Project and natural environment</td>
<td>Substance</td>
<td>Perception of toxicity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Real toxicity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Value of the project</td>
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<td></td>
<td></td>
<td>Localisation of transformation</td>
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<td></td>
<td></td>
<td>Distance to community</td>
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<td>Distance to water</td>
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<td>Distance to protected or fragile sites</td>
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<tr>
<td>Exploitation</td>
<td>Mode</td>
<td>Mode</td>
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<td></td>
<td></td>
<td>Size</td>
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<td></td>
<td></td>
<td>Direct jobs</td>
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<tr>
<td>Community</td>
<td>Economy</td>
<td>Importance of mining in local economy</td>
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<tr>
<td></td>
<td></td>
<td>Population density</td>
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<td></td>
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<td>Post-secondary rate</td>
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<td></td>
<td></td>
<td>Unemployment rate</td>
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<tr>
<td>Sociology</td>
<td>Rate of secondary residence</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Local organisations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Meaning of site</td>
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<td></td>
<td></td>
<td>Use of site</td>
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<tr>
<td></td>
<td></td>
<td>Indigenous peoples’ rights on the site</td>
</tr>
<tr>
<td>History</td>
<td>A round non-mining projects</td>
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<tr>
<td></td>
<td></td>
<td>A round mining projects</td>
</tr>
<tr>
<td>Reactions</td>
<td>Intensity and negative or positive nature of media coverage</td>
<td></td>
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</tbody>
</table>
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References


Predicted Effect of Ore Mineralogy on the Environmental Behaviour of Mine Wastes

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Abstract. Ore mining and processing generate a significant amount of mine wastes. These wastes may have a negative impact on environment due to weathering of minerals as sulphides and sulfosalts which could release potential environmentally harmful elements (As, Cd, Co, Mn, Sb, Se, Ti...). Ten ores from various locations have been characterized using XRD, visible and electron microscopy, chemical electron microprobe analysis and all the results were then reconciliated with the wet chemical assay. A thorough methodology has been followed to allow the detection of harmful elements, even at trace levels. Trace elements as expected have been found in major sulphide minerals in the ore samples: Cd, Mn and/or Ti sphalerite, Cd in chalcopyrite, As in pyrite or Co and Ni in pyrrhotite. Other minor minerals have also been found (tetrahedrite, native bismuth...). Release of acid due to the alteration of the sulphides follows the known weathering kinetics, but the rate of trace poisoning elements release is still under study. Preliminary results gives a key to predict the environmental behaviour of mine wastes produced by ore mining at the early stage of the projects, but can also lead to a future reprocess of wastes with appropriate technologies for valuable elements present in these ores.

Keywords. Mineralogy, environmental prediction, sulphides

1 Introduction

A good understanding of the mineralogy of a potential ore at the exploration stage has significant advantages for the following steps of a mining project: from a mineral processing point of view, technical difficulties could be anticipated; from an environmental point of view, toxicity of the wastes could be evaluated and their management designed. Mine wastes characteristics can vary greatly. Particularly, tailings are dependent on the ore mineralogy together with the physical and chemical processes used to extract the economic product. Ritcey (1989) reported that tailings of the same type may possess different mineralogies and therefore will display different physical and chemical behaviours. Recently, research and industrial work tend to a geometallurgical approach for mining mineral deposits and implementations of the adequate ore processing (Minz et al. 2013; Dold and Weibel 2013; Lund et al. 2013) by integrating the mineralogy in their studies. Nonetheless, common mineralogical characterizations are rarely undertaken at the exploration stage of a mining project. At this stage, the focus is often put on the assay results considering only the valuable elements for which the subsoil is explored.

Mineralogical characterizations are also done directly on mine wastes to assess their potential toxicity, or their possible reprocessing (Brough et al. 2013). Other authors are developing best practices taking account the mineralogy and texture of the waste rocks to evaluate their acid generation potential and to improve the acid rock drainage prediction (Parbhakar-Fox et al. 2011; Parbhakar-Fox et al. 2014). However, direct studies on the ore to try a primary prediction of the environmental behaviour of the wastes resulting of the extraction or processing is not related in the literature.

Thus, the goal of this research is to include an environmental side at the geometallurgical concept by proposing a practical procedure to characterize an ore deposit and to detect the potential contaminating elements at the first stages of a mining development. Ten polymetallic ores from various locations were sampled and characterized using different analytical chemical methods and mineralogical techniques. A complete chemical analysis on a major part of the elements of the periodic table (55 elements) was done to find the harmful elements contained in the ore samples. Harmful trace elements were found in sphalerite (Cd, Mn, Ti), chalcopyrite (Cd), pyrite (As) or pyrrhotite (Co, Ni) and polluting minerals were detected (tetrahedrite, arsenopyrite, ullmannite, native bismuth...). The rate of poisoning elements release is still under study.

2 Materials and methods

2.1 Ores selection and samples comminution

Ten ores were chosen from various deposits to represent a good panel of polymetallic sulphide deposit. All of them are mined for precious metals (Ag, Au, Pd and Pt) as main products (six of them) or as by-products of base metals production (four of them). Only one is at the stage of exploration. The others are in operations, by either underground or open-pit mining. All samples were received from the operators, except three of them, which were prepared in the Research Institute on Mines and Environment (RIME) laboratories. The samples were weighted to reach 1kg each. Samples were quartered into two parts. The first 500g were crushed and screened to reach a size distribution fraction 2-5mm. The second 500g were crushed to reach a typical size distribution of the ore processing plant (d80 ≈ 80µm).
2.2 Preparation for samples analysis

The obtained fractions were sampled and prepared adequately for the different analysis methods. Polished sections were elaborated in a special resin to avoid grains segregation (Figure 1).

![Figure 1. Overview of the two type of prepared polished sections](image)

2.3 Chemical - Mineralogical characterization methods

Samples were analysed by several chemical methods. Firstly, samples were analysed by a portable XRF Niton® XL3t analyser. Secondly, the chemical composition was determined by a Perkin Elmer Optima 3100 ICP-AES following a multi-acid digestion (HNO₃-Br₂-HF-HCl) of 500g of a pulverized aliquot. From another part, the samples were shipped to SGS Lakefield for the determination of fifty-five (55) elements using sodium peroxide fusion and ICP-AES/ICP-M S. The total sulphur and carbon contents were analysed by an ELTRA CS-2000 induction furnace coupled with an infrared analyser. Au, Pd, Pt and Rh content was determined by a Perkin Elmer Optima 3100 ICP-AES and the gold content was conducted in the Accurassay laboratories by combination of pyroanalysis and gravimetry for the gold content and by combination of pyroanalysis and atomic absorption spectroscopy for gold and the other elements contents.

The mineralogical characterizations were carefully undertaken following a specific methodology presented below (Figure 2). For the samples containing little sulphides, the materials were concentrated using centrifugation in pure CHBr₃. Polished sections were observed by a Nikon optical microscopy. The elemental maps were obtained with a JEOL J7600F Field Emission Scanning Electron Microscope (FE-SEM) coupled with an Oxford EDS (Energy Dispersive X-ray Spectrometry) spectrometer. The composition of the minerals and the detection of trace elements were performed by analysing a statistical number of particles of the given minerals from each section using a Cameca SX 100 Electron Probe MicroAnalyser (EPMA) coupled with WDS spectrometers for the microanalysis. All quantitative EPMA analyses were carried out in wavelength-dispersive mode with an accelerating voltage of 20 kV and a constant beam current of 20 nA. The counting time on each peak was 10s for major elements and 40s for trace elements.

![Figure 2. Systematic methodology for the mineralogical characterization of the samples](image)

3 Results

3.1 Data compilation

All obtained data were collected in a table for each ore deposit. An example is given in the Table 1.

The most of the minerals analysed were the sulphides. SEM studies were conducted to analyse them. Possible trace bearing minerals were chosen among microscopically identified phases and then analysed by microprobe. Here, the amount of Se and Cd was either under the limit of detection of the WDS spectrometer in the supposed bearing minerals, or not detected as sulphides with all the different mineralogical techniques (optical microscopy, SEM and EPMA).

3.2 Minerals composition and trace elements

Subsequently, the composition of all detected bearing minerals was determined by EDS and/or WDS microanalyses. Boxplots were established for each bearing-sulphides. An example for the sphalerite in another ore sample is presented below (Figure 3).
1. Results compilation: elements of interest as revealed by ICP-MS assay and bearing-minerals (optical and SEM studies) from an ore sample. Possible trace bearing minerals are chosen among microscopically identified phases

<table>
<thead>
<tr>
<th>Element</th>
<th>Value (in ppm, except S &amp; Fe)</th>
<th>Detected bearing-minerals</th>
<th>Possible bearing-minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>3.90%</td>
<td>Sulphides</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>8.46%</td>
<td>Pyrrhotite, pyrite</td>
<td></td>
</tr>
</tbody>
</table>

**Valuable elements**

| Ni      | 130                           | Ullmannite                |                          |
| Cu      | 110                           | Chalcopyrite, tetrahedrite|                          |
| Zn      | 161                           | Sphalerite, tetrahedrite  |                          |
| Ag*     | <1                            | Tetrahedrite              |                          |
| Au      | 6.6                           | Native gold, arsenopyrite  |                          |

**Poisoning elements**

| Mn      | 2190                          | Carbonates (ankerite)     |                          |
| Co      | 35                            | Ullmannite                |                          |
| As      | 12200                         | Arsenopyrite, pyrite      |                          |
| Se      | 40.3                          | Arsenopyrite, pyrite      |                          |
| Cd      | 0.9                           | Sphalerite                |                          |
| Sb      | 49.4                          | Tetrahedrite, ullmannite  | Arsenopyrite             |

Elements are given by increasing Z-values

*Not detected by the chemical methods but present in observed minerals

4. Discussion and perspectives

Harmful elements as major or traces in common sulphides were found in each ore. These elements are likely to occur in the leachates of the waste rock piles or tailings dams. All ore samples have presented at least one polluting component. XRD was proceeded to propose a mineralogical quantification of the ores, as well as image analysis. Thus, the next step for this study is to apply recovery calculations to estimate the mineralogy of the different ore processing products (concentrates and tailings). The composition of the tailings could therefore be roughly known by these calculations and acid rock drainages could be predicted. Thus, the prediction of the environmental behaviour of tailings could be made in amount of a mining project. Moreover, the mineralogical association and occurrence will be investigated and could allow a prediction of the weathering of polluting minerals. Further investigations are needed to establish the rate of metal releases of specific sulphides and to assess if these metals could exceed the regulation levels in the leachates. Work has already been done on the mobility of metals by Smith and Huyck (1999), but also on specific deposits (Plante et al. 2011) or on pure sulphide minerals (Chopard et al. 2015) or even using specific chemical agent (Plante et al. 2015). The tailings characteristics have to be determined as early as possible to establish the behaviour of the tailings once deposited in their final storage location and to know the potential short and long term liabilities and environmental impacts. Once the likely characteristics of the tailings are determined from laboratory and calculations, the necessary design requirements can be identified to mitigate environmental impact as well as determine optimum operational performance.

Acknowledgements

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characterisation of antimony mineralogy in a geometallurgical context at the Rockliden ore deposit, North-Central Sweden. Minerals Engineering 52:95-103
The Behaviour of Cr and Ni in Mine Spoils and Topsoils before and during Restoration Steps

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Abstract. The ecological restoration of Ni lateritic mines requires specific attention in order to address the following challenges: i) to identify the geochemically adapted endemic and native flora, ii) to construct Technosols with sufficient physical, chemical and biological fertility from mine wastes, iii) to re-integrate local and adapted flora in newly created soil covers, and iv) to prevent from the dissemination of toxic metals to adjacent environments. The acquired experience in different countries (Brazil, New Caledonia) provide examples that allows to draw the outline of a specific methodology to be used worldwide. Careful attention has to be given in restoration processes to the geochemical requirements of the flora (adapted to saprolite or to limonite) before planting Technosols. Vegetating mine spoils will avoid substantial leaching of toxic metals (e.g. Cr and Ni). Also, classical fertilization strategies that are usually applied to mine spoils during revegetation can prove to be risky in terms of metal leaching from soils. Finally, the careful management of Topsoils is also a key to the restoration success because they can bring the required fertility to Technosols built from saprolite and limonite materials.

Keywords. Nickel lateritic mine, ultramafic, revegetation, soil columns, Technosol

1 Introduction

In opencast lateritic nickel mines, the unusual geochemistry is responsible for the presence of ecosystems with irreplaceable endemic vegetation (Reeves et al. 2007; de Andrade et al. 2009). The species composition of the endemic ultrafolic flora of Goias (Brazil) is strongly linked to precise soil geochemistry and, in particular, responds to high Ni availability: for example, several Ni hyperaccumulator species are only found in clay-rich ultramafic soils (de Andrade et al. 2009). Conservation and restoration of the spoils and barren sites require specific attention because recreating a Technosol cover with these soil materials poses a double challenge (Echevarria et al. 2015): 1) The native vegetation is sensitive and sometimes requires some of the geochemical properties of the original ultramafic materials; 2) Disturbing Ni- and Cr-rich materials and expose them to rainfall with limited vegetation cover might generate metal losses through lixiviation. Finally, the conditions of recovery and storage of the topsoil layer, which is often used for Technosol construction, might also play a role in the geochemical behaviour of the newly constructed soils.

This work presents experimental research designed to understand the geochemistry and fate of potentially toxic metals in the early stages of nickel lateritic mine spoil revegetation projects. The possible effect of Nitrogen and Phosphorus fertilisation on spoils is also assessed. Finally, this work provides a special focus on the behaviour of topsoils during stripping and storage and on the possible lixiviation of metals from spoil materials during their exposure to rainfall and to fertilisation.

2 Methods

In tropical ultramafic Ferralsols, the different stages of lateritic weathering has lead to two types of ores, and therefore, to two spoil types. They are mainly either a clay-rich saprolite enriched in phyllosilicates, or a limonitic material, enriched in Fe oxides. Mine spoils were characterized thoroughly in terms of elemental composition, mineralogy and reactivity (Raous et al. 2013). Lysimeter PVC columns (30 cm depth, 4.2 cm diameter) were designed to monitor leaching waters through both spoil materials. Two leaching column experiments were carried out: 1) the influence of various spoil types on the composition of eluted soil solution was studied with three different treatments: pure saprolite or limonite, and a 50:50 mixture column. The total volume of water added to the column was calculated to simulate the usual rainfall during the rainy season. Leachates were collected twice a week at the bottom of the column, then filtered through a 0.22 μm cellulose nitrate filter, acidified with conc. HNO3, and stored at 6 °C before analysis. Columns were replicated four times for each treatment. 2) the influence of mineral fertilisation (N, P) on the dynamics of metal leaching was studied using a 30%-70% saprolite-limonite mixture to mimic the average composition of spoils in Niquelândia mine. Solutions of NH4NO3 (7.6 mg of N) and H3PO4 (6.9 mg of P) were brought 8 days after the recovery of the first eluted waters (input of 55 kg ha⁻¹ of N and 50 kg ha⁻¹ of P respectively). The composition of the filtered eluted solutions was monitored with ICP-OES.

Topsoils on a Geric Ferralsol from Goro (New Caledonia) with continuous iron pan were sampled above the ferricrete (0-20 cm and 20-cm). They were mechanically stripped and piled immediately after in the same area. The pile was 2-m high and samples were taken from the pile at different time at four depths (0, 50, 100, 150 cm). Samples from initial undisturbed topsoil,
removed topsoil and 24-month old piled topsoils were monitored in terms of chemical composition, reactivity and metal availability. Metal extractions were performed with NaOH (0.01M), Na-citrate (0.01M) or Na-EDTA (0.008M) for 24h after adjusting pH at 6.0. Solutions were filtered after 24-h stirring and pH was measured in resulting solutions. The composition of the filtered solutions was also determined with ICP-OES.

### Table 1. Composition of the different materials (S=saprolite; L=limonite) from Niquelândia (Brazil) and (T=topsoil; ST=stripped topsoil; AT=24-mo aged topsoil) from Goro (New Caledonia).

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>S</th>
<th>L</th>
<th>T</th>
<th>ST</th>
<th>AT</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>48.3</td>
<td>2.7</td>
<td>0.49</td>
<td>0.54</td>
<td>0.43</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.0</td>
<td>5.0</td>
<td>3.3</td>
<td>2.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>22.2</td>
<td>72.3</td>
<td>35.6</td>
<td>23.0</td>
<td>59.3</td>
</tr>
<tr>
<td>MnO</td>
<td>0.50</td>
<td>1.2</td>
<td>0.07</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>MgO</td>
<td>4.4</td>
<td>1.6</td>
<td>0.52</td>
<td>0.51</td>
<td>0.52</td>
</tr>
<tr>
<td>CaO</td>
<td>0.30</td>
<td>&lt;0.1</td>
<td>0.13</td>
<td>0.20</td>
<td>0.22</td>
</tr>
<tr>
<td>Carbon</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>26.9</td>
<td>11.5</td>
<td>11.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal elements (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Cation Exchange Capacity (cmol+ kg⁻¹)</td>
</tr>
<tr>
<td>87.1</td>
</tr>
</tbody>
</table>

### 3 Results and Discussion

The concentration of Ni in soil solutions of the saprolite spoil, rich in Fe–Ni smectites, showed a substantial mobilisation of Ni in the first days of elution (concentrations ranged between 1.0 and 2.7 mg l⁻¹). These concentrations were above the limits established by WHO. Nickel was leached exactly the same way as Mg with a constant stoichiometry (Figure 1). After more than 30 days of leaching, Ni concentration stabilised at 0.3 mg l⁻¹. Chromium release appeared to be problematic as its concentration in eluted waters increased regularly with time to reach a final average value of 1.5 mg l⁻¹ (three times more than the WHO limit). Mn-oxide reduction in this material is probably the mechanism that induced oxidation of Cr(III) into Cr(VI), which is rather mobile. In both limonitic spoil and mixed limonitic–garnieritic spoil, the metal concentrations remained low because of the high adsorption capacity of Fe oxides for these metals (for both cations and anions).

Mineral-N fertilisation led to a big and steady increase in Ni and Mg concentrations in waters (0.6 mg Ni l⁻¹) and a decrease in Cr(VI) released into the leachate of about 50% (Figure 2). The application of PO₃⁻ produced an almost insignificant release of extra Cr(VI).

In the second experiment, the storage of topsoils did not seem to affect too much its chemical fertility (most of the organic matter is stable during storage). However, during soil stripping some of the organic matter and exchangeable elements were lost. Secondary metals such as Ni and Cr were only slightly affected by storage. Although Cr concentrations were below WHO limits (they decreased from 0.05 to 0.02 mg l⁻¹ from in-situ topsoil to 24-month aged topsoil), the extraction with citrate revealed a significant pool of available Cr(VI) with no effect of topsoil treatment.

Concerning the nutrient fertility of topsoils during storage, there appears to be a relative stability in the cation exchange capacity (CEC) and in the content of exchangeable cations (K and Ca) although some leaching occurs. Organic matter of the lateritic topsoils seems to be also rather stable and not subject to rapid mineralization. Topsoils may be therefore used for increasing fertility to mine Technosols even after a long period of storage (i.e. more than 24 months).
4 Conclusion

The first experiment has shown that, in several situations for both materials, Cr(VI) may be released at significant concentrations in the leaching waters. Sometimes these concentrations may exceed recommended WHO values for natural waters and need to be monitored as they might impair plant growth and water quality. Nitrate fertilisation can therefore pose many geochemical problems in spoil revegetation. Phosphate fertilisation (in limited concentrations) should not affect too much Cr(VI) release. The storage of topsoils did not seem to affect much metal release properties, even after 24 months. The reuse of topsoils and the loss of fertility is probably due to biological losses rather than to changes in chemical properties.

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Sustainable mining and environmental issues 1513
2 1990's-2000's: The anti-globalization mining industry. It can give clues on how the companies therefore following of their activities, and understanding enormous impact on the social license to operate (SLO). Moffat and Zhang 2014; Parson et al. 2014, Nysten-Blomqvist 2006; Eerola 2003; 2008; 2013; Prno 2013; to global dimension (Phillips 2002; Deegan and important stakeholder groups, whose influence has a local criticism towards the mining industry and one of its very ENGOs are also one of the most pro-eminent agents in promote or difficult the natural resource extraction. The Environmental NGOs (ENGOs) have the power to with the state and corporations (Kröger 2014). They influence the natural resources policy in interaction responsibility and mobilization of environmental protests. (NGOs) have a crucial role in debate on corporate social movements and non-governmental organizations 1 Introduction its stakeholders. the industry looks for the best practices and dialogue with Finnish government is promoting responsible mining and investigate mining. The Mining Act was renewed, the responsibility began and social scientists started to Environmental problems of the Talvivaara nickel mine ceased rapidly when uranium exploration companies left spaces for resistance in the countryside. However, it refreshed the environmental movement and opened up environment back to Finland as a local question. It the "return of politics", the uranium dispute restored the opposition. If the anti-globalization movement represented Uranium exploration restarted at 2005, what raise environmental questions and re-emerged nuclear energy. The climate change debate buried other movement lost its impetus that was followed by years of the environment. After its end, the environmental struggled against global structures, neglecting Finland and beginning of 2000's. The anti-globalization movement anti-globalization movement at the end of 1990's and mobilizations in Finland. The last one of these was the environmental protest waves. There were five main such The Recent Uranium and Current Mining Disputes within globalisation movement started also in Finland. The " The recent uranium and current mining disputes environmental activism, mining, uranium, and International Monetary Fund in Göteborg, Genova, protests against World Trade Organization, World Bank, Ylä-Anttila 2010). Finnish activists participated in 2003; Konttinen and Peltokoski 2004; Lindholm 2005; corporations were questioned and challenged (Eerola 2014 mentioned in the Framework of Environmental Protest Waves in Finland, 2015). According to Kröger (2014), to the current mining boom (Eerola 2013; Sarpo 2008; Kainulainen 2011). The importance of dispute has not yet attracted attention at all. This might be explained by the fact that the whole subject of mining environmental activism related to the ongoing mining Sarpo 2008; Kainulainen 2011). The importance of some authors (Eerola 2008; Litmanen 2008; Karasti 2008; the recent anti-uranium movement has been studied by the mining industry. In order to understand the anti-mining) in Finland. In order to understand the environmental and International Movement;
The Recent Uranium and Current Mining Disputes within the Framework of Environmental Protest Waves in Finland

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Abstract. The recent uranium and current mining disputes in Finland are located within the context of the Finnish environmental protest waves. There were five main such mobilizations in Finland. The last one of these was the anti-globalization movement at the end of 1990’s and beginning of 2000’s. The anti-globalization movement struggled against global structures, neglecting Finland and the environment. After its end, the environmental movement lost its impetus that was followed by years of latency. The climate change debate buried other environmental questions and re-emerged nuclear energy. Uranium exploration re-started at 2005, what raised opposition. If the anti-globalization movement represented the “return of politics”, the uranium dispute restored the environment back to Finland as a local question. It refreshed the environmental movement and opened up spaces for resistance in the countryside. However, it ceased rapidly when uranium exploration companies left Finland due to recession. The activists’ attention shifted towards new mining and development projects. Environmental problems of the Talvivaara nickel mine increased opposition. A discussion on corporate social responsibility began and social scientists started to investigate mining. The Mining Act was renewed, the Finnish government is promoting responsible mining and the industry looks for the best practices and dialogue with its stakeholders.

Keywords. environmental activism, mining, uranium, Finland

1 Introduction

Social movements and non-governmental organizations (NGOs) have a crucial role in debate on corporate social responsibility and mobilization of environmental protests. They influence the natural resources policy in interaction with the state and corporations (Kröger 2014). Environmental NGOs (ENGOs) have the power to promote or difficult the natural resource extraction. The ENGOs are also one of the most pro-eminent agents in criticism towards the mining industry and one of its very important stakeholder groups, whose influence has a local to global dimension (Phillips 2002; Deegan and Blomqvist 2006; Eerola 2003; 2008; 2013; Prno 2013; Moffat and Zhang 2014; Parson et al. 2014, Nysten-Haarala et al. 2015). In other words, they might have an enormous impact on the social license to operate (SLO). Therefore, following of their activities, and understanding their nature and dynamics may be important for the mining industry. It can give clues on how the companies should approach them for a dialogue and eventual cooperation.

Here we focus on environmental activism (especially the anti-mining) in Finland. In order to understand the Finnish environmental activism and its research, it is necessary to review its background and characteristics.

The Finnish environmental activism has been traditionally conceived as a wavy movement (Rannikko 1994; 2003; Konttinen and Peltokoski 2004; Lindholm 2005). Every wave’s mobilization stage has been always triggered by some key event. It raises wide questions for the public debate. A wave is followed by latency. According with Rannikko (1995), this Finnish wave-like environmental protest phenomenon seems to be a quite unique in the world. There have been five environmental protest waves in Finland:

1. 1960’s-1970’s environmental awakening;
2. 1970’s-1980’s alternative way of life, the Koijärvi, and Green Movement;
3. 1980’s-1990’s forest conflicts;
4. 1990’s animal and radical activism;

The succession of waves was followed by years of latency after the anti-globalization movement. The latency ended with disputes over uranium and old forests, followed now by the ongoing dispute over mining.

Regarding the anti-mining activism in Finland, only the recent anti-uranium movement has been studied by some authors (Eerola 2008; Litmanen 2008; K arasti 2008; Sarpo 2008; Kainulainen 2011). The importance of environmental activism related to the ongoing mining dispute has not yet attracted attention at all. This might be explained by the fact that the whole subject of mining dispute is quite recent in Finland. The mining dispute raise together with the current mining boom (Eerola 2013; Nysten-Haarala et al. 2015). A according to K röger (2014), this contentious agency seems to be a quite normal and universal reaction for a change in environment and social space caused by increased natural resource extraction. This is observed also world-wide in the case of mining.

Here we review the development of environmental activism in Finland since the anti-globalization movement from the beginning of 2000 until the recent uranium and ongoing mining disputes. Those disputes are described, and their space and place within the context of Finnish environmental protest waves are located. A special attention is given to an attempt to define if they form a new wave of environmental protest in Finland.

2 1990’s-2000’s: The anti-globalization movement

At the end of 1990’s, the international anti-globalization movement started also in Finland. The “End
Prague and Seattle. The international anti-globalization organization Attac was founded also in Finland. The movement culminated at the World Social Forums in Porto Alegre, Brazil, unifying several types of activists from all over the world (Eerola 2003; Lindholm 2005; Ylä-Anttila 2010). However, at the same time, the anti-globalization movement fragmented the field of environmental activism, diverting its attention from Finland to abroad. Environmental issues were melted within complex global social and economic issues or were even buried by them (Lindholm 2005; Ylä-Anttila 2010). Problems were looked in complex international political-economic structures and struggled against them in developing countries.

The terrorist strike on World Trade Center in New York restricted civil rights all over the world, which had an impact on social movements. After a great initial enthusiasm, the anti-globalization movement started to exhaust, and break up because of violence used in protests. The media’s interest was reduced. After the beginning of 2000’s, the anti-globalization movement vanished, what was reflected also in the Finnish activism (Lindholm 2005; Ylä-Anttila 2010). Stranius (2006) identified a post-anti-globalization movement latency during 2004-2006 in Finland.

3 2005 to 2008: Uranium dispute

The latency that followed the anti-globalization movement’s end was abruptly interrupted locally, when a dispute over old forests begun in Northern Lapland at 2004-2005 (Valkonen 2007). At the same time, the climate change debate re-emerged the nuclear power in the energy policy agenda and the uranium spot price raise in the world market. The French company Areva applied for large claim areas for uranium exploration in Southern Finland at 2005 (Litmanen 2008, Sarpo 2008). The dispute over uranium started at Eastern and Western Uusimaa at 2006 and spread quickly to Northern Karelia and Kuusamo, where Areva and other companies applied for other claims for uranium exploration, (Eerola 2008; Karisti 2008; Litmanen 2008; Sarpo 2008; Kainulainen 2011).

The movement against uranium exploration was characterized by its networking and international connections (Litmanen 2008). The dispute over uranium can be considered as a moment of a re-awakening of the anti-globalization movement against multinational mining industry in Finland (Eerola 2005). The movement against uranium presented characteristics of previous environmental protests, such as anti-authoritarianism, distrust on authorities and experts, spirit of structural renewal (e.g. Mining Act), criticism on modernism and anti-nuclear attitude. However, the resource nationalism (Eerola 2008) and involvement of the church (Kainulainen 2011) were completely new phenomena in the Finnish environmental activism.

The foreign uranium exploration companies left Finland at 2009-2010 because of global recession and long periods of license processing, which lead to the end of dispute over uranium. The major achievements of this movement were the public discussion on the subject and renewal of the Mining Act in 2011. Its main result was the alteration of the permit system. Earlier, the licensing for uranium and thorium mining and processing was granted exclusively by the government, but according with the new Mining Act, now there is also a need for approval by the local municipality of the area in which the applied mine site is located. In practice, this means a significant improvement of local possibilities to influence the decision making, by which the local municipality can obstruct uranium mining in its area. This produces challenges for uranium explorers and mining companies for their investigations, security, and environmental impact assessments, as well as in their dissemination for the general public and decision makers in order to obtain approval for the projects. In this sense, the mining permit system turned to be much more complex, which corresponded to the public opinion.

4 2010 – ongoing: Mining dispute

The last years Finland has experienced a mining boom with lot of mineral exploration and development projects as well as opening of new mines for exploitation of nickel, copper, and gold. Mining is an important sector that has grown during the last years. Before this boom, started at 2005, the mining industry was in recession during almost all of the last 20 years in Finland. Earlier, mineral exploration and mining were carried out by domestic, state-owned companies, such as Outokumpu Oy. During this recession, people in certain areas became unfamiliar with mineral exploration and mining, especially close to major urban centers. The environmental awareness increased in that period. Therefore the current, increased need for natural resources and a consequent mining boom, mostly carried out by foreign companies, has surprised many in a negative way. This has created an urgent need for information on geology, exploration, and mining in an accessible mode for the general public and decision-makers.

The public debate on mining started already during the uranium dispute (Eerola 2008), and it grew at the same time when climate change debate was ceasing and environmental problems of the Talvivaara nickel mine began at 2010 (Eerola 2014; Nysten-Haarala et al. 2015). Application for uranium uptake by Talvivaara and constant environmental problems increased its opposition (Tiainen et al. 2014). However, a leakage of its tailing ponds formed a key-event for mobilization at the autumn of 2012 (Tiainen et al. 2014). The Stop Talviivaara movement was founded and anti-mining protests and camps have been organized together with major Finnish and international ENGOs operating in the country. In this moment, there are four mines, and five development projects which have been opposed. In some of these the opposition is local, when as in others the pressure is external (e.g. ENGOs). Some of the projects have been also challenged by local tourism entrepreneurs that fears that mining will affect their business.

According to Nysten-Haarala et al. (2015), a suspicion towards mining is especially strongly developed among environmental activists, whom the companies have not managed to draw to their co-operation groups. Inclusion of ENGOs as an important stakeholder and co-operation has been suggested by Eerola (2003, 2008, 2013).
Operation of mining and mineral exploration companies within or close to nature conservation, touristic, and aboriginal Sámi people areas will probably maintain mining in the ENGOs' agenda for a long time in Finland. There is also potential to turn local Finnish mining dispute in an international conflict by international ENGOs' campaigns.

5 Discussion

The main point of this paper is to locate the uranium and mining disputes within the context of Finnish environmental protest and to discuss if they compose a new wave of environmental protest in Finland.

In fact, the uranium dispute re-activated the Finnish ENGOs and local activists in Finland after years of latency. It brought the environment back as a local question from global trade policy arenas and developing countries to Finnish countryside provinces and municipalities after the end of the anti-globalization movement. Therefore, it might be attempting to call the uranium and mining disputes as a new wave of Finnish environmental protest. However, the dynamics of the loose and anarchistic networks, individual migration of activists from one campaign to another (the "backpack" activism, Stranius 2006), and concentration only in one issue can probably explain why the uranium and mining disputes have not been able to construct a such a strong phenomenon as the previous waves of Finnish environmental protests, at least until this moment. In this sense, the disputes seems to be more like part of a "swell" described by Konttinen and Peltokoski (2004) that followed the anti-globalization movement. A swell is composed by minor disputes and protests, that does not necessarily have a common agenda or requests, and which does not raise such wide questions for public debate as the waves have done (Konttinen and Peltokoski 2004). If uranium and mining disputes would produce larger mobilization together with those wider questions, they probably could be considered as a new wave. In this sense, there has been now a tentative to join the discussion on free trade agreements (Transatlantic Trade and Investment Partnership and Comprehensive Economic and Trade Agreement) between the EU and North American countries, opposition to NATO, peat production, and deregulation of bog and environmental restrictions together with the debate on mining.

In all cases, the development from uranium dispute to mining dispute shows a clear continuation and a long term concentration against the mining industry, if compared to other waves of environmental protests in Finland.

As consequences of the uranium and mining disputes, the Mining Act was revised, and a discussion on the corporate social responsibility (CSR) is now dealing also with the multinational mining industry operating in Finland (Sairinen 2011; Mononen and Sairinen 2011; Mononen 2012; Ryterri 2012; Eerola 2013; 2014; Jartti et al. 2014, Nysten-Haarala et al. 2015). The Finnish state, universities and research institutes started to investigate and promote CSR and social license to operate of mining industry (Eerola 2014). Because mining is an important and growing industry in Finland, the Finnish government published an action plan with a goal to turn Finland as a forerunner of sustainable mining (TEM 2013). The industry is now looking for the best practices in sustainable mining and dialogue with its stakeholders and local communities (Eerola 2013; Nysten-Haarala et al. 2015). The Independence Fund of Finland (Sitra) founded The Sustainable Mining Network, which is a forum for dialogue and cooperation between the mining industry and ENGO’s (Eerola 2014).

Unfortunately, the current Finnish social science research on mining is concentrated only in companies, mines and local communities (Eerola 2014). Although the environmental activism has a strong role to play in SLO, also with its own corporate social responsibility issues (Jepson 2005, Crowson 2009), unfortunately it has been completely ignored by the current Finnish academic debate. Therefore, it might be “missing the point” in its studies on the SLO of mining.

However, with 46 operating mines in Finland and considering the amount of opposition, it can be concluded that at least in this moment the anti-mining movement is not widespread and it is concentrated on some of the new mines and development projects, as was seen above. The study of these mines and projects and the issues and mechanisms that turned them as focus of anti-mining campaigns can give important clues to develop toolkits to obtain SLO for future projects in Finland and abroad. In any cases, it seems that at least the presence of uranium, and nature conservation and touristic areas within or close to the project areas, as well as communication and stakeholder engagement methods used by the companies (or their lack) are issues that can generate opposition for mining in Finland.

6 Conclusions

A dispersion of attention from the local environmental problems to complex global issues by the anti-globalization movement made the Finnish environmental activism to lose its impetus, and there have been no new wave after that. In this sense, even that the uranium and mining disputes does not seems to form a new wave of environmental protest in Finland, the uranium and mining disputes were able to refresh the Finnish environmental activism after years of post-anti-globalization “hangover” and its subsequent latency. Therefore, if the anti-globalization movement was the “return of politics” for Ylã-Anttila (2010), for the author the uranium dispute was the “return of the environment” back to Finland as a local question. However, in order to generate a new wave of Finnish environmental protest, there is a need for wider questions associated with mining and natural resources. In order to avoid the increasing of opposition for their activities, the mining companies need to include ENGOs within their stakeholders, practice dialogue and try to establish cooperation with them.

In all cases, the full importance and dimension of the uranium and mining disputes within the history of Finnish environmental protest can probably be completely evaluated only after some chronological distance.
Data compilation for South-East Sulawesi was the first time the prospectivity maps and sustainability maps based on environmental, community, and sustainability factors, which both have a significant impact on the ability of exploration and mining companies to operate. A pilot project was undertaken in South-East Sulawesi, which in turn offers opportunities for economic growth. Any map produced "sustainable prospectivity maps". This allows to produce "sustainable prospectivity maps". This allows one way to utilize this data is to generate mineral prospectivity maps, which can assist in the mapping. In this case, datasets found to be inconsistent with the corresponding geology and contained information relating to the formation name and age. A geological map was available at 1:250,000 scale (in Finnish). Unpublished MSc thesis. Yhdyskuntatieteiden laitos, Tampereen yliopisto.

Abstract

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A GIS-Based Exploration Initiative to Help Steer Sustainable Development

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Abstract. The aim of this project was to build on the traditional GIS-based prospectivity analysis for mineral deposits, and integrate data relevant to environmental, community, and infrastructure development, in order to produce “sustainable prospectivity maps”. This allows target areas to be highlighted based on both geological and sustainability factors, which both have a significant impact on the ability of exploration and mining companies to operate. A pilot project was undertaken in South-East Sulawesi, Indonesia, which clearly highlighted areas that showed both geological potential for orogenic and placer gold mineralization, as well as favourable sustainability. This approach to sustainable exploration potentially de-risks investment in exploration and mineral resource development.

Keywords. GIS, Gold, Indonesia, Prospectivity Analysis, Sustainable Development

1 Introduction

It is a common problem that large amounts of geoscience data are acquired by national and provincial geological surveys but underutilized due to lack of resources or in-house expertise. One way to utilize this data is to generate mineral prospectivity maps, which can assist with exploration and other land management decisions.

In Australia and elsewhere, exploration has been promoted through the release of pre-competitive datasets in the form of GIS databases and prospectivity (mineral potential) maps (e.g. Joly et al. 2013; Ford and Mühler 2014; Witt et al. 2014).

Similar to Australia, Indonesia is a nation of interest for the global mineral exploration and mining sector, which in turn offers opportunities for economic growth and employment. The aim of this project was to: (1) assess the quality of the available GIS data for the South-East Sulawesi province in Indonesia, specifically the Bombana region; (2) develop a series of prospectivity maps for varying styles of mineralization; (3) generate sustainability maps based on environmental, community, and infrastructure requirements; and (4) integrate for the first time the prospectivity maps and sustainability maps to produce a set of “sustainable prospectivity maps”.

2 Data and Methods

2.1 Data

Data compilation for South-East Sulawesi was undertaken in collaboration with the regional Energy and Mineral Resources office in Kendari. This database contained numerous datasets. To be of practical use in a mineral prospectivity analysis, the digital geoscience datasets must have complete coverage over the study area, and have a relatively homogeneous level of detail in the mapping. In this case, datasets found to be inconsistent or incomplete were not included in the analysis.

The following GIS datasets were acquired for potential use in the sustainable prospectivity analysis:

- A geological map was available at 1:250,000 scale and contained information relating to the formation name and age.
- Free air gravity map produced from data available from Scripps Institute of Oceanography.
- A structural map at 1:250,000 scale. This was found to be inconsistent with the corresponding geology map, and revised using the gravity map that was produced.
- Digital elevation model produced from SRTM data - used to validate hydrology.
- Landsat images - used to validate hydrology.
- Hydrology map (rivers and other water sources).
- Mineral deposit map – a small number of accurately located mineral occurrences in South-East Sulawesi were collated into a spreadsheet. This contained a total of 20 occurrences (4 gold, remainder were nickel laterite).
- Administrative maps included: administrative boundaries, environmental data, land-use, transportation infrastructure, water resources, etc. Many of these maps contained a large number of GIS objects, but were of limited use due to missing metadata or lack of information in the corresponding attribute tables.

2.2 Methodology

Given the lack of known mapped occurrences within the mineral deposit database for South-East Sulawesi, this restricted the prospectivity analysis to a knowledge-driven approach. In this case, a fuzzy logic analysis (Bonham-Carter 1994) was undertaken to assess the mineral prospectivity and sustainability. Fuzzy logic relies on an expert to determine the inputs for the prospectivity map by selecting the data layers believed to be the most important for the style of mineralization being targeted, the critical thresholds that should be applied (e.g. proximity threshold from a structure), and
what weightings to assign to the different areas of favourability.

Previous case studies suggest that the best practice is to assign a class weight, map weight, and uncertainty weight to each favourability class, where the weights are in the range between 0 and 1 (Joly et al. 2013; Ford and Miller 2014). A class weight (C.W.) indicates how favourable each class within an individual map is, a map weight (M.W.) indicates how important that overall map is relative to other maps, and an uncertainty weight (U.W.) represents the measure of the quality of the input map. These three weights are then multiplied together to produce the fuzzy membership (F.M.) value for each favourability class in each map. The maps are then combined using the fuzzy PRODUCT operator (Bonham-Carter 1994).

3 Sustainable Prospectivity Mapping

3.1 Mineral Prospectivity Maps

Gold mineralization in South-East Sulawesi is mapped in the Bombana Regency. Current mining efforts are focused on alluvial gold occurrences in the Lower Miocene Langkowala Formation. However, the source of this alluvial gold has not been determined. Based on its proximity to greenschist-grade metamorphic rocks, granites, and an alteration zone that includes assemblages similar to those typically seen near orogenic gold deposits, we suggest that the likely source of the alluvial gold is orogenic in nature. The targeting parameters for orogenic and placer gold are shown in Tables 1 and 2, respectively.

Table 1. Prospectivity mapping parameters for orogenic gold mineralization in the Bombana region of South East Sulawesi

<table>
<thead>
<tr>
<th>Input Layer</th>
<th>Distance to Fault</th>
<th>Distance to Metamorphics</th>
<th>C.W.</th>
<th>M.W.</th>
<th>U.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dist. to Fault</td>
<td>0-2 km</td>
<td>0.98</td>
<td>0.90</td>
<td>0.60</td>
<td>0.5292</td>
</tr>
<tr>
<td></td>
<td>&gt;2 km</td>
<td>0.01</td>
<td>0.90</td>
<td>0.60</td>
<td>0.0056</td>
</tr>
<tr>
<td>Dist. to Metamorphics</td>
<td>0-3 km</td>
<td>0.95</td>
<td>0.80</td>
<td>0.70</td>
<td>0.5320</td>
</tr>
<tr>
<td></td>
<td>&gt;3 km</td>
<td>0.01</td>
<td>0.80</td>
<td>0.70</td>
<td>0.0054</td>
</tr>
</tbody>
</table>

Table 2. Prospectivity mapping parameters for placer gold in the Bombana region of South East Sulawesi

<table>
<thead>
<tr>
<th>Input Layer</th>
<th>Distance to Langkowala f.m.</th>
<th>Distance to Fault</th>
<th>Distance to River</th>
<th>C.W.</th>
<th>M.W.</th>
<th>U.W.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-3 km</td>
<td>0.95</td>
<td>0.80</td>
<td>0.70</td>
<td>0.5320</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;3 km</td>
<td>0.01</td>
<td>0.80</td>
<td>0.70</td>
<td>0.0056</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0-2 km</td>
<td>0.98</td>
<td>0.90</td>
<td>0.60</td>
<td>0.5292</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;2 km</td>
<td>0.01</td>
<td>0.90</td>
<td>0.60</td>
<td>0.0054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0-5 km</td>
<td>0.70</td>
<td>0.80</td>
<td>0.75</td>
<td>0.4200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;5 km</td>
<td>0.01</td>
<td>0.80</td>
<td>0.75</td>
<td>0.0060</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0-500 m</td>
<td>0.70</td>
<td>0.80</td>
<td>0.75</td>
<td>0.4200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;500 m</td>
<td>0.01</td>
<td>0.80</td>
<td>0.75</td>
<td>0.0060</td>
<td></td>
</tr>
</tbody>
</table>

Additional models included nickel laterite and iron laterite targeting models. These were generated based on information available from van Leeuwen and Pieters (2011). The mineralization is believed to be Pliocene to Late Miocene in age, and is related to the presence of ultramafics in the region. The nickel is hosted in the upper limonite zone of the laterite profile, which has an Fe content between 45-47% and is depleted in SiO₂ and MgO. However, despite these targeting models being generated, the lack of available geochemistry data and the limited information contained within the geology map, as well as its poor resolution for the scale of investigation meant that the models could not be implemented. In order to enable an analysis of these styles of mineralization, a comprehensive geochemistry database would be required, including a full suite of both major and trace elements for stream sediment samples within the region. Additionally, a high resolution geological map, containing information on the stratigraphy, lithology, and alteration would be necessary.

3.2 Sustainability Maps

A sustainability map for South-East Sulawesi was generated using the parameters shown in Table 3. Other sustainability factors not included in this study due to data availability include access to electricity infrastructure, proximity to historical or sacred sites, and proximity to national parks.

Table 3. Sustainability map parameters for Southeast Sulawesi

<table>
<thead>
<tr>
<th>Input Layer</th>
<th>Distance to Protected Forest Area</th>
<th>Distance to Residential City</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-5 km</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>&gt;5 km</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>0-2 km</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>&gt;2 km</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>0-1 km</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>&gt;1 km</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>0-3 km</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>&gt;3 km</td>
<td>0.95</td>
</tr>
</tbody>
</table>

3.3 Sustainable Prospectivity Maps

Through integration of the inputs contained in Tables 1, 2, and 3, sustainable prospectivity maps were generated for both orogenic and placer gold within the Bombana region of South-East Sulawesi. Areas of favourability are shown in red, with areas of reduced favourability shown in blue. The green stars in Figures 1 and 2 represent the known gold occurrences, and the yellow circles represent the geochemical sample points which may be representative of mineralization. A positive correlation can be seen between the sustainable prospectivity maps and the known mineralization. Although it is not a strong correlation, this may be due to the limited information available regarding the known mineral occurrences, and potential misclassification regarding the style of mineralization.

The results of the sustainable prospectivity analysis clearly highlight areas with potential for gold mineralization, as well as favourable sustainability measures.

Taking this approach, the areas highlighted can be investigated with higher resolution mapping and sampling, while taking into consideration measures of sustainability and existing land-use, in order to de-risk exploration programs and promote a favourable relationship with local communities and government.
Mineralization in the Bombana region of South East Sulawesi is mapped in Table 1 and Table 2, respectively. Table 1 shows prospectivity mapping parameters for orogenic gold, while Table 2 focuses on placer gold. These parameters were combined using the fuzzy PRODUCT operator to derive a fuzzy membership (F.M.) value for each input layer. The input layers included distance to river, distance to metamorphics, distance to fault, and Langkowala input layer. The process involved assigning a class weight (C.W.), map weight (M.W.), and uncertainty weight (U.W.) to each input layer, with weightings for orogenic and placer gold evaluated in conjunction with these weights. The fuzzy membership values were then calculated for each favourability class within an individual map. The maps were then combined to produce a single sustainability map for South-East Sulawesi. The maps are used to identify areas with potential for gold mineralization, as well as favourable sustainability factors. These maps provide a valuable tool for sustainable exploration and environmental management in the region.
Acknowledgements

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References

Environmental Impacts and Management of Ancient Abandoned Mines in the French Alps

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Abstract. The French Alps have a long mining history that span the last 2,500 years. Despite low tonnages, thousands of small deposits have been mined from Antiquity to the 20th century. These mines are currently abandoned, some even forgotten. Even though Fe, Cu, and Pb-Zn were mostly extracted, the ore deposits display a great variety of mineralisation (Ag, Au, U, Hg...). The mining industry was quite important (several million tons of iron, 200 000 t Pb, 100 000 t Zn and 500 t Ag) and thus contributed to human settlement and economic development of the French Alps. Now abandoned, the mines and their waste dumps are subjected to alteration and slow degradation over time, a probable source of cavity collapse, soil and water pollution. Considering the high amount of scattered mines, post-mining management only concerns a few sites with top priority. For most mines, the environmental impact and potential hazard are not yet evaluated. However the mining heritage has not been forgotten as evidenced by the development of interpretive boards and theme trails, the number of museums (about 10) and the possibility of underground guided tours.

Keywords. Abandoned mines, French Alps, water pollution, risk prevention, tourism development

1 Introduction

The complex Variscan and Alpine orogeneses were associated to fluid flows that were locally responsible for metal concentrations that have been mined since Antiquity (e.g., Goldenberg and Rieser 2004; Py et al. 2014). However, the distribution and size of ore deposits is very heterogeneous depending of the geological setting. The Eastern Alps hosted some world class Fe-Cu-Sn deposits that have been mined since the bronze age (Schibler et al. 2011); some being still operated as open pits. On the opposite, the French Alps is characterized by numerous and disseminated small size ores deposits; about 350 ore deposits have been reported by the French geological survey (BRGM; Figure 1, Table 1). However, this number is underestimated as some deposits have been grouped, while others are not even reported (e.g., iron mines and deposits from the Chartreuse and Bauges massives, between Grenoble and Annecy). In the French Alps, all mines were operated underground.

Iron ore and base-metal deposits (Cu, Pb-Zn-Ag) are the most common in the French Alps. With the exception of some sedimentary iron ores, most deposits occur as vein-type and stratumfied mineralisation. They are mainly hosted in the external crystalline massifs or in sediments, at the Permain-Trias transition, and with carboniferous rocks of the external Alps (Figure 1; M eloux 1975, Rossi and Gasquet 2014). Therefore most ore deposits result from hydrothermal activity associated with the Variscan and Alpine orogenic cycles.

Table 1. Inventory of alpine ore deposits and mine districts for the seven alpine departments (data from the BRGM website: http://sigminesfrance.brgm.fr).

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Fe</th>
<th>Cu</th>
<th>Pb</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haute-Savoie</td>
<td>21</td>
<td>3</td>
<td>-</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>Savoie</td>
<td>54</td>
<td>12</td>
<td>8</td>
<td>21</td>
<td>-</td>
</tr>
<tr>
<td>Isère</td>
<td>62</td>
<td>22</td>
<td>3</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>Hautes-Alpes</td>
<td>52</td>
<td>1</td>
<td>11</td>
<td>16</td>
<td>1</td>
</tr>
<tr>
<td>Alpes de Haute Provence</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Alpes-Maritimes</td>
<td>49</td>
<td>4</td>
<td>20</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Var</td>
<td>104</td>
<td>8</td>
<td>5</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>352</td>
<td>50</td>
<td>47</td>
<td>78</td>
<td>4</td>
</tr>
</tbody>
</table>

If many alpine mines were operated since Antiquity, mining activity reached its maximum during Middle-Age and the 19th century, as evidenced by lead records in lake sediments (e.g., Arnaud et al. 2005, Giguet-Covex et al. 2011, Py et al. 2014). The activity started to decline at the end of the 19th century due to (i) resource depletion in some districts, (ii) the difficulties and costs of operating in high-altitude (most mines are located above 2000 m. asl.), and (iii) the discovery of world-class deposits with higher metal content and where metal treatment was easier. Accordingly, the last Fe mine closed in the 1930s and the last Pb-Zn mine closed in the 1970s. Mining activity has thus been a long-time central in the Alps, as suggested by the high number of mines: more than 650 mines entrances have been reported by Durand (2014, 2010) for the Savoie department only, and the mine of M acôt-La Plagne was the third provider of French Pb-Ag in the 20th century (156 000 t Pb and 350 t Ag; Meloux 1975). Meloux (1975) estimated that several millions tons of iron have been mined in the Alps, together with 200 000 t of Pb, 100 000 t of Zn and 500 t of Ag. The abundance of ore deposits of various metal contents (Fe, Cu, Pb-Zn-Ag, etc.) and the development of the mining activity thus strongly contributed to human settlement of the Alps for more than 2 000 years (Py et al. 2014).

After closure, the alpine mines were abandoned, and their infrastructures mostly dismantled. Vegetation developed and covered up the waste dumps that were affected by weathering. The existence of many abandoned mines scattered throughout the Alpine area, at all altitudes, is thus a real socio-environmental issue. This paper presents the main issues and stakeholders of post-mining in France before discussing the issue of hazard and risk prevention and of soil and water pollution. It finally focuses on valorisation strategies of the alpine mining heritage.
2 Post-mining in France

After mine closure, the operator companies were responsible of the mining sites, which were left abandoned and sometimes even forgotten. After the 1996 gallery collapses in Lorraine (NE France), France revised its Mining Code so that the French authorities became responsible in case of renunciation, failure or disappearance of the mining operator. At the same time several administrative structures were created in order to analyse and prevent risks related to mining activity.

GEODERIS was created in 1998 from a joint venture between BRGM and INERIS (the national institute of industrial environments and risks) in order to perform hazard diagnostics and to provide risk reducing solutions. The DPSM (department of prevention and mining security) was created in 2007 by the BRGM in order to manage post-mining activities such as monitoring, safety engineering, disaster response, archive management, etc. GEODERIS and DPSM work in collaboration with and under the supervision of the French Ministry of Ecology, Sustainable Development.
and Energy, which is regionally represented by the DREAL. The expertise of GEODERIS allows the DREAL to establish Mining Risk Prevention Plans (MRPP). The DREAL determines whether risks are acceptable or not. If not, it either supervises the work of the DPSM to secure the site or proceeds to expropriation, if required.

3 Hazard and risk prevention

Common mining hazards are (i) localized or widespread mass movement, such as collapse, subsidence and land settling, (ii) water and soil pollution, (iii) flooding, (iv) gas or ionizing radiation, and (v) coal waste dump mass movement and/or heating. Mass movement and pollution are of main concern in the Alps (Figure 2).

In order to prevent people for going in the ancient mines, the DREAL sealed most gallery entrances by locked doors or surrounding rock blocks. However, considering the high amount of galleries widespread on the northern alpine territory—more than 40 gallery entrances have been reported for the Cu-Fe district of Saint-Georges d’Hurtières (Savoie) only—only a minority of galleries is actually sealed, so that most galleries are still accessible for the joy of speleologists.

Prevention measures can also lead to gallery filling. In 2012, the DPSM proceeded to filling of a gallery from the ancient coal mine located 25 m underneath the school in the village of La Motte d’Avelians (Isère). The gallery was filled with 600 m³ of concrete that was injected by drilling and stopped by new build walls.

The DPSM is also in charge of monitoring the environmental evolution of selected sites. In the northern Alps, only 5 concessions and an additional site are under monitoring for either soil pollution or monitoring of the mining drainage waters. Most of them are located in the ancient coal district, South of Grenoble (Isère). The DPSM thus concentrates on a few sites, while most mines and ore treatment sites are under no supervision, nor monitoring.

The DREAL is responsible for the development and implementation of Mining Risk Prevention Plans (MRPP). These MRPP define perimeters of building lands without or under given conditions and unconstructible zones. In the northern Alps, the MRPP of Macôt-La Plagne (Savoie; Figure 3) has been adopted in 2014. Macôt-La Plagne was the part of the main Pb-Zn-Ag district of the French Alps. Nowadays, some galleries are located under the skiing resort of La Plagne, sometimes less than 20 m from the surface. The DREAL thus evaluated the risk of collapse and provided a MRPP to the municipality, highlighting unconstructible zones. Such MRPP is of capital importance and can be source of tension for the stakeholders in such a touristic place. Except that of Macôt-La Plagne, five others MRPP are being established by the Rhône-Alpes DREAL for the northern Alps.

4 Soil and water pollution

Despite monitoring of few drainage waters by the DPSM, no systematic environmental diagnostic has ever been performed on ancient mining sites. However, many small waste dumps are scattered in the mountains, often covered by vegetation. Meteoric water flows through the ore-rich dumps, most probably remobilizing some metals. Similarly, meteoric water percolates through the galleries leading to partial or full flooding, and leaching of the remnant ore (Figure 4). Leached metals are then transported by the drainage water to surface and groundwater. Arsenic has been a major problem in the northern Alps, especially in the Savoie department. Indeed, between 1998 and 2008, about 80 water catchments had to be cancelled in Savoie because of high As ratios. Tisserand et al. (2014) noted that 28% of the 257 springs of Savoie present an As content higher than the European potability threshold of 10 ppb. Among them, 9 springs have As in the 50-100 ppb range, and 2 contain more than 100 ppb As. Such high As values in spring waters are very well correlated with the presence of As and other base metal deposits in the vicinity.

With a few exceptions, no monitoring or diagnostic of water and soil pollution have been established in the ancient mining districts. One could think that it’s not so...
important as there has been no complains, and as most mining sites are located in high altitude, more or less far from the villages. However, agricultural and pastoral activities, tourism, as well as lumbering, play an important role for the local economy and might be affected by soil and water pollution.

Figure 4. Fe, Pb and Cu-rich alteration in the Cu-Fe mine of St-Georges d’Hurtières in Savoie (© Robert Durand).

5 Mining heritage and valorization

Most traces of the mining activity are slowly disappearing: the gallery entrances are being sealed, the waste dumps are most of the time covered with vegetation, and most of the mining infrastructures were dismantled. However, some ruins of buildings and furnaces remain, as well as remnants of cable-cars or railways.

During the last decades, the remaining traces of the alpine mining heritage have been highlighted, through interpretative boards along thematic trails, museums and even some underground guided tours. Interpretive boards are either used to promote mining sites located in remote places, such as the Saint-Véran copper mine (Haute-Alpes), which is located more than 2 700 m asl, or to promote important place such as the building that first hosted the French Mining High School (École des Mines). About 10 museums focus on the local mining activity, presenting various aspects such as mining techniques, ore minerals and extraction tools, economic and social development, etc. Finally, three mines propose guided tours in the underground galleries: (i) the “Musée souterrain de la Mine-image” welcomes about 20 000 visitors each year in the ancient coal mine of La Motte d’Avellians (Isère), (ii) about 10 000 persons visit the Pb-Ag mine of Argentière (Haute-Alpes; “Mines d’Argent du Fournel”), and (iii) “Le Grand Filon” recently opened to visits about 500 m over the 22 km of galleries of the Cu-Fe mine of St-Georges d’Hurtières (Savoie).

6 Conclusion

Post-mining national issues were only recently considered in France. The French authorities are responsible of the post-mining activity; it supervises hazard studies conducted by GÉODERIS and hazard prevention management conducted by the DPSM. It provides Mining Risk Prevention Plans (MRPP) to the concerned municipalities. The French Alps are a particular case considering the high amount of scattered and abandoned small mines with low-tonnage. A systematic monitoring and environmental diagnostic is thus unrealistic. Therefore, very few sites are currently monitored and only a few MRPP have been adopted (1) or are being established (6) in the Alps. The environmental impact (soil and water pollution) of all these mines is unknown, so that monitoring and evaluation of potential pollution is thus required, at least for the largest mining districts. Finally, the mining heritage as been valorised through underground guided tours, museums, boards and theme trails.

Acknowledgements

The authors are very thankful to Carole Christophe from the Rhône-Alpes DREAL for her help in clarifying the role of the various administrative stakeholders, and for giving us access to some reports concerning the post-mining activity in the northern French Alps. The authors are very grateful to Robert Durand, who gave the authors access to his huge personal database (pictures, archives, etc.) concerning all mines from the northern Alps.

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Occurrence of Rare Earth Elements in Ecosystems and Assessment of their Ecological Impacts: Research Approaches used in the French Programme Labex Ressource 21

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Abstract. The Rare Earth Elements (REEs) are a group of metals, including lanthanides, yttrium and scandium, with a strategic importance in several economic sectors (agriculture, medicine, motor industry...). The rising use of REEs has triggered renewed interest in exploring new sources, which will likely result in increasing public and environmental exposure to these elements. Their global production has increased exponentially in the last decades and human use is disrupting their biogeochemical cycles (e.g. gadolinium anomalies in freshwater and tap water, REEs enrichment of soils). However, studies about toxic effects following environmental exposure as well as the mechanism of action of these elements are much less known. In this study, the aquatic ecotoxicity of three lanthanides: Cerium as a light-REE, Lutetium as a heavy REE, and Gadolinium with an intermediate position, was studied using a test battery. Laboratory tests showed that ecotoxicity of lanthanides may increase with increasing atomic number (Ce<Gd<Lu), but variability among species was detected. At present, the environmental risk of these elements can be considered as acceptable except in some particular hot spots. However, their growing industrial use is promoting their release into environment and their risk could be higher in the future.

Keywords. Rare Earth Elements, Ecotoxicity, Environmental risk assessment

1 Introduction

The lanthanide group includes 15 elements, from lanthanum (Z = 57) to lutetium (Z = 71), that have atomic properties very close to lanthanum and very similar among themselves (Yosida et al. 1997; Greenwood and Earnshaw 1997). Generally, based on the electronic configuration of each element, lanthanides can be divided into two groups: light lanthanides, from Lanthanum to Europium (La-Eu) and heavy lanthanides, from Gadolinium to Lutetium (Gd-Lu), but there is no worldwide accepted definition for which lanthanide belongs to the heavy or the light group. Along with yttrium (Y) and scandium (Sc), they form the rare earth elements (REEs), which have a broad spectrum of applications in agriculture, clean energy and other industrial sectors (EPA 2012). Commonly low concentrations of lanthanides occur in soil and water, but their low mobility could promote their accumulation in the environment (Cao et al. 2000; Zhang and Shan 2001) following anthropogenic inputs. In 2008, 129,000 metric tons of REEs oxides were consumed worldwide (Cordier and Hedrick 2010). Mature markets (e.g. metallurgy, lighting, catalysis and glassmaking) consume 60% of the total, and high-growth markets (e.g. battery alloys, permanent magnets and ceramic) consume the remaining (Goonan 2011). Their wide range of applications is causing lanthanide enrichment in the environment as microcontaminants in the hydrosphere (Kulasiz and Bau 2011a) or in tap water (Kulasiz and Bau 2011b). Their uses as fertilizers in oriental agriculture and mining activities associated with REEs extraction are being associated with bioaccumulation in soils and vegetables (Xiao et al. 2013) and also in human hairs (Wei et al. 2013) in China. However, critical knowledge gaps exist regarding lanthanide ecotoxicity (Gonzalez et al. 2014). Their atomic properties are quite similar, varying in a predictable way, but no consensus exists on the variations of their related ecotoxicity.

Single test does not provide a global and representative vision of the environment (Repetto et al. 2001) and could over- or underestimate the potential toxicity of a substance (Davoren and Fogarty 2004). However test batteries are considered as good tools for detecting different effects using a variety of endpoints (Rojickova-padrova et al. 1998; Fochman et al. 2000). Although reported cases on lanthanide contamination are scarce, they are emerging in recent literature, highlighting the need to develop a general understanding of lanthanide ecotoxicity, as well as their bioaccumulation and mode of action, to predict the possible risks associated with the current anthropogenically-driven release in environment. In this research we assessed the ecotoxicity of three lanthanides: cerium (Ce) and lutetium (Lu) representing light and heavy lanthanides respectively, and gadolinium (Gd) with middle position, using a test battery. The aims of this study were: (1) to generate ecotoxicological information regarding these poorly studied elements, (2) to identify, if possible, an ecotoxicity order between them and (3) to compare ecotoxicity endpoints with concentrations already found in the environment to determine current risk associated to these elements.

2 Material and Methods

The experiments were conducted using commercially available chemicals (purity >99.99%): Cerium chloride (CeCl₃·7H₂O), gadolinium chloride (GdCl₃·6H₂O) and lutetium chloride (LuCl₃·6H₂O).

The test battery included: (1) Daphnia magna (Crustacean: Branchiopoda): The 48-h immobilization test with D. magna was performed according to the international guideline ISO (2012); (2) Heterocypris
incongruens (Crustacean; Ostracod) : The 6-d mortality and growth inhibition test was performed according to the Standard Operational Procedure (Microtoxtest, 2001); (3) Hydra attenuata (Cnidarian;Hydrozoa) : The 96-h acute toxicity test was performed according to Environment Canada (1996); (4) Brachionus calyciflorus (Rotfiera: Monogononta) : The 48h population growth inhibition test was performed according to the standardized French Guideline (NT F 90-377, 2000); (5) Pseudokirchneriella subcapitata (Chlorophyta: Chlorophyceae) : The 72-h growth inhibition (Korshikov, strain 61.81 SAG, Göttingen, Germany) was performed according to ISO (2011) standardized protocol; (6) Alliivibrio fischeri (Proteobacteria: Gamma proteobacteria) : The bacterial (Alliivibrio fischeri formerly known as Vibrio fischeri) luminescence inhibition test was performed according to ISO (1998) and (7) LuminoTox ®: The test uses stabilized photosynthetic enzyme complexes (PECs), isolated from spinach plant extract (LabBel Inc., Shawining, QC, Canada), and was performed according to Dellamatrice et al. (2006).

Risk characterization: The predicted no effect concentration (PNEC) is commonly known as the concentration below which an ecosystem is not expected to suffer an unacceptable damage. In this study EC10, based on time-weighted mean concentration (OECD 2008), were calculated with the excel macro REGTOX® for the different tests organisms. We used these values for estimation of the species sensitivity distribution (SSD) and to calculate PNEC values (Aldenberg and Jaworska, 2000) by using the software ETX 2.0 (Van Vlaardingen et al. 2004). The measured environmental concentrations (MEC) were found in bibliography or obtained through collaboration with other researchers. The ecological risk quotient (RQ=MEC/Lower limit-PNEC) was calculated for each element and environmental location. If RQ<1, then risk was considered as acceptable.

Main results and conclusions

Ecotoxicity of lanthanides seems to increase with increasing atomic number, but variability between species was detected. This order was only significant in bacteria (A. fischeri) and alga (P. subcapitata). Considering the toxicity of the three lanthanides studied, crustaceans (D. magna and H. incongruens) were the less sensitive species and rotifer (B. calyciflorus) and cnidarians (H. attenuata) were the most sensitive ones. These differences were partly explained by the formation of insoluble species during exposure and require further investigation.

For risk assessment purposes, Predicted Non Effect Concentration (PNEC) for each lanthanide was estimated (table 1). For calculation, we used EC10 data, based on measured concentrations in each test, minimizing a possible underestimation of toxicity because of metal precipitation. PNEC values for Lu are much lower than for Ce and Gd, highlighting the higher toxicity of heavier lanthanide, but a comparison with environmental concentration of these elements is needed for risk assessment. The RQ were calculated for mean values of each dataset, and for minimum and maximum values. The risk is considered acceptable when it is below 1. So, at current environmental levels, no harmful effects on aquatic ecosystems were likely to occur when mean values were selected for risk calculation. In all scenarios, risk quotients were below 1, although close in some cases with values around 0.8. However, RQ can be above 1 when it is calculated by using the maximum concentration found in some locations. In this case, some peak concentrations could present a high risk for aquatic ecosystems.

With the information currently available, these elements do not appear to be the cause of significant environmental impacts; but the growing industrial use of lanthanides will result in their increasing release into the environment and could induce a higher risk in the future. Special mention should be made to the exponential increase in the REE demand; it is anticipated that over the next 25 years the demand for neodymium and dysprosium will rise by 700% and 2600% respectively (Alonso et al., 2012), and the commercial recycling of these elements is extremely low, less than 1% of REEs were being recycled in 2011, due to inefficient collection, technological difficulties and lack of incentives (Reck and Graedel 2012). Landfill deposition is predicted as main end use of REE from the consumer products, based on assumption about previous production and consumer product life (Goonan, 2011). Medical applications, agriculture or mining activities could be other important sources of REEs; however, release and transfer quantities of these elements cannot be obtained, since they are not contemplated in any Pollutant Releases and Transfer Registers (PRTR).

Table 1. Effect on endpoints of different lanthanides, measured as EC10 based on measured concentration and estimated PNEC (HC5, the hazardous concentration protecting 95% of the species) derived from the EC10 values of the aquatic organism battery.

<table>
<thead>
<tr>
<th>Species</th>
<th>Endpoint</th>
<th>Ce</th>
<th>Cd</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brachionus calyciflorus</td>
<td>Reproduction</td>
<td>0.059</td>
<td>0.173</td>
<td>0.050</td>
</tr>
<tr>
<td>Hydrilla verticillata</td>
<td>Scour</td>
<td>1.50</td>
<td>2.60</td>
<td>1.53</td>
</tr>
<tr>
<td>Periclimenes schmitti</td>
<td>Reduction</td>
<td>0.18</td>
<td>0.26</td>
<td>0.17</td>
</tr>
<tr>
<td>Vibrio fischeri</td>
<td>Fluorescent</td>
<td>0.145</td>
<td>0.204</td>
<td>0.124</td>
</tr>
<tr>
<td>Chlamydomonas</td>
<td>Fluorescence</td>
<td>0.0015</td>
<td>0.0006</td>
<td>0.0012</td>
</tr>
<tr>
<td>Nitrobacter</td>
<td>Growth</td>
<td>0.0006</td>
<td>0.0004</td>
<td>0.0002</td>
</tr>
<tr>
<td>Growth</td>
<td></td>
<td>0.0006</td>
<td>0.0004</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

Acknowledgements

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1. Introduction

Waste rocks are one of the two main solid mine wastes produced by mine sites, along with mill tailings. They come from the rock materials surrounding the ore, which are extracted by explosion and stockpiled (Brooks 2011). To reclaim forests on waste rock dumps, the main strategy consists in tree planting on flat areas after soil layering on the waste rocks. Information is available used strategy consists in tree planting on flat areas after soil layering on the waste rocks. However, the plantation design that should be used to achieve both objectives remains unknown. To overcome this knowledge gap, two hybrid poplar plantations were established in 2013 on the waste rock slopes of the Canadian Malartic gold mine in Quebec. Tested factors were tree spacing, soil type, plantation material, and natural colonization of revegetated slopes by forest trees.

2. Material and methods

2.1 Mine site and waste rocks

The experiments were conducted at the Canadian Malartic gold mine, Quebec, Canada (48°13'N, 78°12'W). The production of this open-pit mine begun in 2011 and around 55,000 tons of ore are processed each day. Canadian Malartic ore is a mineralized greywacke. Calcium carbonate is the dominant mineral, and the waste rocks have low-sulphur content (around 1 % S) and contain calcite, which can neutralize acidity.

2.2 Tree plantation

Improve Revegetation of Mine Waste Rock Slopes

Fast-Growing Plantations as an Ecoengineering Tool to catalyze plant succession and accelerate the conversion of revegetated waste rocks into forest, restoring the quality substrates for tree establishment, especially waste rocks. Tree plantation after soil layering can allow the evolution of revegetated areas towards the closure, mine revegetation, root development, soil hydroseeding of herbaceous species. Tree responses to soil, vegetation cover, and soil erosion, and 2) microclimatic conditions controlling seed germi-

Pioneer tree species like poplar, which are able to one hand, fast-growing trees like hybrid poplar, develop forest reclamation, hybrid poplar, mine and hydroseeding of herbaceous species. They come from the rock materials surrounding the ore, which are extracted by explosion and stockpiled (Brooks 2011). To reclaim forests on waste rock dumps, the main strategy consists in tree planting on flat areas after soil layering on the waste rocks. Information is available, and seedling development of forest trees. Tested factors were tree spacing, soil type, plantation material, and light with trees (Rizza et al. 2007; Franklin et al. 1999), as well as a canopy which protects the soil from rain drop impacts. On the other hand, the facilitation herbaceous species often compete for water, nutrients, limit soil erosion (Helm 1995). However, used seeding allows to rapidly stabilize soil surface and to herbaceous seeding after soil layering. Herbaceous species which come later in forest succession. tree spacing, soil type, plantation material, and light with trees (Rizza et al. 2007; Franklin et al. 1999), as well as a canopy which protects the soil from rain drop impacts. On the other hand, the facilitation herbaceous species often compete for water, nutrients, limit soil erosion (Helm 1995). However, used seeding allows to rapidly stabilize soil surface and to herbaceous seeding after soil layering. Herbaceous species which come later in forest succession. This study mainly aims at determining if hybrid poplar plantations on waste rock slopes can limit soil erosion, tree recruitment by changing the undergrowth herbaceous species that are below Quebec regulatory concentrations that are below Quebec regulatory concentrations that are below Quebec regulatory concentrations that are below Quebec regulatory concentrations that are below Quebec regulatory concentrations.
Fast-Growing Plantations as an Ecoengineering Tool to Improve Revegetation of Mine Waste Rock Slopes

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Abstract. In forested regions, mine wastes are poor quality substrates for tree establishment, especially waste rock dumps. Tree plantation after soil layering can catalyze plant succession and accelerate the conversion of revegetated waste rocks into forest, restoring the traditional use of closed mine sites. Fast-growing trees may be used to quickly stabilize waste rocks slopes against erosion while facilitating forest reestablishment. However, the plantation design that should be used to achieve both objectives remains unknown. To overcome this knowledge gap, two hybrid poplar plantations were established in 2013 on the waste rock slopes of the Canadian Malartic gold mine in Quebec. Tested factors were tree spacing, soil type, plantation material, and hydroseeding of herbaceous species. Tree responses to varying designs were evaluated by measuring aerial growth, root development to insure soil fixation, and forest tree colonization.

Keywords. forest reclamation, hybrid poplar, mine closure, mine revegetation, root development, soil erosion, tree recruitment

1 Introduction

In Canadian forested regions, the revegetation of mine wastes should aim at reclaiming the forest environment to increase the social acceptability of mine projects as well as to decrease their environmental impacts. In consequence, mine revegetation techniques should both allow the evolution of revegetated areas towards the surrounding natural ecosystem and stabilize mine wastes.

Waste rocks are one of the two main solid mine wastes produced by mine sites, along with mill tailings. They come from the rock materials surrounding the ore, which are extracted by explosion and stockpiled (Brooks 1990). To reclaim forests on waste rock dumps, the main used strategy consists in tree planting on flat areas after soil layering on the waste rocks. Information is available in the literature regarding tree plantations in waste rocks, in particular to reclaim coal mines, in USA (Drake 1986; Kost and Vimmerstedt 1994; Angel et al. 2006; Emerson et al. 2009; Aiphy 1997), in Europe (Katzur and Vimmerstedt 1994; Angel et al. 2006; Emerson et al. 2009; Aiphy 1997), in India (Singh and Singh 2006, Maiti 2007) and in Canada (Sloan and Jacobs 2013; Landhäuser and Sloan 2012; M. Mosser et al. 2014).

In waste rock slopes where soil erosion constraint is important, revegetation methods generally consists in herbaceous seeding after soil layering. Herbaceous seeding allows to rapidly stabilize soil surface and to limit soil erosion (Helm 1995). However, used herbaceous species often compete for water, nutrients, and light with trees (Rizza et al. 2007; Franklin et al. 2012), and are low quality nurse plants to enhance natural colonization of revegetated slopes by forest trees. Thus, tree seedling survival and growth are often found very low on revegetated mine sites using herbaceous seeding (Anderson et al. 1989).

On the contrary, the use of fast-growing tree plantations on waste rock slopes could facilitate forest trees recruitment by changing the undergrowth microclimatic conditions while limiting soil erosion. On one hand, fast-growing trees like hybrid poplar, develop an extensive root system which rapidly colonizes the available soil volume (Douglas et al. 2010; Wilkinson 1999), as well as a canopy which protects the soil from rain drop impacts. On the other hand, the facilitation theoretical model (Connell and Slatyer 1977) tells us that pioneer tree species like poplar, which are able to colonize disturbed sites, prepare the environment for tree species which come later in forest succession.

This study mainly aims at determining if hybrid poplar plantations on waste rock slopes can limit soil erosion and act as nurse plants vis-à-vis boreal forest trees. To fulfill this goal, two field experiments were conducted to evaluate the influence of differing plantation designs on: 1) root development in superficial soil, vegetation cover, and soil erosion, and 2) microenvironmental conditions controlling seed germination and seedling development of forest trees. Tested factors were tree spacing, soil type, plantation material, and hydroseeding of herbaceous species.

2 Material and methods

2.1 Mine site and waste rocks

The experiments were conducted at the Canadian Malartic gold mine, Quebec, Canada (48°13′N, 78°12′W). The production of this open-pit mine begun in 2011 and around 55,000 tons of ore are processed each day. Canadian Malartic ore is a mineralized greywacke. The waste rocks have low-sulphur content (around 1% S) and contain calcite, which can neutralize acidity. Canadian Malartic waste rocks have mean trace metal concentrations that are below Quebec regulatory...

2.2 Experimental setting

In 2013, two experimental plantations were established on 33% waste rock slopes. The first plantation consists in 15 experimental plots (8 x 12 m): 3 replication blocks x 5 randomly distributed treatments (tree spacing 1x1m, 2x2m, 4x4m without hydroseeding, 2x2m with hydroseeding, control without trees or hydroseeding) x 12, 35 or 117 poplars (according to tree spacing). The second plantation consists in 18 experimental plots (8 x 8m): 3 replication blocks x 6 randomly distributed treatments (one-year-old whips, 50 cm cuttings, or bare root trees planted on 50 cm topsoil or on 40 cm mineral soil covered with 10 cm topsoil) x 25 trees. In this last plantation, the tree spacing was established at 2 x 2m. In both plantations, experimental plots were separated by 4-m wide buffer zones without trees.

Overburden soil that was used to cover the waste rocks was a luvis gleysol (Soil Classification Working Group, 1998) that was derived from a swampy area above the pit that had been previously colonized by conifers. The overburden topsoil consisted of the uppermost 30 cm of dark (organic-rich) soil (O- and A-horizons) that had been set aside prior to the excavation of the open-pit. The overburden subsoil consisted of the remaining mineral sandy clay loam soil (several meters thick), which was excavated down to bedrock after the overburden topsoil had been removed.

Hybrid poplar stock consisted of clonally propagated one-year-old whips (i.e. 1-m long stem cuttings), cuttings (i.e. 50-cm long stem cuttings), or bare-root trees (i.e. one year old stem with developed root system) from Populus maximowiczii Henry × P. balsamifera L. (M×B, clones number 915319 and 915318).

2.3 Experimental following

Tree growth

In both plantations, survival, stem height, and basal diameter were measured at planting and at the end of 2013 and 2014 growing seasons for each planted tree. Cumulative height and diameter increments were calculated as (value at the end of the experiment - value at planting).

Soil erosion

Surface soil loss (erosion pin method, Loughran 1989, Haigh, and Gentcheva-Kostadinova 2002) was measured in Spring, Summer, and Fall in 2013 and 2014, along 5-m long transects established perpendicularly to the slope axis. These measures were then related to a) root development (fine < 2mm, and coarse >2mm diameter) in the soil first 10 cm (soil coring), b) tree canopy development (densitometer), and c) undergrowth cover and biomass (hydroseeded or naturally established, point intercept method, Jonasson 1983) along the same transects as the one used for soil loss measurement.

Low diameter roots (1-20mm) especially contribute to soil erosion control (Van Beek et al. 2005; Styczen and Morgan 1995). Specific root length (root length to biomass ratio) and root length density (root length to soil volume ratio) are recognized indicators of soil occupation efficiency (Grams et al. 2002) and of soil cohesion (Styczen and Morgan 1995), two factors which control soil erosion. Thus these two parameters were assessed with WinRhizo software.

Tree recruitment

In June 2014, three 110 x 90 cm microsites were systematically positioned in each experimental plot. The microsite center was at the diagonal intersection of the square formed by four planted trees. A microsite half was seeded with 40 seeds of white spruce while the other half was seeded with 40 balsam fir seeds. Seed germination and seedling survival was followed every two weeks. At the same moment, each microsite microclimatic conditions were measured. Isolated measures of soil temperature (A-corn probe, Oakton Instruments) and light intensity at ground level (Sunfleck radiometer, Decagon) were taken, as well as continuous measures of soil water volumetric content at +/-3 cm depth (ECH2O probe, Decagon).

In each plot, nine 1-m² squares were randomly positioned and tree seedling presence was noted in each square at the beginning, the middle, and the end of Summer. Finally, seedlings survival rates were calculated by species and by treatment.

3 Preliminary results

3.1 Plantation design effect on tree growth and survival

At this stage, no treatment effect was found on planted tree survival. In the first plantation, tree height after two growing seasons (2014) was significantly lower in hydroseeded plots, and height increased with planting density (4x4 < 2x2 < 1x1). Basal diameter was also minimal on hydroseeded plots but also in plots with 1x1m tree spacing compared to the two other treatments. In the second plantation, after two growing seasons (2014), tree height and basal diameter was lower for cuttings compared to whips and bare root trees. Moreover, tree height was greater in plots with mineral soil covered by 10cm topsoil compared to topsoil alone.

3.2 Plantation design effect on soil erosion

Soil erosion

In the first plantation, repeated measures in 2013 and 2014 allowed to evidence a soil loss after snow melting, followed by a soil deposition in the second part of the growing season. Soil loss was the lowest in hydroseeded plots while it was the greatest in control plots without trees or without hydroseeding. Plots planted with hybrid
poplars showed intermediate soil losses. Soil deposition was the lowest and similar in hydroseeded and control plots. It was the greatest in planted plots without hydroseeding. Tree spacing had no influence on soil loss or soil deposition dynamics at this stage. The global balance of soil movements along 2014 resulted in no soil loss in hydroseeded plots (soil deposition compensated soil loss), a slight loss in planted plots (around 1 cm soil loss), and a greater soil loss in control plots (around 2.5 cm soil loss).

**Undergrowth and tree canopy covers**

In the first plantation, at the beginning of the second growing season (May 2014), undergrowth cover was clearly greater in hydroseeded plots (75%) compared to planted or control plots (30%). At the end of the second growing season (October 2014), cover differences between hydroseeded plots (90%) and the other plots (75%) attenuated thanks to natural vegetation colonization of non-hydroseeded plots. Tree canopy cover was greater in high density plantations (1x1m) compared to the other treatments (2x2, and 4x4m).

**Root development in superficial soil (0-10cm)**

In the first plantation, among planted plots, root length density was greater in high density plots (1x1m). At the end of the second growing season (October 2014), even if the undergrowth cover was important in all plots, herbaceous root length density was greater in hydroseeded plots compared to planted or control plots.

**3.3 Plantation design effect on forest trees establishment**

In July 2014, the water volumetric content of the superficial soil was the greater in plots with intermediate tree density (2x2m) compared to other plots without hydroseeding. The same treatment with intermediate planting density showed the greatest number of naturally colonizing tree seedlings. Balsam poplar was the more frequent tree species occurring from natural colonization (73% of relative abundance), followed by willows (13% relative abundance). At this stage, no clear effect of the treatments was found on seed germination and seedling survival of white spruce and balsam fir.

**4 Conclusion**

At the short term, herbaceous hydroseeding remained the most efficient method to limit soil erosion in waste rock slopes thanks to a greater aerial cover and root development of the undergrowth vegetation as soon as the first year after planting. On the other hand, tree growth was decreased in herbaceous hydroseeded plots. Fast-growing plantations also decreased soil erosion compared to control plots without trees and without hydroseeding. Their positive effect improved the second year after planting according to tree growth and undergrowth vegetation development.

The treatment with high planting density (1x1m) could better protect the soil from erosion from the third year after planting (2015) onwards because it presented a greater tree canopy cover and a greater root development of trees compared to lower planting densities. However, this high density treatment also presented lower soil water volumetric content which was less favorable to natural colonization of forest trees compared to intermediate planting density (2x2m).

Additional data will be collected during a third sampling season this summer 2015. Our findings will have practical implications for the development of innovative revegetation techniques on mine wastes in the boreal forest region.

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Sustainable mining and environmental issues 1533
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Abstract.
Mining and mineral exploration activities have
potentially negative impacts on the economy.
In addition to the major land use types, the people who
are living on these regions have their own silent
knowledge over their use of land and places. This refers
to places used for, for example, fishing, berry picking,
hiking, hunting, relaxation and other recreational and
minor economic activities. Mining has, on the one hand,
been seen as a problem for the environment, bringing
expectations towards the socio-economic benefits
exploration activities will return to the previous level.
to reconcile different interests on mining intensive areas.
the expectation is that in a relatively short period of time
The current decrease of metal prices has affected
the metal prices will start to rise again, and the mining and
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The newly awaken interest towards the Finnish
interest towards the use of mineral resources has
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Keywords. Land use, mineral exploration, mining, social

Introduction
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Land Uses
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Discussion and conclusions
The future of mining and mineral exploration activities in the
will be uncertain. The most important factors for the future
will be the prices of metals and the potential of finding new
mineral resources. It is also important to consider the
factors that have an impact on the future of mining and mineral
exploration activities in the

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Land use, mineral exploration, mining, social.
Developing Tools for the Integration of Mining with other Land Uses

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Abstract. Mining and mineral exploration activities have increased notably in Finland during the last 20 years. This has created challenges in land use planning in the municipalities where the activities are intense, and affects the social licence of the industry to operate. The aim of our research is to contribute in improving the pro-activity in land use related decision-making and strengthening the prerequisites in gaining a social license to operate. This is done by investigating 1) the potential future overlap of different land use types (such as exploration, mining, forestry, reindeer herding, and tourism and recreation), 2) the dialogue mechanisms between interested parties, and 3) the opportunities and limitations that legal frameworks provide for adaptive decision-making. Our multidisciplinary approach enables in gaining a deep understanding on how to reconcile different interests on mining intensive areas.

Keywords. Land use, mineral exploration, mining, social licence, adaptive law, stakeholder dialogue

1 Introduction

Rapidly increased prices of metals, favourable mineral potential, and inviting minerals policy have attracted multiple exploration and mining companies into Finland since mid 1990s (Eilu 2012; Jackson and Green 2015). Before this, the mining and exploration business in the country went through a recession during the previous two decades, even though the industry was a fundamental part of the economy of Finland before.

The newly awakened interest towards the Finnish mineral resources has resulted in opening of several new mines, especially targeted for gold, nickel, copper and platinum group metals (Fig. 1). The new mines are based on old findings that have now reached the economic feasibility, whereas the recent exploration has produced a number of discoveries not yet in production. Most of the present mining and exploration takes place in the eastern and northern parts of the country.

The current decrease of metal prices has affected strongly on exploration activities and, also, several mine projects have been placed on hold in Finland. However, the expectation is that in a relatively short period of time the metal prices will start to rise again, and the mining and exploration activities will return to the previous level.

The interest towards the use of mineral resources has brought expectations towards the socio-economic benefits that the mining industry could bring on economically recessive northern and eastern Finland (Tuusjärvi et al. 2014). However, at the same time, there are uncertainties over the possible negative effects especially towards the nature and the livelihoods depending on its pristinity, such as tourism. In addition, mining activities require space, and combined to the geology-confined location, they usually supersede other land use types. In the northern and eastern Finland, the main competing land use types are forestry, nature conservation (such as national parks and NATURA 2000 areas), tourism and reindeer herding.

Figure 1. Operating and currently suspended mines and advanced mine projects in Finland. Case study areas are in the northern Finland in the squared area (see Figure 3 for enlargement).

In addition to the major land use types, the people who are living on these regions have their own silent knowledge over their use of land and places. This refers to places used for, for example, fishing, berry picking, hiking, hunting, relaxation and other recreational and minor economic activities. Mining has, on the one hand,
a capacity to hinder or eventually prevent these activities in restricted areas, and people have, on the other hand, capacity to delay or eventually prevent mining at places valuable for them. In this situation, a proactive and iterative research over different competing and overlapping land use preferences and opportunities benefits all parties. This includes better possibilities for gaining social licence to operate for the mining companies. In addition, it supports the development of collaborative governance instruments which has a capacity to enhance the agility and case-specificity of the decision-making.

For this purpose, we combine expertise from five disciplines: 1) economic geology, 2) ecology, 3) economics, 4) law, and 5) sociology (Fig. 2), to study the current and potential future overlap of different land uses, and improved governance mechanisms in the case areas in northern Finland (Fig. 1 and 3). The work started on the fall 2014. In this report, we summarise the research methods, case study areas, and expected outcomes.

2 Methods

In this project, all researchers and institutions bring in their own methods and knowledge which enables a deeper, cross-disciplinary understanding over the land use related discrepancies of northern Finland (Fig. 2).

The expected outcomes of the research are 1) decision-support tools for proactive land use planning, 2) dialogue methodology to support conflict prevention and 3) understanding how the law could be improved to support adaptive decision-making.

![Figure 2. Our research combines expertise from different disciplines for deeper understanding over how to proactively respond to the land use challenges and improve the social acceptability of mining.](image)

2.1 Locating conflicting land uses

Sustainable land use planning involves integrated assessment of ecological, social and economic values of the landscape. In order to evaluate the needs and possibilities for adaptive coordination of land uses, we will develop and test a new GIS-based approach.

Firstly, we classify the ecological value of the case areas based on the conservation value of the habitats and species in the area. Secondly, we evaluate the social values of the areas by collecting information from local people and tourists via internet-based PPGIS survey (e.g., Brown and Kytta 2014). This method provides spatial information on respondents’ recreational use as well as opinions relating to the management and use of the focal area. Thirdly, we estimate the economic potential of the case areas from the viewpoint of mining and timber production. Finally, the spatial datasets are integrated in GIS to assess the location and overlap of different land uses and to identify possible future conflict sites.

2.2 Assessing possible future mining and its environmental and social effects

The locations of the future mining activities cannot be known for certain in advance. This is because the mineral exploration constantly provides new information about the existence and non-existence of mineral deposits, new technologies emerge, and the uses of minerals and metals and the commodity prices change.

To provide support for the integrated land use assessment, we evaluate the focus areas for mineral development in the case areas, with an estimation of the economic potential. The assessment is based on existing knowledge on the location of mines, deposits and mineral showings, and a probability modelling over the possible new mineral deposit findings, and the potential to proceed to the mining stage.

In addition, we will develop a tool which can be used to estimate potential environmental and socio-economic effects of the future mining projects at a coarse level. The tool will be based on characteristics of the existing mining projects and will be derived from the technical qualities of the deposits, characteristics of the operating companies, and the societal and environmental context in which the mining sites occur. The tool will also serve as a communication tool between various actors; authorities, industry, residents and other stakeholders as well as the general public.

2.3 Developing stakeholder dialogue

Various kinds of expertise and lay knowledge through administrational, scientific and participatory processes are used to support land use planning. However, especially collected participatory knowledge is not always included in to the governance processes. The focus here will be in developing a dialogue methodology to support conflict prevention in areas with competing land uses identified by the integrated assessment (see chapter 2.1).

To study the role of participatory knowledge in relation to the more traditional expertise knowledge, the examples of existing land use related dialogue processes are analysed and compared to the processes without such established communicative structures. In the areas that lack land use related dialogue, variety of relevant (government, market, and civil society) actors are studied, to generate knowledge for potential change and improvements in the dialogue (Johnsen et al. 2014). In the cases with evolved conflicts, joint fact finding (Karl et al. 2007) is used as a tool to create common understanding of the situation between parties involved.
2.4 Developing law relevant for the integration of land uses

In relation to alternative land uses, the law defines ownership and rights to use the resources, and provides mechanisms to change those rights, coordinate uses in other ways, and resolve disputes. Law always provides some mechanisms for all the functions mentioned. However, the law may be rigid and unable to support integration of alternative land uses in a way that would satisfy the legitimate needs and desires of those involved. Our research aims to understand whether the law could be improved for this purpose.

The research is based on assumption that land use issues significantly vary from case to case and law should be able to take into account this variation. This calls for adaptive law, i.e. law which is able to cope with changing conditions.

To develop an analytic framework to assess adaptive and non-adaptive features of law (A mold and Gunderson 2013) we employ the adaptive law theory (Craig and Ruhl 2014, Ruhl 2011). This framework is then used to study how law performs in the coordination of land uses and in resolving disputes. In addition, we will use literature study, interviews and doctrinal legal analyses.

2.5 Case-study areas

Two case study areas will be used to develop and test the methodology described above: 1) Kittilä-Kolari and 2) Sodankylä (Fig. 3). These cover a region from 100 to 200 km north of the Arctic Circle. Both areas have had active exploration and mine planning activities during the 2000s.

Two new mines have been opened in these areas during the last ten years: Kevitsa Ni-Cu-PGE mine in the Sodankylä area and Kittila gold mine in the Kittilä-Kolari area (FODD 2014). In addition, there is a Pahtavaara Au-mine (currently on hold), an iron mine project (Hannukainen) in feasibility stage, and a recent worlds-class, grass-roots, Ni-Cu discovery (Sakatti) within the case areas.

Three municipalities cover nearly all of the case-study areas: Sodankylä, Kittilä and Kolari. In total, these municipalities have 19,000 inhabitants (approx. 1.0 inhabitant/km²). The present important livelihoods in the region include services (tourism & administration), mining, forestry, and mining and mineral exploration.

The biggest town in the region is Sodankylä (8,800 inhabitants) and there is an international airport at Kittilä. Major tourist attractions in the region are two ski resorts (Levi and Ylläs) and the Arctic nature. The region holds several nature conservation areas including nature parks, strict nature reserves and NATURA 2000 areas with an extensive trekking trail network.

The mining and exploration companies operating at the case-study areas have different approaches in communication and dialogue processes. Kittilä mine, for example, has been active in creating dialogue with the local community. There is a cooperative forum where local interest groups can make their opinions heard. Also in different EIA processes social impact assessment has been performed although these processes can be criticised, for example, for not taking into account the diversity of local communities (Suopajärvi 2013).

Figure 3. An insert from Figure 1 representing the case-study areas (marked with thick, grey borders): Kittilä-Kolari on the left and Sodankylä on the right. Areas with green colour are nature conservation areas with various statuses, and areas with grey lineation are exploration tenements. Data sources: TUKES (2015), FODD (2014). Base map: National Land Survey.
3 Discussion
Mining and mineral exploration industries are heavily subjected to the changes in market-driven metal prices. This creates uncertainty onto the business, which is drifted also on to the expectations and long-term planning possibilities of local residents, local entrepreneurs, and authorities in the mining regions. On the one hand, uncertainty over the extent of actual environmental and socio-economic effects can generate resistance towards mining industry. On the other hand, potential for increased economic activities can raise hopes in local people for increased well-being.

To support the positive development, more information about the potentially overlapping land use types and their potential ecological and socio-economic pros and cons is needed. In addition, to proactively prevent possible discrepancies and conflicts, the dialogue and communication practices between the entrepreneurs, authorities and residents should be improved with strengthening the possibility of people to contribute to the economic development of the area where they are living. The integrated assessment gives information on the location of the valuable sites in terms of different land uses, and the location of sites with small or high risks of conflicts between land use alternatives. The spatial analysis based on a GIS approach is used in order to concretise the land use issues and to reconcile differing ecological, social, cultural and economic values.

Finally, the examination over the features of law will give a signal on how the governance system could be improved to support the reconciliation of the different interests. That promotes the capacity of law to support, in a flexible way, the region’s preferred development.

4 Conclusions
Tools to reconcile land use related conflicts, to support flexible governance mechanisms and to create prerequisites for the mining industry to gain social license to operate are developed in this research via multidisciplinary approach. By bringing together researchers with different backgrounds and expertise, we aim towards a deeper understanding over the complex land use planning problematic.

Our research will provide a variety of tools for proactive planning, but also for improving communication and dialogue processes between involved parties. By this, it supports the sustainable development of northern Finland from the socio-economic and ecological viewpoints, and strengthens the possibilities of the decision makers to better prepare for the changing societal environment.

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Abstract. Demand for mineral commodities has increased in the world and this leads to discover new reserves worldwide; thus that the Republic of Guinea has become a destination for mining giants since the turn of the century. Guinea is endowed with rich and diverse renewable and non-renewable natural resources, but largely under-exploited until now. Social and environmental issues relating to mining impacts remains a real concern in Guinea. With one of the world’s most important bauxite concentrations, yet Guinea remains among the poorest country in the world.

Keywords. Mining, Guinea, Sustainable development

1 Introduction

Located in West Africa, the Republic of Guinea covers an area of about 246 x 10^3 square metres and its population is estimated at about 11 million people. The mining potential of Guinea was probably perceived well before the thirteenth century, when gold was already the greatness and prosperity of the western African empires. Guinea has very rich and varied mining potential such as world reserves of bauxite, gold deposits and very high quality diamond reserves, iron ore with high grade are. Despite its vast mineral potential under-exploited, social and environmental issues related to mining operations remains a major concern for the sustainable development of Guinea. The aim of this paper is to dress an overview of relationships between mining impacts and sustainable development in Guinea.

2 Geology and economy of Guinea

2.1 Geologic setting

Major parts of Guinea are underlain by Precambrian rocks, which form the southern portion of the West African Craton (Schluter 2008) (Fig. 1).

The eastern two-thirds of the country are dominated by rocks of the Kenema-Man domain and the Paleoproterozoic Birrimian System. Neoproterozoic and Paleozoic sediments with a basal tillite and overlying sandstones, marls and quartzites form wide parts of northern Guinea. Along the coast occurs a strip of Neogene marine and alluvial sediments (Schluter 2008) (Fig. 1).

2.2 Economic Geology

Guinea is a country rich in various mineral commodities (Fig. 2) and was the second largest world producer of bauxite in 2002. All bauxite deposits occur in the western and central parts of the country and were formed through the alteration of dolerites, crystalline schists and nepheline syenites from Neoproterozoic and Paleozoic strata during the penneplanation and laterization of this region (Schluter 2008).

Diamonds of gemstone quality occur in southern Guinea, and originate from Mesozoic kimberlite dykes and pipes, which are controlled by deepseated fracture systems. Diamonds can be found in Guinea also in alluvial and eluvial deposits. Gold is found primarily in shear-zone hosted Paleoproterozoic greenstone. Major iron ore deposits originating from Banded Iron Formations (BIF) of Archean rocks occur for instance at Mt Nimba in the east of the country. Other mineral products include a nickel deposit in the Kakouilama-Kaloun range, about 50 km away from Conakry (Schluter 2008). Uranium deposits occur in the north of Guinea along the border to Mali. Economical deposits of ilmenite, rutile, zircon, tourmaline, etc. associated with sands from shorelines and large watercourse beds are also known in Guinea, but not yet exploited. Hydrocarbon exploration in Guinea began already in 1968, and the existence of oil resources in the Guinean of shore has since then been confirmed, but no production unit is yet in operation (Schluter 2008).

For the last decade, Guinea has been the destination of world’s mining giants (CBG, Alcoa, Gac, Bhp Billiton, Rio Tinto, and Valley) to discover different mineral and energy resources reserves. Over 900 exploration licenses have been granted by Guinea government for bauxite, iron ore, gold and diamonds (M anedov 2004). Currently, three mining companies mine bauxite and alumina industry (Rusal Frigulia, CBG and CBK), three others for gold processing (SAG, SM D and SEM AFO).

3 Sustainable development and mining in Guinea

One of the major challenges of sustainable development in the context of non-renewable resource is to use the wealth it creates as an engine of growth and development and sustain it long after the minerals have been depleted. This is a challenge relevant to Guinea where mining operations have social and environmental impacts. For social aspect, two mining giants serve as example: the "Compagnie des Bauxites de Guinée" (CBG) for bauxites, Rio Tinto SIMANDOU for iron ore. The environmental aspect is illustrated by two mining companies: SM D (Mining Company Dinguiraye) for gold processing and Rusal Frja for alumina refining (Fig. 3).
3.1 The social impacts

Since 1973, the “Compagnie des Bauxites de Guinée” (CBG) operates and exports the bauxite deposits in Boke region. After 42 years, the impact on local development in the region remains insignificant. However, the production increases year by year (Fig. 4). According to statistics published by company, its production has greatly increased over the past decade, but the development index and the poverty reduction are very low.

Despite the increase in production, the Boké region has not significant development (Fig. 5). In addition, the mining giant Rio Tinto has soon open one of the largest iron mines (Fig. 6) for 100 years production minimum in the forest region of Guinea (N’zérékoré, 1000 km from Conakry).

According to the latest report published by Rio Tinto, Simandou project is at final stage of feasibility study. However, no local development project has yet until now and N’zérékoré national road is one of the examples (Fig. 7). This road is the means connection between the forest region of Guinea and the capital Conakry along 1000 miles. It remains impassable for population while Rio Tinto personnel airlifted (Fig. 7).
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3.2 The environnemental impacts

In the Republic of Guinea, environmental considerations have gained increasing importance since the UN Conference on Environment and Development (UNCED) of 1992. Issues of environmental protection in Guinea are still at the stage of speeches and laws elaborations. However, the degradation and pollution caused by the uncontrolled deposits exploitation and metal processing greatly affect natural environment (Fig. 8). Major environmental impacts of mining occur in RUSAL Fria (first alumina refining company in Africa) are: threats from bauxite mining and processing in ecologically-sensitive area, and water contamination by the discharge of effluents which contain toxic chemicals. SMD produces large amounts of gold per year. Since the start of operations, environmental impact is on health effects from exposure to mercury and cyanide (for gold miners).

Both of RUSAL Fria and SMD are known for the obsolescence of its installations. These polluting companies have their factories which are no modernization technically, even at the level of treatment processes.

Figure 8. Pollution from RUSAL and SMD

4 Conclusion

The contribution of mining revenues to the socio-economic development of the Republic of Guinea remains very low despite huge reserves and others deposits present in Guinea. Even social and environmental impacts also occur more and more since there is no effective scientific organization for the monitoring of mining companies in their mineral processing.

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Technosols of Mining and Quarrying Areas: Toward Multifunctionality

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Abstract. The soils of mining and quarrying areas, characterised as Technosols, are deeply modified soils. The intense degradation they are subject to has altered their capacity to support ecosystem services. However rehabilitation issues are now considering the multifunctionality of mining and quarrying Technosols, i.e. their capacity to provide altogether several ecosystem services. Integrated rehabilitation techniques encompassing physical, chemical and ecological aspects are now being designed to ensure sustainable multifunctional soils in mining and quarrying areas. The aim of this position paper is to assess the multifunctional potential of Technosols of those areas and, thus, to determine its implications for the establishment of rehabilitation schemes.

Keywords. Ecosystem services, SUITMAs, rehabilitation.

1 Introduction

With the rising of anthropogenic pressures on the Earth system, many natural resources are going toward shortage and planetary boundaries are being threatened or even transgressed (Rockström et al. 2009). Soil is one key natural capital which supports critical ecosystem services but has often been overlooked (Breure et al 2012, Dominati et al. 2010). Today, sustainable soil management is needed to meet the environmental challenges of our era (Lal 2009).

Soils of Urban, Industrial, Traffic, Mining and Military Areas or SUITMAs are among the essential soils to manage as they represent increasing land surfaces (EEA 2010) and are expected to support a wide variety of ecosystem services like regulating, provisioning and cultural services (Morel et al. 2014). SUITMAs are mainly “soils dominated or strongly influenced by human-made material” called Technosols (IUSS 2014).

As for agricultural soils (Kibblewhite et al. 2008), sustainable management of Technosols should integrate their potential multi-functionality, i.e. their capacity to provide altogether several ecosystem services. Steps toward the integration of multi-functionality for the management of urban Technosols have been made (Morel et al. 2014). However such a work is still needed for Technosols of mining and quarrying areas whereas they represent large areas and are subject of major environmental disturbances (Echevarria et al. 2015).

Thus, the aim of this position paper is to assess the multifunctional potential of Technosols of the mining and quarrying areas and, thus, to determine its implications in rehabilitation schemes.

2 Technosols of mining and quarrying areas: from degradation to rehabilitation

2.1 Characteristics of Technosols right after mining and quarrying

In this paper, we first examine the characteristics of Technosols left after the mining and the quarrying activities. In a detailed literature review, briefly summarised here, we identify the various mining and quarrying processes, their consequences on soil chemical, physical, and biological properties, and, lastly, their impact on supported ecosystem services.

Mining and quarrying can be the source of largescale ecosystem degradation. For example, mining for strategic metals often implies contamination of surface environments with hazardous trace metals or metalloids. Mining of sulphide minerals induces soil acidification as well as trace metal transfers. Opencast coal mining and aggregate quarries do not have such an acute geochemical impact on the environment, but they strongly modify the geochemical cycles, the agro-ecosystems, the geomorphology and the landscapes. Deep mining also produces large quantities of spoils and tailings, which cover huge surfaces.

In consequence, mining and quarrying activities generally generates degraded Technosols with low carbon content, very low pH, very high bulk densities, coarse or fine textures, and low nutrient contents in comparison with initial soils. Such changes induce a dramatic alteration of the supported ecosystem services and rehabilitation is needed to enhance the multifunctionality of the soils of those areas.

2.2 Rehabilitation issues

Concerns about the rehabilitation of mining and quarrying sites have emerged as early as the beginning of the 20th century (Plass, 2000). The rehabilitation efforts first focused on a return of the mines soils to a productive use (e.g. wood, agriculture) and then on environmental quality (e.g. spoil toxicity, water quality). Issues were pointed by the public, the politicians, the scientists and the mining industry. Now, regulations have emerged worldwide to limit adverse effects of mining activities and to define rehabilitation strategies and goals. Thus,
according to changing regulations and emerging social demand, the way degraded land and mine wastes were handled has changed with time (Plass 2000, Schulz 1996). Some mining companies are now implementing real sustainable strategies for mined land reclamation (Toy and Griffith 2001).

An increasing number of ecosystem services are now considered when establishing a rehabilitation scheme. At first, mine Technosols are engineered to render local ecosystem services, which include: food and non-food biomass production, geotechnical stability, soil erosion and runoff control, groundwater level and quality, landscape and cultural services. Furthermore, they must ensure that no geochemical contamination of adjacent environments occurs: air (dust emissions), water (particulate and soluble contaminant transfer) and biota (soil-plant or soil-animal transfer). Finally, more global goals, such as carbon sequestration or the preservation of endemic species can even be set for rehabilitated mined Technosols.

Multi-functionality is thus today a common goal for soil rehabilitation in mining and quarrying areas.

### 2.2 Rehabilitation techniques

One of the most important steps of land reclamation is landscaping the site by implementing new vegetation covers and create a surface water flow network. Technosols are therefore created at large scales in post-mining sites. The first purpose of landscaping mined areas was to properly handle geotechnical risks. Sloping spoil heaps and dumps is basically intended to avoid dump collapse, to provide stability over time and to avoid excess water runoff. For this purpose, rock stability, porosity, density, hardness, rainfall are among the main criteria taken into account for designing landscapes, sloping spoil or tailing dumps.

Designing new soil covers for landscape issues has emerged in the last decades. As an example, it became a legal standard and requirement for coal mining in the Ruhr area (Germany) in 1985 or in 1982 in Spain. A holistic approach started to be needed and land reclamation plans for ecological and landscape purposes became a requisite for post-mining rehabilitation. Consideration of the integration of the geomorphology of dumps with surrounding landscapes, the composition of the vegetation, the future land use (secondary natural sites, forests, agricultural areas, urbanised or industrial areas), and the need for infrastructures became of high importance in the landscaping process.

Soil construction and amendment are more often used to ensure a sustainable rehabilitated ecosystems. As for other engineered soils, the construction of Technosols follows some basic rules in order to make them fulfill essential ecological and environmental functions (Séré et al. 2008). Basically, as the raw materials (spoils, stripped soils, tailings) are the main geochemical driving forces of the system a careful characterisation, including physical, chemical and biological properties, is required prior to soil construction. Assessment of the re-colonisation of soil biota is also a critical feature to assess in order to design sustainable rehabilitated system (Frouz 2013).

Numerous techniques have been developed and tested over the years to integrate a wider variety of ecosystem services in the rehabilitation of mining and quarrying Technosols. Mid-term surveys point the importance of integrating the rehabilitation goals and techniques right at the beginning of the mining or quarrying operations in order to preserve the physical, chemical and ecological properties of the raw materials that are used for soil reclamation.

### 3 Conclusion

From degraded soils, Technosols of mining and quarrying areas are now more often expected to be multifunctional and to support a wide range of ecosystem services. Relevant rehabilitation techniques have been designed to enable this multi-functionality but they have to be integrated right at the beginning of the mining or quarrying operations to be successful.

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Lighting Up the Subsurface

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Abstract. Our future use of the subsurface, particularly for energy (subsurface gas storage, compressed air energy storage, shale gas, coal bed methane, underground coal gasification, enhanced oil recovery, geothermal) and waste disposal relating to energy (carbon capture and storage, radwaste), but also for mineral resources, depends on much greater understanding of subsurface flow and processes. This is particularly pertinent to low-carbon energy because the feasibility of three low carbon energy solutions rely on understanding of subsurface geological containment or flow: carbon capture and storage (CCS), shale gas and radwaste. Mineral deposit development and extraction, particularly near urban areas must be mined responsibly. Lack of understanding and uncertainty feeds through to lack of confidence amongst policy makers and industrial investors, and most of all to lack of public confidence.

Keywords. Energy, minerals, subsurface responsible development

1 The concept

We propose an infrastructure “the Energy Test Bed” to allow the subsurface to be monitored at time scales that are consistent with our use of the subsurface, to increase efficiency and environmental sustainability but also to act as a catalyst to stimulate investment and speed new technology energy and mining options to commercialisation.

• the role of biological mediation in the subsurface in shallow to deep environments;
• processes at basin and reservoir scale in reservoir stimulation and enhanced oil recovery (EOR);
• ground deformation and induced seismicity associated with enhanced geothermal systems in hot-rock-dry-rock environments.
• Large subsurface and open surface mining operations and associated waste management

We will develop a unique package of monitoring capability where monitoring at the surface and in the critical zone will be coupled with deep borehole monitoring of variables such as pressure, temperature, heat flow, seismicity, tilting, strain accumulation, fluid chemistry, pH and biological properties. Monitoring will also include satellite and remote sensed data such as InSAR (Interferometric synthetic aperture radar) and gravity, electrical, spectral and magnetic data.

Infrastructure that underpins research into subsurface activity will make us better at monitoring and managing these new and continuing activities safely and sustainably, including optimising exploration practices. Industry would benefit in being able to access state-of-the-art monitoring data to maximise efficiency of extraction and subsurface management, as well as maximising environmental sustainability.

2 Impact of the Infrastructure

The economic impact is potentially very large in developing (1) untapped energy resources like shale gas, CBM, UCG, geothermal and new occurrences; (2) methods to sustain fossil fuel reserves e.g. EOR; (3) understanding of storage processes including CCS, gas storage and radioactive waste disposal; and (4) subsurface energy storage such as compressed air energy storage (CAES).

Economic value will also stem from management and minimisation of environmental impacts which will protect the environment, ecosystem services, property and infrastructure. Greater understanding of subsurface processes, if communicated properly, will also allow better public buy-in to subsurface usage and therefore more efficient, streamlined development.
The scientific impact of this new infrastructure will be far reaching, including understanding of subsurface flows, geochemistry and physics of rock matrices, and the interaction of surface carbon and other geochemical cycles and subsurface flows.

The new infrastructure will act as a catalyst for industry both onshore and offshore to stimulate investment and speed new technology options to commercialisation. It will thus act as a bridge from ideas to application and would attract support and possible co-funding from oil and gas companies, mining companies, utilities and energy and environment consultancy.

Figure 1. Schematic model of the Energy Test Bed

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Traceability of Base Metals Ores Using Mineralogical and Microtextural Parameters

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Abstract. The demand in mineral resources is increasing rapidly, but there is a lack of transparency in the trade of concentrates raw mineral materials because of speculation and involvement in the finance of armed conflicts. Because of the distance between primary extraction and the final production sites it is difficult to check the origin of these products. An identity card is required for mineral commodities, so that trading in the industry can be verified and the traceability of concentrates ensured. This problem may be considered as an inversion process: studying the products sold to identify the original ore. The discriminant parameters are mineralogical composition, identification of textural microfacies of the target minerals (pyrite, sphalerite and chalcopyrite), “pseudo-paragenetic sequence”, and the contents and distributions of minor elements of target minerals. Statistical tests are used to compare the chemical composition of three target minerals. The application to Volcanic Massive Sulphide ore deposits shows that it is possible to distinguish target minerals between ore deposits in the Iberian Pyrite Belt province and from the Urals province using the selected characteristics. Ore deposits from different provinces may be discriminated using the identity cards, as well as different deposits in the same province.

Keywords. Traceability, identity card, target minerals, Volcanic Massive Sulphide

1 Introduction

Metal mining and marketing have an impact on the economy, society (negative or positive) and the environment. The metal market is a major factor in economic development. This is a major concern in developed countries, which are anxious to secure supplies in view of the strong demand for mobile phones, digital tablets, solar panels, batteries, ... It is also growing concern for the “citizen-consumer”, who needs to be sure that these items have not been produced contrary to his or her ethical or moral values. To avoid parallel markets of certain mineral resources, solutions have been proposed to locate the extraction sites of these resources for diamond via Kimberley Process (www.kimberleyprocess.com), for emeralds (Giuliani et al. 1998a, b), sapphire (Giuliani et al. 2005), ruby (Giuliani et al. 2005) and “coltan” (Gäbler et al. 2011, 2013; Melcher et al. 2008a, b, 2013; Savu-Krohn et al. 2011). A chain of control and certification has been set up by the diamond producer countries under the supervision of international experts.

All diamonds must be accompanied by a certificate of origin (Kimberley process). The development of the $^{3}O_1^{18}O$ isotopic identity card for emeralds helps to distinguish the source of a large number of high quality emeralds (Giuliani et al. 1998b). Fingerprints of coltan can be determined to find the place of origin of the mineral (Gäbler et al. 2011, 2013; Melcher et al. 2008a, b, 2013; Savu-Krohn et al. 2011). A similar need sometimes arises during mineral processing when multiple sources are used. The Luossavaara Kirunavaara A B plant (LKAB) in Sweden produces iron ore from Kiruna and Malmoberget mines. These minerals are mixed. Iron oxides of Malmoberget are different from those from Kiruna (coarser-grained, different types of joints of grains,...) (Oghazi et al. 2009) and behave differently during treatment. To clarify the importance of the source of the ore on the difficulties observed during treatment, a traceability study was attempted (Kvarnström and Oghazi 2008; Machault et al. 2013). However, there are very few studies on the traceability of base metals. These metals are mainly used in industrial sectors and the evolution of their price depends to a large extent of the growth of the global economy.

The aim of this work is to establish parameters to be included in an identity card for each deposit, which will allow it to be discriminated from other deposits. This requires a method of traceability with low analytical cost, using easily accessible techniques mineralogical and microtextural characterization allow an unique signature to be established for each ore and each deposit studied (Machault et al. 2014). The ultimate objective of this study, which is part of a global programme to create an ore identity card, is the establishment of a database incorporating the characteristics of each deposit and each mineral processing plant (Machault et al. 2013). Periodic reviews of the database will ensure monitoring of traceability parameters over time.

2 An approach for the traceability of base metals in Volcanogenic Massive Sulphide

Traceability refers to the ability to track a product at different stages of its production, its transformation and its commercialization from the source of the product up to the end of its life, including possible recycling. It must allow the origin of the source concentrate to be determined at each of these stages. Procedures to
achieve a good traceability are governed by standards and/or national or international control organizations. In the case of mineral resources, traceability consists of associating a commodity to the mine from which it has been extracted. For base metals, the bulk ores bear mineralogical differences, which may provide characteristics to track the bulk ore. These characteristics may “survive” during mineral processing, so that we can find “footprints” of bulk ore in the concentrate. Hence metal ore traceability implies that, in the ideal case, for each province and also for each deposit, valuable mineral have an unique signature. The characteristics that can be observed in concentrated at grain-scale (mineralogical composition, chemical composition of the phases, microtexture) will depend on (1) the process of formation of the mineralization and its post-deposit history (type of ore deposit) and (2) the local geological setting including the host rocks (regional setting which is sometimes poorly understood). The concentrate is derived not only from natural processes, but also from industrial processes, which must be taken into account. In addition to the processing difficulties like mixing of bulk ores (Kvarnström and Oghazi 2008) we cannot exclude variations over time in the operation of a given mineralogical plant. Finally, within a given mine, the nature of the bulk ore may vary over time as the exploitation of the site progresses. Hence, the signature of the concentrate depends on the characteristics of useful minerals, the type of deposit, the metallogenic province and the treatment the ore is subjected to. This signature is rigorously established only at a given moment of observation. In the case of base metals, traceability is the ability to find, for a given concentrate, the trace of all manufacturing stages (mineral processing) and the provenance (deposit) of all its components. The traceability of a metal concentrate would be possible to determine: (1) the province, the district, the deposit and bulk ore from which it was extracted; (2) the mining company; (3) the different places where it has been stored; (4) the manipulations and the equipment used in its manufacturing; (5) its transportation to its final destination; (6) its end-use; (7) its recycling; (8) its possible reutilization.

3 Methodology of traceability in the case of base metals in Volcanogenic Massive Sulphide

Figure 1 is a flowchart illustrating the methodological procedure followed in this study. We have selected the samples we considered as the most representative ones according to their texture and mineralogical compositions. Variability within a deposit can be significant. Comparisons are only valid at the time of sampling. That raises the problem of feasibility. The bulk ore characterization was conducted using a metallurgical microscope, a scanning electron microscope (SEM) and an electron microprobe. These techniques are used to study the textures, mineralogical composition, and chemistry of the minerals. Statistical analyses are then performed on the individual mineral phases to finally obtain an identity card of each studied ore (Fig. 1). During observations, a particular attention has been paid to: the identification of characteristics microfacies, the presence of trace minerals and finally the minor elements contained in the “target minerals”. The “target minerals” are: (1) Pyrite for its ubiquity in the studied bulk ore deposits which allows to compare bulk ores from different mines; (2) Sphalerite, which can incorporate into its structure a large number of potentially valuable elements (Ge, Ag, In, Ga) or non-valuable elements (Fe, Cd, Hg, Mn, Sb); (3) Chalcopyrite that is repeatedly found associated with pyrite and sphalerite.

![Figure 1](image)

**Figure 1.** Organization chart of the method used for establishing identity cards

4 Presentation of the metallogenic context of the two studied provinces

We limit this study to a single type of deposit: Volcanogenic Massive Sulphide (VMS) deposits in order to consider a single metallogenic process. We chose to study bulk ores of nine deposits from two different provinces: the South-Iberian province and the Urals province.

5 Results

Bulk ores of deposits from the South-Iberian and Urals provinces have been characterized. It should be noted again that the observations and the measured parameters and therefore the ore comparisons, have been inferred only from the samples collected so that the conclusions are therefore only valid for the set of studied samples. In consequence such a traceability study requires to be updated periodically. Results will be expressed in qualitative or semi-quantitative form. The different parameters of the identity card (Fig. 2) from bulk ore of each ore deposit allow us to differentiate deposits from a single province and also to distinguish different provinces. We can evaluate the effect of regional heritage on the mineralogical composition and the chemistry of the bulk ore minerals.

The parameters of the identity card are: the mineralogical composition in the form of relative abundance, the microtextures of target minerals (the following provides a description as well as a tentative evolution in time of these microtextures, Fig. 3), the pseudo-paragenetic succession, the chemical composition and the distribution of target minerals and when possible, the “memory loss” parameter which is a characteristic of mineral processing (Machault et al. 2013).
6 Discussion

6.1. Appropriateness of the methodological approach used

We have established an original traceability method for base metals. This traceability method can be used to obtain a comprehensive identity card of the deposits. Mineral chemistry is considered to be the most promising tool for provenance analyses. The comparative results obtained from the statistical tests (Kolmogorov Smirnov and Colin White) are roughly similar, regardless of the elements or considered target minerals. Therefore the Colin White test appears to be the most effective test to compare the minor elements content in ore, since (1) it necessitates fewer individual data; (2) it is not influenced by the value of individual data and (3) it is not sensitive to element distribution heterogeneity.

6.2. Utilisation of discriminative parameters for ore traceability

This study contributes to the establishment of various parameters that differ from a deposit or a province to another. Some of these parameters are discriminative but a single characteristic is generally not enough to obtain a successful discrimination of all the deposits. It is therefore necessary to combine parameters, as provided in the ore identity card to get a satisfactory result. In our case, there is not any unique parameter that could provide a satisfactory differentiation between the nine deposits. A flow chart using logical criteria to discriminate ore deposits can also be established (Melcher et al. 2008a, b), but it requires a hierarchy of the considered parameters or criteria. At this stage of method development, the establishment of a hierarchy between the retained characteristics, valid for all VMS deposits, seems premature. However, we are able to produce flow charts for each parameter showing their discriminative or satisfactory features (Fig. 4).

Figure 2. Identity card of Neves Corvo. Experimental memory loss refers to a characteristic of the mineral processing (Machault et al. 2013).

Figure 3. A. Framboidal pyrites evolution from Neves Corvo and Tharsis deposits (pictures taken through a metallographic microscope) stage 1- framboidal pyrite, stage 2- crusting-fibro-radial structure, stage 3- crusting with chalcopyrite- coprecipitation pyrite-chalcopyrite, stage 4- disappearance of spherulites in the inner part, stage 5- cristallization continues- growth of large crystals, stage 6- brecciation- deposition of other sulphides; B. Sphalerites associated with pyrite and chalcopyrite from Neves Corvo and Tharsis bulk ore (pictures taken through a metallographic microscope) stage 1- sphalerite, chalcopyrite, pyrite (micro-crusting), stage 2- the pyrite growth, stage 3- microfracturing- filling by sphalerite, stage 4- filling continues, stage 5- chalcopyrite inclusions in sphalerite. The scale shown is valid throughout the figure.
7. Conclusions

This study has contributed to: (1) establish nine ore identity cards for two metallogenic provinces: Neves Corvo and Tharsis in South Iberian province; Alexandrinka, Dergamish, Yaman Kasy, Safyanovka, Ivanovka, Mauk and Sibay in the Urals province; (2) discriminate the bulk ores from deposits in a given province and the bulk ores between distinct provinces; (3) reveal pyrite as a characteristic microtexture parameter for performing bulk ore traceability. This parameter is not influenced by the age of the deposit, the tectonics zone where the deposit is located and the nature of the rocks hosting the deposit.

This method forms the basis of a necessary protocol to establish base metals ore traceability. For this, to achieve the monitoring of ore parameters, it is necessary throughout the life of a mine, including costs for analyses and competent operators. Such studies will also contribute to increase the amount of data usable for understanding the genesis of an ore deposit and the metallogenic processes involved. The deposits are unpredictable by nature. It is difficult to take into account the internal variability of the deposit. This leads to the necessity to ensure a continuous watch, which also provides a better understanding of deposits in particular on valuable low grade elements. The industrial and academic communities will also benefit from traceability monitoring, which will provide regular quantitative data throughout mineral processing potentially improving its efficiency. Finally, the establishment of traceability methods based on minor element contents will have an effect on mineral resource management especially for strategic (critical and valuable) elements which are sensitive to market fluctuations.

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Science Outreach and Mining Heritage: Drivers to the Rehabilitation of the Mining Village of Lousal, Portugal

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Abstract. The Lousal deposit was mined continuously between 1900 and 1988, exploiting pyrite for sulphur. This mining village is currently an international example of success in socio-economic, environmental and mining heritage rehabilitation. The program resulted from the joint efforts of the local municipality - Grândola - and the mine owner company – Sapec, SA. It was responsible for the restoration of the mineshafts and conversion of the old power plant into a mining museum. The main warehouse was transformed into a regional restaurant, the administration house was converted into a rural hotel, and the mine offices into a handicraft centre. A rehabilitation plan directed to reclaim the contaminated areas was developed. Some other mining facilities gave rise to a Science Centre that promotes non-formal, science outreach educational activities, which represent a very strong attractor for public that definitely changed the daily life scenario of Lousal. The strong commitments of many institutions, with emphasis on the University of Lisbon, have raised very high the scientific standards of the whole initiative.

Keywords. Lousal Mine, Mine rehabilitation, RELOUSAL program, Iberian Pyrite Belt

1 Introduction

The Lousal mine was an important massive sulphide deposit of the Iberian Pyrite Belt located in its NW sector, in an area limited to the N, E and S by the Tertiary sediments of the Alvaiade basin (Schmerhorn et al. 1987; Matos and Oliveira 2003). The deposit consists of several ore lenses that are lined up along 1.5 km length in strike (Strauss 1970). It consisted of about 50 Mt of ore at 1.4% zinc, 0.8% lead and 0.7% copper (Strauss 1970). The massive sulphide mineralization occurs in close dependence to felsic volcanic centres, where intense ore-forming hydrothermal activity led to extensive chloritic-sericitic alteration and stockwork mineralization (Fernandes 2011). The mine was active for sulphur between 1900 and 1988 and part of its surface infrastructures are rather well preserved.

In the past, the safety, environmental and social risks arising from badly conducted mine closures resulted in severe distress for communities due to environmental, social and economic collapse, as in most cases very little environmental obligations were imposed by law and mines were simply boarded up and abandoned. However, it is currently accepted that mine closure requires the return of land to a viable post-mining use, and that the socio-economic impacts of the closure must be assessed and managed. Therefore, the Lousal mining village is being rehabilitated not only as a geological and mining heritage site, but also as a centre for education for science and technology and a destination for tourism of nature, culture and patrimony. Here, we address the main components of this successful rehabilitation program.

2 The past

The discovery of the Lousal deposit took place in 1882 by a local farmer. However, the area shows several signs of mining activity since the Bronze Age (ca. 3300 BC), with particular emphasis on constructions probably built for defense as well as for ore storage. Between 1900 and 1934, the exploitation rights were property of several individual persons and companies. In 1936, the Belgian corporation Société Anonyme Mines et Industries S.A., which preceded SAPEC, became the owner of the Lousal mine (Rodrigues 2005). SAPEC still owns the mine despite the shut down of the operation in 1988. The urban structure of the Lousal village is centred on the buildings related to the mining activity - headframes, workshops, stores and laboratories -, which spread out over the entire mining perimeter. Besides the mining buildings, there are two other groups of structures in the area: the social support buildings – medical ward, school, church and market – and the housing buildings, including accommodation for the miners and for the technical personnel, and the administration building. In 1958, Frédéric Velge, son of Antoine Velge, the main holder of Société Anonyme Mines et Industries, SA, became director of the Lousal Mine and opened an epoch of great expansion for the mine. With the help of the on-site geologist Günter Strauss, he modernized the management and introduced new methods of mechanised mining production. The closure of the Lousal Mine, in 1988, followed the unsustainability of sulphur production out of pyrite.
3 The present

Less than ten years after the closure of the mine, it was decided to promote an integrated rehabilitation program in Lousal, encompassing several complementary features, aiming to rehabilitate the village in environmental, economic and social terms. Emphasis has been given to the cultural and scientific aspects, but the touristic potential of the whole project was strongly valued as well. The name of the program - RELOUSAL - stands for REvitalization, REnewing, Rcovery and REnhabilitation of the Lousal village. The program required a solid institutional framework, which catalyzed the joint efforts of the mine owner - the SAPEC corporation - with the local authorities - the Municipality of Grândola -, leading to the creation of the Frédéric Velge Foundation. Several facilities have been created in the framework of RELOUSAL, aimed at adding value to the Lousal mining heritage via reuse of the industrial complex, equipment and objects of the old mine.

The positive impacts of the program in terms of socioeconomic regeneration of the local community have been notable. Since 1996, the RELOUSAL program has supported a number of different activities and projects of different nature, including partial re-accommodation of the resident population, professional training for the examiners and their families, promotion of handicraft activities and family-scale manufactories, public-awareness equipment, a handicraft centre (1999), a restaurant in the main storehouse of the mine ("Armazém Central", 2000), patrimonial valorization, soil decontamination, reforestation and a visitor welcoming centre (2001). In 2003, a local technical office of the Grândola Municipality was installed in Lousal, and, in 2005, a charming hotel located in the ancient house of the mine administration was inaugurated (Sta. Bárbara Lodge).

The Urban Plan for the village was formally ratified in 2007, fuelling the requalification of the urban space, the marketing of touristic projects and the internationalization of the whole initiative.

A rehabilitation plan directed to reclaim the Lousal contaminated area was defined by EDM (Empresa de Desenvolvimento Mineiro). Due to the RELOUSAL program, the strategy adopted by EDM to the Lousal area aimed to preserve as much as possible the memory of the mining activities, with significant protection of the mining landscape, essential to the development of mining heritage projects (Matos et al. 2008). Their intervention was delineated to confine within the impacted perimeter the environmental aggressions identified, and sort them out without obliterating from the landscape the visual impressions left by almost a century of mining. The contamination sources at this area were assessed and a variety of combined interventions have been implemented.

One of the first big projects that have been completed under the scope of the RELOUSAL program was the mining museum. The project was promoted by the Frédéric Velge Foundation, and developed between 1998 and 2001 with the technical support of APAI, the Portuguese Association for Industrial Archaeology. This industrial museum was installed in a large building formerly hosting the electrical plant of the mine ("Central Eléctrica"). The installation accommodates several rehabilitated equipment that possess valuable significance from an industrial archaeological standpoint. Among the pieces contained therein standout a number of huge electrical alternators and air-compressors that closely follow the major steps of the evolution of the mining exploitation methods through time (Tinoco et al. 2002). The museum has multiple focal points, including an exhibition, inaugurated in 2006, of over fifty scale-models made of wood and metal that perfectly represent machines and devices used for mining exploitation during the 19th century.

The Mine of Science - "Ciência Viva" Centre of Lousal was inaugurated in 2010. It was set up in two buildings that were associated with the past activity of the mine (geology office, lanterns room, miners' locker room and bathhouse). The exhibition strategy was conceived for a large-spectrum audience in terms of age, education and social or geographic origin. The general idea consists of taking advantage of the old mine environment to use the concept of "georesource" as a window opened through a wide range of fields of knowledge that include the natural and exact sciences, applied technologies and several fields of engineering. In the Mine of Science, one exploits science and extracts knowledge, always with interactivity at the fingertips. There, the visitors may discover some of the most fascinating phenomena of the world of science and technology, through tens of interactive experiences and "hands-on" exhibits. The Centre is extremely dynamic and promotes also many educational activities that go far beyond the walls of the building: guided visits to the open-pit, geo- and bio-field trips, astronomy observations, scientific camping, among many others.

In four years, more than sixty seven thousand people, including scholar groups, families and tourists, have visited this Science Centre, and many other persons visited or benefited from the remaining components of the RELOUSAL program. Lousal also receive frequent visits from under- and post-graduate students, professors and researchers, both from Portuguese and foreign universities, mostly interested in ore geology, mining engineering, environmental sciences and sociology.

4 The future

The above circumstances completely changed the daily life scenario in Lousal. The dynamic activity of the "Ciência Viva" team brought a new reality to the village, pushed forward new economic activities, justified new job opportunities for the local population, and for the youth in particular, and opened a new cycle in the revitalization program initiated more than two decades ago.

The rehabilitation of Lousal is an on-going process that has already reached a point that allows one to look at the future with justified expectations. An important evidence for this is the recent recognition made to the Municipality of Grândola by PROGEO, which have attributed the 2013 Geconservation Award to the Lousal mining village for its rehabilitation program and consistent defense of its mining patrimonial heritage. Moreover, in 2014, the program was awarded with a
“Social Entrepreneurship Award”. The steps forward that have been pursued so far have put together, in a consolidated way, a number of relevant partners with different, but complementary and compatible motivations. The key words for the future are now consolidation, step-by-step development and economic sustainability. Sooner or later, Lousal should pass from a mining village under a rehabilitation program, to a territory able to attract investments and where better economic opportunities may emerge.

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and Finch 1989; Levay et al. 2006; Somot et al. 2012) is order to decrease volume management and treatment (Rao 2013; Wang and Peng 2014) and recirculated water in Peng and Zhao. 2012; Drelich and Miller 2012; Ozdemir al. 2001; Castro et al. 2012 a and b; Alexander et al. 2012; concept of using locally available saline water (Hancer et al. 2006; Hawkins and Smoyer 2011; EEA 2012). The part of the NI 43-101 and JORC Codes technical reports). The tightening of environmental regulations, the question of the sustainable management of water is raised earlier least through sedimentation in tailings/sludge ponds. With groundwater or even tap water) are generally deviated towards the mining site (concentrator). These have to be targeted deliverables for sustainable mining: (1) an effective management of process water and of residual process waters management. This allowed reaching two simple but reliable analytical method for starch separation processes, as well as for pelletizing. More specifically, this abstract underlines how the use of a R&D approach in green mining initiatives, based on real case study investigations. Starch was selected as an concern. The aim of this extended abstract is to expose a waters, following the legal guidelines of the country of included through the management of mine and process feasibility studies are initiat ed, sustainable mining is explored.

This global context leads to a dynamics of mine water Large volumes of fresh waters (i.e., from rivers, lakes, industrial minerals and iron ores. We focus here on iron ores Starches are widely used in the mineral processing of ores 2  Use of starch for inverse flotation of iron (i.e., while floating gangue depress iron values during the commonly practiced selectively flocculate iron at a pre-concentration stage the environment (US EPA 2004). Starches are used to recover ultrafines for pelletizing. However, starch has to be caustified prior to use. The use according to the collector chemistry. Caustic soda properties of value and gangue minerals as well as additions, varying according to the relative surface of starch also often involves the adjustment of the however, the use of starch is not new (Read and Manser 1975) but is still poorly encouraged through the literature review (Jones and Woodcock 1984; Hao et al. 2008; Greet et al. 2010) that dosage of reagents was also shown to be highly sensitive to water quality in flotation of Gehr et al. 1989). The dosage of reagents was also shown to be unacceptable performance losses (Rao and Finch 1989; 10% was fresh water and 8% of it was discharged back to approximately 650 billion of gallons used in 1984, about iron ore facilities in the US (US EPA 2004). From 1989: direct flotation of sparingly soluble ores was shown to be the reverse flotation of low-grade oxide ores or during the exploited.

Starch was one of the first reagents used in flotation, according to the collector chemistry. Caustic soda was also used in the flotation process. However, the use of starch is not new (Read and Manser 1975) but is still poorly encouraged through the literature review (Jones and Woodcock 1984; Hao et al. 2008; Greet et al. 2010) that dosage of reagents was also shown to be highly sensitive to water quality in flotation of Gehr et al. 1989). The dosage of reagents was also shown to be unacceptable performance losses (Rao and Finch 1989; 10% was fresh water and 8% of it was discharged back to approximately 650 billion of gallons used in 1984, about iron ore facilities in the US (US EPA 2004). From 1989: direct flotation of sparingly soluble ores was shown to be the reverse flotation of low-grade oxide ores or during the exploited.
An Approach in Water Management for Sustainable Mining: Residual Reagents Concentrations Optimisation in Recirculated Process Waters

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Abstract. As soon as ore deposit exploitation pre-feasibility studies are initiated, sustainable mining is included through the management of mine and process waters, following the legal guidelines of the country of concern. The aim of this extended abstract is to expose a R&D approach in green mining initiatives, based on real case study investigations. Starch was selected as an example since it is a reagent widely used in iron ore beneficiation, during the flotation and flocculation separation processes, as well as for pelleting. More specifically, this abstract underlines how the use of a simple but reliable analytical method for starch quantification was applied at the pilot-plant scale to process waters management. This allowed reaching two targeted deliverables for sustainable mining: (1) an effective management of process water and of residual reagents recirculation without impairing flotation performance and (2) survey for residual starch in tailings waters, which would become part of the concentrator effluents.

Keywords. Sustainable mining, residual reagents, process water, starch analysis, iron ore flotation

1 Introduction

A n important factor in the concept of sustainable mining is the management of local waters available on-site (Levay et al. 2006; Dunne 2012; Connelly 2012), in terms of volumes and flows used for ore processing as well as in terms of quality to reach acceptable mineral processing performances (Brown 2003; Johnson 2003; Drelich 2012).

Large volumes of fresh waters (i.e., from rivers, lakes, groundwater or even tap water) are generally deviated towards the mining site (concentrator). These have to be treated before being released back to the environment, at least through sedimentation in tailings/sludge ponds. With the tightening of environmental regulations, the question of the sustainable management of water is raised earlier and more concretely while mining projects go from the exploration stage to the exploitation one (e.g., the environmental impact studies systematically required as part of the NI 43-101 and JORC Codes technical reports).

This global context leads to a dynamics of mine water valorisation (Merritt and McIntosh 2006; Ringwood 2006; Hawkins and S moyer 2011; EEA 2012). The concept of using locally available saline water (Hancer et al. 2001; Castro et al. 2012 a and b; Alexand er et al. 2012; Peng and Zhao. 2012; Drelich and Mil ler 2012; Ozbekemir 2013; Wang and Peng 2014) and recirculated water in order to decrease volume management and treatment (Rao and Finch 1989; Levay et al. 2006; Somot et al. 2012) is not new (Read and Manser 1975) but is still poorly exploited.

In particular, the recirculation of process water during the reverse flotation of low-grade oxide ores or during the direct flotation of sparingly soluble ores was shown to be difficult so far: negative interactions between flotation reagents, process waters and/or mineral surfaces may lead to unacceptable performance losses (Rao and Finch 1989; Gehr et al. 1989). The dosage of reagents was also shown to be highly sensitive to water quality in flotation of industrial minerals and Nb-oxides (Pawlik and Smoyer 2003; Rao and Finch 1989). It was speculated, and then encouraged through the literature review (Jones and Woodcock 1984; Hao et al. 2008; Greet et al. 2010) that the development of easy to use but reliable reagent analytical methods could allow (1) effectively designing recirculated flows, (2) controlling residual reagents as a mean to check sorption performance during mineral processing (dosage and addition points) and (3) minimising and surveying residual concentrations at the effluents, serving both the industry and the environment.

We present here the concept through the example of starch flow management and survey, which was validated at pilot-plant scale.

2 Use of starch for inverse flotation of iron ores

Starches are widely used in the mineral processing of industrial minerals and iron ores. We focus here on iron ore flotation. Process water is recirculated at 90%-95% by iron ore facilities in the US (US EPA 2004). From approximately 650 billion of gallons used in 1984, about 10% was fresh water and 8% of it was discharged back to the environment (US EPA 2004). Starches are used to selectively flocculate iron at a pre-concentration stage (Houot 1983; Iwasaki 1983; Mathur et al. 2000), to depress iron values during the commonly practiced inverse flotation of iron (i.e., while floating gangue minerals) (Houot 1983; Iwasaki 1983; Ravishankar et al. 1995; Araujo et al. 2005), sometimes to improve agglomeration in pelleting stages (Haas et al. 1989; Halt et al. 2014) and finally, to clarify process water and to recover ultrafines for pelleting.

Natural starches are considered to be non-toxic. However, starch has to be caustified prior to use. The use of starch also often involves the adjustment of the flotation pH, generally at pH =10.5 through acid/base additions, varying according to the relative surface properties of value and gangue minerals as well as according to the collector chemistry. Caustic soda
represents a major cost for the mineral processing operation and thus, the industry is willing to minimise its consumption: recirculating process water is one way to reach such a target.

3 Process water sampling and analysis

3.1 Sampling points strategies

The circuit studied at the pilot-scale was a typical column flotation circuit. Process stages succession was resembling the one illustrated below (Fig. 1).

![Schematic flowsheet of a reverse flotation circuit for an iron ore used at pilot-scale.](image)

**Figure 1.** Schematic flowsheet of a reverse flotation circuit for an iron ore used at pilot-scale. It is considered a typical one to serve the concept of residual reagents concentrations optimisation and survey in recirculated process waters: starch (and other reagents) concentrations are optimized, according to records at the monitoring points.

Moreover, in case of difficulty to reach targeted iron recovery and grade at the final product, the methodology could be used to diagnose process issues by collecting complementary process waters.

Finally, effluent could be monitored over time to state the starch decay rate to be expected in sedimentation basins. Starch is not considered a toxic reagent but its biodegradation consumes oxygen and may lead to unacceptable levels of turbidity for water release to receiving natural water streams.

3.2 Analytical procedure

Dewatering of process waters was conducted by filtration on standard industrial membranes (ca. 22 μm pore-size). Special attention was given to the pore-size of microfiltration membranes in order (1) to remove spectral interferers between solids and the light beam and (2) to avoid losing some starch during this preparation step. Water was filtrated on 6 μm micro-filtration membrane prior to starch analysis. Lower pore size microfiltration led to the loss of a fraction of the starch. The turbidity of the micro-filtrated process water was checked by a light transmittance method to ensure minimum interferers.

In order to stabilize the circuit during the pilot-scale adjustment, residual starch was collected from the rougher feed, from the rougher and scavenger iron-rich tailings - these both being the flocculated value-rich final products - and from the silica tailings, which in the case of reverse flotation is actually a froth concentrate of gangue minerals. Water flows are indicated in grey on Figure 1. Dewatered iron-rich products are indicated by the black-filled side of the liquid-solid separation process symbol, while the gangue-rich product is represented by the white-filled side.

A colorimetric method in the presence of molecular iodine (I₂) was used to quantify stachs (namely, its amylose) and its derivative, dextrin (adapted from Badenhuizen and Chandorkar 1964). The method was adapted to test conditions (maize and wheat starches), calibrated and its reliability was validated using the "known addition" method.

4 Results and discussion

During the pilot-scale operation, as expected, residual starch was recovered mostly from the iron-rich pulp. Knowing how much was recovered by recirculating process water flows, the circuit could be stabilised efficiently and quickly.

The effluent flow was reduced significantly by recirculating process water recovered by dewatering. Flotation performances were not affected by recirculation and results over 95% recovery with a grade of silica below 1.5% were achieved. In practice, all "mineral waters" (i.e., as opposed to "organic waste and sanitary waters") collected on-site would be sedimented in thickeners/clarifiers in order to collect back iron-rich ultrafines for pelletizing. This water includes the equivalent to process.
waters described in Figure 1 and excess process water from the primary stages of ore concentration (the comminution, pre-concentration stages, froth wash waters and dust abatement water were excluded from Figure 1, for simplicity purposes). A thickening aid (starch, eventually) may be added at this stage. Thus, in real-life operations, such a control of residual starch concentration in the thickener overflow is important as well. At the same time, it may help adjusting the thicker operation conditions when the process efficiency is impaired (e.g., over seasons or during process design changes).

These results are in agreement with previous ones in that, the development of simple, dedicated, cost effective and reliable analytical methods for mineral processing circuits control and optimisation (Gelinias et al. 2005; 2007; Zangooi et al. 2010; Zhang et al. 2013) are welcome on several points of view:

- The basis of classical quantitative sorption studies, here under complex pluminerals systems, as long as analytical interferences can be avoided and analytical results reliability kept demonstrated
- Optimisation of the circuit
- Stabilisation of the circuit in recirculated water
- Lowering the consumption of reagents
- Control of discharge levels to the environment
- Cost effective tool for reagents biodegradability tests by reagents suppliers

5 Conclusion

An improvement, both for mineral processing operations and for the environment resulted from the application of simple but reliable analytical methods applied on-line. This allowed operators to check residual starch concentrations in process water. Several advantages for both the industry and the environment are:

- Lower fresh water use by recirculating process water flows without impairing flotation performances
- Lower reagents consumption, and thus, lower release to the environment, by optimising the dosage while processing
- Lower volumes of effluents to be treated and managed prior to release to the environment

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SYMPOSIUM A
Metallogeny of North and West Africa

Convenors
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Cu-Pb-Zn-Au-Ag; Pb-Ag and Mo Mineralizations South of the Imiter Mine (Precambrian Saghro Massif, Eastern Anti-Atlas, Morocco): Geodynamic and Metallogenic Implications

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Abstract. The study area is located at the south-Eastern of the silver Imiter mine and north-Eastern of the gold Tiouit mine, on the northwest flank of Jbel Saghro (eastern Anti-Atlas). This area is characterized by the outcrop of a Cryogenian basement (Saghro Group (PII)) which consists essentially of regular alternation of low metamorphic sandstone and shale levels, intruded by calc-alkaline granitoids. Detailed mapping allows to identify several occurrences and precious metals, base metals and molybdenum deposits. Preliminary studies show a wide diversity of petrographic facies composed mainly of two plutons and three types of mineralizations: the Bou- Teglimt massif to which N45°oriented, Pb-Zn-Cu-Au-Ag mineralized structures are associated, a new biotite granite, which is crosscutted by E-W quartz-molybdenum veins, and Pb-Ag mineralized structures hosted by the Cryogenian basement. Field observations and preliminary metallographic studies of two types of polymetallic structures, allow to link Pb-Zn-Cu-Au-Ag mineralizations to the gold Tiouit mine and Pb-Ag mineralization to that of the Imiter silver mine. The aim of this study is therefore to characterize the molybdenum mineralization from mapping, petrographic, mineralogical and geochemical a point of view and the hosted granite, recently discovered in the region, and to integrate these features in the geodynamic context of the Imiter inlier.

Keywords. Molybdenum, quartz vein, granitoids, Cryogenian, Imiter, Saghro, Anti-Atlas

1 Introduction

The Imiter inlier is located on the northern side of the Saghro massif, which constitutes, with the other Proterozoic inliers (Ifni, Kerdous, Akka, Bou Azzer, Sirwa and Ougnat) the Anti-Atlas orogenic belt of Morocco bordering the north side of the western African craton (Clauer 1974; Ennih and Liegeois 2001; Fekkak et al. 2001). It is known by its famous silver epithermal deposit and the Porphyry type Tiouit Au-Ag-Cu (Fig 1). The new molybdenum mineralization recently discovered in this region would be a new contribution to a regional metallogenic and geodynamic features of the Imiter inlier. The aim of this study is to characterize the molybdenum mineralization from mapping, petrographic, mineralogical and geochemical a point of view and the hosted granite, recently discovered in the region, and to integrate this in the geodynamic context of the Imiter inlier.

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2 Geological setting

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This area is characterized by the outcrop of a Cryogenian basement (Saghro Group (PII)) which consists essentially of regular alternation of low metamorphic sandstone and shale levels, intruded by calc-alkaline granitoids.

3 Petrographic description

Field observations show the diversity of petrographic facies in the study area. Two main plutonic rocks were distinguished: the Bou Teglimt massif which is composed of quartz, biotite, plagioclase, amphibole and accessory minerals (zircon, apatite). The second pluton called biotite granite is discovered for the first time, and is crossed by E-W quartz-molybdenum veins. It is composed chiefly of quartz, plagioclases, biotite, K-feldspaths (especially microcline) and a minor amount of zircon and apatite (Fig. 2).

4 Ore mineralizations

Preliminary studies show a wide diversity of mineralized structures. We have observed three types of mineralizations.

4.1 Pb-Zn-Cu-Au-Ag structures

The Pb-Zn-Cu-Au-Ag vein structures hosted by Bou Teglimt granodiorite are oriented N-S and N 45°. They are consisted by: arsenopyrite, chalcopyrite, sphalerite, grey copper, quartz, hematite, covellite (Fig. 3 A and B).

4.2 Mo structures

The N 90° trending Mo-quartz veins are hosted by biotite granite. They are composed mainly of quartz and molybdenite (Fig. 3 C).

4.3 Pb-Ag structures

The N 45° trending Pb -Ag mineralized structures are hosted by the Cryogenian basement (PII). They are composed of argentiferous galena and quartz (Fig. 3 D).

5 Perspectives

In light of these preliminary results of the petrographic and mineralogical study obtained, it is carried out:

- Firstly, a semi-quantitative chemical analyses point using the scanning electron microscopy (SEM) to confirm and discover other mineral phases existing at the ore deposit.
- Secondly, to perform geochemical and geochronological analyses for granitoid rocks in order to project it within the regional geodynamic setting.
- At the end, to characterize the molybdenum mineralization and the hosted granite, and to integrate this in the geodynamic context of the Imiter inlier.

Figure 3. Mineralized structures. A. Chalcopyrite associated with grey copper within siliceous gangue; B. Quartz was corroded by chalcopyrite, galena and sphalerite assemblages; C. molybdenite flake within quartz gangue; D. galena contains quartz inclusions.

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Tectonic Evolution of the Gaoua Region, Burkina Faso: Implications for the Mineralization

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Abstract. The interpretation of high-resolution airborne geophysical data integrated with field structural and lithological observations were employed in the creation of a litho-structural framework for the Gaoua region, Burkina Faso. The Paleoproterozoic granite-greenstone terrain was affected by multiple deformation and mineralization events. The early tectonic phase is characterized by emplacement of voluminous tholeiitic and calc-alkaline lavas, probably in a volcanic arc setting. The copper mineralization is concentrated in a diorite / andesite breccia, and is interpreted as an early-stage porphyry style deposit. Evidence of the first deformation event D1Ga, corresponding to N-S shortening, was only found in the E-W trending mafic unit bordering the Gaoua batholith to the south. A second deformation phase D2Ga lead to a development of metamorphic foliation and its subsequent folding under an overall E-W compression. At later stages, the D2Ga switched to a transient regime characterized by intense N-S to NW-trending steeply dipping shear zones. The first significant gold mineralization event is related to this transient tectonic phase. During subsequent D3Ga, an intense network of brittle to brittle-ductile NW and NE faults developed. Economic gold concentrations are attributed to the D3Ga event and are associated with the remobilization of early, disseminated low-grade gold concentrations.

Keywords. West African Craton; Burkina Faso; Paleoproterozoic; Tectonics; Porphyry copper deposit; Orogenic gold deposit

1 Introduction and geological setting

Precambrian granite-greenstone terrains of southern West African Craton (SWAC) host many gold and base-metal deposits (Markwitz et al. submitted; Milési et al. 1989, 1992; Schwartz 2008). While gold deposits were extensively studied in the past (e.g., Allibone et al. 2002; Béziat et al. 2008; Bourges et al. 1998; Kadio et al. 2010; Klemd and Ott 1997; McFarlane et al. 2011; Milési et al. 1989; Tshibubudze and Hein 2013) only limited information exists on copper deposits in West Africa (Bouladon et al. 1973; Marcellin 1971; Milési and Feybesse 1993; Ouedraogo 1991; Schwartz 2008; Sillitoe 1979). Unraveling the structural context of a metal deposit is a key to understanding the whole mineral system, in particular for deposits affected by multiple deformation and hydrothermal events.

The Boromo belt, where the Gaoua deposit is located, hosts several metal deposits including zinc at Perkoa (Napon 1998; Schwartz and Melcher 2003) and gold at Poura – Laraffella area (Bamba et al. 1997; Béziat et al. 2008; Lompo 1991; Milési et al. 1992) and Batli west. The N-S trending Boromo greenstone belt is composed of mafic and intermediate volcanics at the flanks and intermediate volcano-sedimentary and sedimentary units in the central zone. The study area is located at the western margin of the Boromo belt, at the southern extremity of the Gaoua batholith. The stratigraphic sequence of the study area is starting with 4 to 6 km thick sequence of tholeiitic mafic rocks followed by more intermediate calc-alkaline intrusive, effusive and eruptive members such as diorites, andesites, dacites, rhyolites and a large range of pyroclastic flows, tuffs, and interstratified volcano-sedimentary members (Naba 2010; Wemmenga and Affaton 2003). The uppermost unit consists of volcano-sediments and fine grained sediments. All volcanic rocks in the Boromo belt were affected by regional metamorphism reaching greenschist to amphibolite facies conditions.

A rhyolite included in the Boromo calc-alkaline volcanic sequence was dated at 2171±7 Ma (U-Pb on zircon; Castaing et al. 2003). A diorite and a gabbro from Gongondy were dated at 2185.3 ± 12 M a and 2171.6 ± 9.3 M a, respectively (U-Pb on zircon; Browncombe 2009). A volcaniclastic rock N of Bati was dated at 2170 ± 9 M a and the granitoids truncating the Boromo belt S of Gaoua range in age between 2168 ± 10 M a and 2149 ± 12 M a (U-Pb on zircon; Parra et al. submitted). The granitoids east and west of the Boromo belt yield ages between 2175±1 M a and 2104±1 M a (U-Pb on zircon; Agyei Duodu et al. 2009; Castaing et al. 2003; Davis in Schwartz and Melcher 2003; de Kock et al. 2011).

The Gaoua region in south-west Burkina Faso is a multi-commodity copper and gold deposit, which was formed during a polyphase tectonic history during the Eburnean orogeny (ca 2.15 – 2.1 Ga). The major copper and gold mineralized body is located between Mt Biri and the Dienerema and Gongondy villages; however, several gold-only deposits have been found in the same
area (Nassara, Gomblora, Batié West, and Kampti). This leads to the question as to whether the copper and gold mineralization were contemporaneous and to which structures and deformation events they are related.

2 Structural evolution

Four deformation phases related to the Eburnean orogeny can be distinguished in the study area. The first metamorphic phase D1GA can only be identified in the mafic rocks limiting the Gaoua batholith to the south. The magnetic anisotropy susceptibility measurements indicate E-W trending magnetic foliation dipping to the south at variable dips (Fig. 1), supporting the map observation of E-W oriented layers of intercalated high and low magnetic massive undeformed basalts and andesites. The E-W units appear to turn around the Gaoua batholith. Outcrop scale foliation or other deformation features corresponding to the D1GA deformation event were not found in the massive mafic volcanics.

The second deformation phase D2GA resulted in penetrative metamorphic fabric of variable intensity and overall N-S orientation (Fig. 1). A penetrative metamorphic foliation S2GA defined by chlorite and actinolite is best developed in fine-grained tuffs and volcano-sediments. The N-S strongly elongate form of units of alternating magnetic and non-magnetic basalts, gabbros and andesites at the western margin of Boromo belt suggests the presence of rootless isoclinal folds. The curved shape of the E-W oriented mafic units south of Gaoua batholith is interpreted as an open fold related to the D2GA deformation.

N-S oriented steeply dipping shear zones are typical for the later stages of the D2GA (Fig. 1). They may be locally oriented NW (Nassara) or NE (N of Dienemera). The mafic and intermediate rocks of the Mt Biri - Dienemera - Gongondy area are affected by a large-scale C-C' sigmoidal shear band defined by N-S sinistral and NE-dextral shear zones. Andesite / diorite breccia bearing the copper mineralization are affected by the S2GA shear zones, which implies that hydrothermal brecciation occurred before the onset of D2GA. South of the Gaoua batholith, the domain with E-W oriented structural pattern is bounded by NW- and N-S trending S2GA shear zones from the west and east, respectively.

The third deformation D3GA marks a transition from ductile to brittle deformation. NW and NE-trending normal faults and fractures, affecting the pre-existing fabrics, are abundant particularly in the eastern part of the study area (Fig. 1). Brittle faults in the zone south of Gaoua have more variable orientation due to spatial accommodation related to folding of the mafic units at the southern limit of the Gaoua batholith.

The last deformation event D4GA is characterized by an E-W trending S4GA spaced cleavage, crenulation cleavage, and chevron or kink folds. The cleavage and fold axial planes are in general steeply dipping and cross-cut the S2GA and S3GA fabrics at a high angle.

Figure 1. (a) Structural map showing field and ASM measurements. The map was realized using the method described in Metelka et al. (2011). Blue and green colour: mafic and intermediate volcanic rocks, yellow and light green: volcano-sediments and sediments, pink: granitoids. (b) Lower hemisphere equal-area stereoplots of field structural measurements. Measurements of Anisotropy of Magnetic Susceptibility are plotted for the D1GA as there is only one field measurement corresponding to this deformation phase.

3 Mineralization events within the structural framework

3.1 Copper mineralization

The copper mineralization in Gongondy, Dienemera and Mt Biri is concentrated in a diorite / andesite breccia. The brecciation and mineralization are contemporaneous or shortly follow emplacement of the diorite / andesite and precede the D2GA deformation phase. The relationship between the D1GA and mineralization could not be constrained. Cu-mineralization occurs in the form of chalcopyrite associated with a first generation of pyrite, anhydrite, carbonate and quartz, which infill cavities within the breccia or form related vein networks.

In the vicinity of Cu-mineralized breccia, the diorite is altered to various extents, with local enrichments in
pyrite ± carbonate, forming a zone known as the “pyrite front”. Brecciated diorite / andesite is locally affected by N-S oriented S2 Ga shear zones which caused further crushing of the breccia, leaching of anhydrite and carbonate, and closure of all open space. Detailed mineral assemblages, mineral chemistry, and Re-Os dating of pyrite (isochron age of 2161 ± 23 Ma) can be found in Le Mignot et al. (submitted).

3.1 Gold mineralization

Gold is associated with N-S and locally NE- and NW-oriented steeply-dipping S2 Ga shear zones (Fig. 2). In the field, these structures are characterized by strong carbonation, chloritization and sericitization, accompanied by intense quartz veining. Gold occurs as disseminated grains in these shear-zones, associated with second-generation pyrite.

A last generation of gold occurs in an intense network of brittle to brittle-ductile NW and NE steeply-dipping faults related to D3 Ga, which are rich in chlorite and locally carbonate and quartz. This deformation event caused crushing of pre-existing pyrites and remobilization of first-generation disseminated gold. This mineralization event is the richest of the Gaoua deposit. Similar gold mineralization occurs in the nearby Nassara deposit.

Gold was essentially transported by hydrothermal fluids under greenschist facies conditions during D2 Ga transcurrent ductile deformation. Disseminated low-grade gold concentrations are discordant with the copper-rich zones, transecting them at several places. This is further evidence that the two mineralization events are not related to each other. Based on the relative chronology it can be interpreted that the first gold mineralization occurs around or after ~2150 Ma, which is the youngest age of the N-S oriented granulite suite affected by D2 Ga deformation (Parra et al. submitted), which is intruding the Boromo greenstone belt.

Remobilization and economic concentration of gold is associated with the D3 Ga deformation event, of brittle to brittle-ductile character. The last phases of NE dextral shearing (equivalent of D2 Ga) were interpreted as young as 2081 ± 1 Ma in Ivory Coast (U-Pb on zircon; Delor et al. 1992) and 2088 ± 1 Ma in Ghana (U-Pb on zircon; Hirdes et al. 1992; Jessell et al. 2012). The D3 Ga deformation phase must therefore predate it. No mineralization is associated with the D4 Ga event. Orogenic gold related to late shear zones is very common in West Africa (e.g., Allibone et al. 2002; Béziat et al. 2008; Bourges et al. 1998; Klemd and Ott 1997; Milesi et al. 1992).

The structural patterns show that most of the lithological units were affected by ductile deformation in a regime of E-W shortening. Consequently, the rock units are no longer in their original structural position, which must be kept in mind when establishing the geometrical configuration of the porphyry copper deposit. Deformation and metamorphism typically obscure the primary features in most Precambrian porphyry copper deposits (Laznicka 2006).

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Seismic Velocities, Anisotropy, and Shear Wave Splitting of Antigorite (Ait Ahmane Serpentinites, Bou Azzer Inlier, Morocco)

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Abstract. Serpentization is an important process that influences the seismic and mechanical properties in subduction zones. We report here electron backscatter diffraction (EBSD) measurements of antigorite crystal preferred orientations (CPOs) in samples of antigorite schist from serpentinite of the Ait Ahmane sector in the Bou Azzer inlier of the central Anti Atlas. In this study, the (CPOs) and seismic anisotropy of natural serpentinite from the Ait Ahmane fault zone are studied. It is found that the [001] axes are aligned subnormal to the foliation but the [010] axes of the serpentine are subparallel to the lineation, which is significantly different from that produced in a recent high pressure experimental study. Seismic anisotropy increases with the antigorite volume fraction. The seismic anisotropy of shear waves is large. The sample having the lowest serpentine content (30%) shows the lowest P- and S-wave anisotropy (VP=7.2% and AVS=6.55%), and the sample with the highest serpentine content (85%) shows the highest P-wave and S-wave anisotropy (VP=8.6% and AVS=11.06%). Effects of the degree of serpentization and composition on seismic anisotropy are shown in equal area and lower hemisphere projections.

Keywords. Serpentization, electron backscatter diffraction, Crystal preferred orientation, seismic anisotropy.

1 Introduction and analytical methods

Serpentinite samples having different amounts of antigorite serpentine were studied. Antigorite lattice preferred orientations were measured on the rock sample from which the single crystal was extracted for elasticity measurements using the electron back-scattering diffraction (EBSD) technique. The mineral phases present in the specimen mainly comprise serpentine (antigorite) with a small amount of magnetite. Sample AABH9 contains the lowest serpentine content (30%), sample AABH4 has the highest serpentine content (85%). The foliation of each sample was determined from the compositional layering and elongation of serpentine, where as the lineation was determined from the elongation of serpentine and diopside by performing a grain shape analysis of digitized lines in a plane (Panozzo 1984). The samples were cut parallel to the lineation (x) and perpendicular to the foliation (z) for microstructure analysis. The CPO of antigorite was measured by performing (EBSD) (Jung et al. 2006). The EBSD patterns were measured on an JEOL 6380 SEM at the School of Earth and Environmental Sciences at Seoul National University, and the resulting patterns were analyzed using HKL Channel 5 software. An accelerating voltage of 30 kV at a working distance of 15 mm was employed for the SEM. At each point, the EBSD pattern was indexed manually to ensure an accurate solution. The CPOs of the serpentine are measured for individual grains (n=564–642). Seismic velocity and seismic anisotropy were calculated from the orientation data of the serpentine (antigorite) using the elastic constants of antigorite (Bezacier et al. 2010) and a software program (Miniprice 1990). Minor phases such as diopside and magnetite were ignored in the calculation of seismic anisotropy.

2 Result

2.1 Crystal preferred orientation (CPO) of antigorite

The CPO of antigorite is shown in pole figures (Fig. 1). CPOs of antigorite in sample AABH9 and AABH4 are different. The serpentine [001] axis is strongly aligned subnormal to the foliation; whereas the [010] axis is strongly aligned subparallel to the lineation (x). This pattern of CPO is significantly different from the CPOs of the serpentines produced in experimentally deformed antigorite (Katayama et al. 2009), for which the [100] axis is strongly aligned subparallel to the lineation. The CPO of the serpentines in sample AABH4, which contains the highest proportion of magnetite, is different from that of sample AABH9, indicating that the CPO of the serpentines in sample AABH4 was probably affected by the presence of large amounts of magnetite.

2.2 Inverse pole figure of antigorite

To infer the dominant slip system that causes the natural deformation in antigorite serpentines, inverse pole figures were drawn, as shown in Fig. 2 (right panel). The sample AABH9 shows that the serpentine [001] axis is aligned normal to the foliation and the [010] axis is aligned subparallel to the lineation, indicating that the dominant slip system of antigorite is (001) [010]. Sample AABH4
shows that the serpentine [001] axis is aligned normal to the foliation, but both the [100] and [010] axes are subparallel to the lineation, indicating a mixed slip system of (001) [010] and (001) [100].

2.3 Seismic velocity and anisotropy of antigorite

The seismic anisotropy of the P- and S-waves was calculated from the CPO of the serpentine. Figure 2 shows the seismic anisotropy in a horizontal flow. The seismic anisotropy in Fig. 3 is plotted in such a way that the center of the pole figure (z) corresponds to the direction normal to the horizontal plane (foliation) and the E-W direction corresponds to the flow direction (lineation, x). P-wave velocity is the fastest in the direction subparallel to lineation (x: flow direction). The P-wave velocity is slow near the center of the plot where the slowest serpentine [001] axis is aligned subnormal to foliation (Fig. 3). For all specimens, the polarization direction of the fast shear wave (Vs1) is oriented nearly normal to the flow direction (lineation, x) which is shown at the center of the pole figure for Vs1 polarization. The effect of the degree of serpen tinization on the magnitude of seismic anisotropy is also shown in Fig. 3. The sample having the lowest serpentine content (30%, sample AABH4) shows the lowest P- and S-wave anisotropy (Vp=7.2% and AVs=6.55%), the sample with the highest serpentine content (85%; AABH9) shows the highest P- and S-wave anisotropy (Vp=8.6% and AVs=11.06%). Seismic anisotropy produced by the CPO of the serpentine (30% in the sample) is more than three times higher than that produced by the CPO of the olivine alone. The magnitude of seismic anisotropy increases with increasing serpentine content in the specimens (Table-1). For sample AABH9 consisting of 85% serpentine, the seismic anisotropy of S-waves (AVs) is 11.6%. In this case, serpentine layers having a thickness of only ~13 to 26 km to explain the delay time of 1–2 s for shear wave splitting.

Table 1. Sample descriptions and results: (Ant: Antigorite, Mg: Magnetite).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>ABBH9</th>
<th>ABBH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ant (%)</td>
<td>85</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Mg (%)</td>
<td>8</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>CPO of Antigorite</td>
<td>001 F 010 L</td>
<td>001 F 010 L</td>
<td></td>
</tr>
<tr>
<td>Max. Vp (%)</td>
<td>8.6</td>
<td>11.06</td>
<td></td>
</tr>
<tr>
<td>Max. AVs (%)</td>
<td>7.2</td>
<td>6.55</td>
<td></td>
</tr>
</tbody>
</table>

3 Conclusion

Upward flow of deeply formed serpentinites and in situ hydration in the mantle wedge contribute to the accumulation of large bodies of serpentinite. In most subduction zones, the mantle wedge is likely to be infiltrated with water and undergo serpentinitization (Bostock et al. 2002; Christensen 2004; Kamiya and Kobayashi 2000; Tibi et al. 2008). The current study suggests that the serpentine CPO of the flow parallel [010] axis maximum can develop in the mantle wedge above subducting slabs (Figs. 2 and 4).
To understand the development of anisotropy within aggregates of antigorite, we measured the crystal preferred orientations (CPOs) of antigorite grains. The CPO of antigorite serpentine was studied in natural specimens from Ait Ahmane in central Anti Atlas. Strong CPOs of antigorite were observed. These are represented by the [010] axes aligned parallel to lineation and [001] axes aligned normal to foliation (Fig. 1), indicating that the serpentine was deformed by a dominant slip system of (001) [010]. The seismic anisotropy caused by the CPOs of antigorite has much broader implications for interpreting the trench-parallel seismic anisotropy in the cold mantle wedge than previously thought. For the vertical propagation of S-waves in horizontal shear, the polarization direction of the fast shear wave (Vs1) is oriented nearly perpendicular to the flow direction. Therefore, the CPOs of antigorite can be used to explain the seismic anisotropy in mantle wedges in many subduction zones, even though the serpentine is deformed at low angles from the surface such as by horizontal shear. It is also found that the magnitude of seismic anisotropy caused by the CPO of serpentine strongly depends on the degree of serpentinization and that the polarization anisotropy of the S-waves depends on the flow geometry in the subduction zone.

Acknowledgements

This study was supported by Manager Mining Company (SA) and the School of Earth and Environmental Sciences at Seoul National University.

References

Mainprice D (1990) A Fortran program to calculate seismic anisotropy from the lattice preferred orientation of minerals. Comput Geosci 16:385-393
the fluid flow path. mineralizing system, and water-rock interactions along mantle versus crustally derived fluids in the MVT Morocco (Fig. 1) in order to assess the contribution of Touissit-Bou Beker MVT district of northeastern hydrothermal fluids trapped in sulphides from the MVT s the helium isotopic compositions of present for the first time at the scale of North African Kendrick et al. 2002a, 2006). In the current study we crustally derived volatiles into the hydrothermal system as well as to assess the involvement of mantle and/or fluid-rock interaction(s) during fluid migration, as including MVT s, to further constrain fluid origin(s) and Noble gases in paleofluids are being increasingly used 1 Introduction mineralization, helium isotopes. basement-derived hydrothermal brines triggered depo-

Paleozoic basement. Mixing of Messinian seawater and basement-buffered dense brines stored within the water, which ultimately promoted the mobilization of older fluid convection of downward-flowing Messinian sea-

increased geothermal gradient initiated buoyancy-driven fluids. The associated elevated heat flow and subsequent component are in the range of ~3-8% in the mineralizing Estimated contributions of the mantle-derived (4He) crustal He components along the fluid flow path. reflect different degrees of mixing between mantle and paragenetic stage. The highly variable 3He/4He values overall lowering from 0.5 RA to <0.01 RA with advancing dolostones. The distribution of 3He/4He ratios shows an to massive replacements of medium- to coarse-grained sphalerite, and occurs as open-space fillings and partial mineralization consists principally of galena and Aalenian-Bajocian (Middle Jurassic) age. The sulphide hydrothermally dolomitized carbonate platform rocks of thick sequence of flat-lying, diagenetically and metal Zoning 3 Ore mineralogy, textures, paragenesis, regionally developed shale unit up to 100 m thick bearing silty limestone with intercalated ferruginous Zn mineralization and its formation significantly cement.

related, vug- and fracture-filling saddle dolomite diagenetic replacement dolomitization that formed 70 vol % of the dolostone; and (2) epigenetic, ore-

major ore deposits and their peripheries, fills open, D1, D2), having a spatial distribution restricted to the two types of dolomite led to the development of spaces created within replacement dolostone. Formation 2 Geological setting regionally extensive, pre-ore and metal Zoning 2012), specifically (1) regionally extensive, pre-ore alteration. Two major stages have been distinguished Dolomitization is the principal form of wall-rock alteration. Two major stages have been distinguished D1, D2), having a spatial distribution restricted to the two types of dolomite led to the development of spaces created within replacement dolostone. Formation 2 Geological setting regionally extensive, pre-ore and metal Zoning 2012), specifically (1) regionally extensive, pre-ore alteration. Two major stages have been distinguished Dolomitization is the principal form of wall-rock alteration. Two major stages have been distinguished
Helium Isotopic Constraints on the Genesis of the Touissit-Bou Beker Mississippi Valley-Type District of Northeastern Morocco

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Abstract. The Touissit-Bou Beker Mississippi Valley-type (MVT) district of northeastern Morocco and adjacent western Algeria represents the largest MVT district in North Africa. Economic orebodies are hosted by a 25-m-thick sequence of flat-lying, diagenetically and hydrothermally dolomitized carbonate platform rocks of Aalenian-Bajocian (Middle Jurassic) age. The sulphide mineralization consists principally of galena and sphalerite, and occurs as open-space fillings and partial to massive replacements of medium- to coarse-grained dolostones. The distribution of 3He/4He ratios shows an overall lowering from 0.5 RA to <0.01 RA with advancing paragenetic stage. The highly variable 3He/4He values reflect different degrees of mixing between mantle and crustal He components along the fluid flow path. Estimated contributions of the mantle-derived (4He) component are in the range of ~3-8% in the mineralizing fluids. The associated elevated heat flow and subsequent increased geothermal gradient initiated buoyancy-driven fluid convection of downward-flowing Messinian seawater, which ultimately promoted the mobilization of older basement-buffered dense brines stored within the Paleozoic basement. Mixing of Messinian seawater and basement-derived hydrothermal brines triggered deposition of Pb- and Zn-rich ores.

Keywords. Touissit-Bou Beker district, Morocco, MVT mineralization, helium isotopes.

1 Introduction

Noble gases in paleofluids are being increasingly used in studies of sediment-hosted hydrothermal deposits, including MVTs, to further constrain fluid origin(s) and fluid-rock interaction(s) during fluid migration, as well as to assess the involvement of mantle and/or crustally derived volatiles into the hydrothermal system (Kendrick et al. 2001; Ballentine and Burnard 2002; Kendrick et al. 2002a, 2006). In the current study we present for the first time at the scale of North African MVTs the helium isotopic compositions of hydrothermal fluids trapped in sulphides from the Touissit-Bou Beker MVT district of northeastern Morocco (Fig. 1) in order to assess the contribution of mantle versus crustally derived fluids in the MVT mineralizing system, and water-rock interactions along the fluid flow path.

2 Geological setting

The district stratigraphy consists of Paleozoic basement made of Ordovician pelitic schist locally intruded by Visean (347-331 Ma) rhyodacite overlain unconformably by a succession of unmetamorphosed Mesozoic-Cenozoic to Quaternary strata (Fig. 1). The unconformably overlying Mesozoic sequence consists of a thin unit of basal conglomerate and fine-grained limestone assigned to the Early Jurassic (Sinemurian-Carixian?) overlain by the Aalenian-Bajocian carbonate sequence. The Aalenian-Bajocian sediments consist of a succession of interbedded gray to brown, medium- to coarse-grained dolostones with interlayered thin (0.1 to 1 m) marl and clay layers. The 10- to 20-m-thick “Toit Jaune” unit, which constitutes the hanging wall rocks for the MVT mineralization, consists primarily of a succession of yellow sandstone and silty shale interlayered with argillaceous carbonate, which grade upward into a Bathonian (Middle Jurassic) condensed succession (<2 m) of clay-rich siltstone and ammonite-bearing silty limestone with intercalated ferruginous oolitic beds. Overlying the Bathonian marker is a regionally developed shale unit up to 100 m thick that forms the cap rock for Pb-Zn mineralization.

3 Ore mineralogy, textures, paragenesis, and metal Zoning

Dolomitization is the principal form of wall-rock alteration. Two major stages have been distinguished (Bouabdellah 1994; Abou tahir 1999; Bouabdellah et al. 2012), specifically (1) regionally extensive, pre-ore diagenetic replacement dolomitization that formed 70 vol % of the dolostone; and (2) epigenetic, ore-related, vug- and fracture-filling saddle dolomite cement.

The replacement dolomite (D1, D2) pre-dates the Pb-Zn mineralization and its formation significantly enhanced porosity and permeability of the precursor limestones. In contrast, ore-related dolomite (HD1, HD2, HD3), having a spatial distribution restricted to the major ore deposits and their peripheries, fills open spaces created within replacement dolostone. Formation of the two types of dolomite led to the development of
diagnostic structures and textures that are common in MVT deposits, such as saddle dolomite-cemented crackle, mosaic, and rubble breccias, rock-matrix ("trash") breccias, zebra dolomite, and snow-on-roof texture (Bouabdellah et al. 2012).

The sulphide mineralization consists principally of galena and sphalerite, and occurs as open-space fillings and metasomatic replacements of carbonate. Field observations, together with mineralogical and textural relationships, show that ore deposition occurred in three major stages, progressing from Zn-rich stage I to Pb-rich stage II, and finally to a late Pb-rich cuboctahedral stage III (Fig. 2). The transition from stage I to stage II mineralization is marked by the development of an intermediate Pb-Zn paragenesis in which co-genetic, fine-grained galena and sphalerite are intimately intergrown. Further evidence for the progressive evolution of the mineralizing fluid, from the Zn-rich to the Pb-rich ore stages, is shown by distinct metal zoning both vertically and laterally: a gradual decrease in Zn/Pb ratios occurs from east to west, and upward from ores hosted in the lower part to the uppermost part of the Aalenian-Bajocian dolostones, with Zn/Pb ratios approaching unity in the Bou Beker and Touissit deposits (Bouabdellah et al. 2012).

**Figure 1.** Geological map of Touissit-Bou Beker district (TBD) showing regional geology, major faults, distribution of ore-bearing dolostone, and associated MVT deposits (projected to surface). Regional geology simplified from Voirin (1965), Samson (1973), Owodenko (1976), and Valin and Rakus (1979). Red rectangle shows the position of the TBD. Inset shows the location of "la chaîne des Horsts" A tectonic belt, the eastern portion of which hosts the TBD.

**Figure 2.** Summary paragenetic sequence of pre-ore, main-stage, and post-ore minerals in the TBD. Abbreviations: Ang, anglesite; Azur, azurite; Cer, cerussite; Gn, galena; Gyp, gypsum; Mal, malachite; Pr, pyromorphite; Py, pyrite; Smith, smithsonite; Sp, sphalerite; Van, vanadinite; Wul, wulfenite.
4 Results

Helium isotopic compositions were determined at GFZ Potsdam, Germany, following the experimental protocol described by Niedermann et al. (1997). Seven pure sulphide separates spanning the main ore stages, of which one fine-grained sphalerite from the paragenetically earlier Zn-rich ore-stage (I), two galenas from the Pb-dominant main ore-stage (II), together with two sphalerite and two galena crystals from the later Pb-rich cuboctahedral stage (III), were analyzed for helium abundances and isotopic compositions. The measured He abundances and isotopic ratios are presented in Table 1 and plotted in Figure 3.

The $^{3}$He/$^{4}$He ratios show a wide range from completely radiogenic values of −0.003 R_A to a maximum of 0.514 R_A (Table 1, Fig. 3). The $^{3}$He/$^{4}$He ratios display a distinct overall decrease with advancing paragenetic stage from early to younger sulphides. In this respect, fine-grained sphalerite from the paragenetically earlier Zn-rich stage I exhibits the highest $^{3}$He/$^{4}$He ratio of 0.514 ± 0.028 R_A, whereas galena and sphalerite from the later Pb-rich cuboctahedral stage III have the lowest $^{3}$He/$^{4}$He ratios of −0.003 to 0.017 R_A (Table 1). The two galena separates from the Pb-rich main ore stage II show intermediate $^{3}$He/$^{4}$He ratios of 0.15 ± 0.11 and 0.245 ± 0.080 R_A.

5 Discussion and conclusion

The range of $^{3}$He/$^{4}$He ratios in the fluids extracted from sulphide separates suggests that diverse sources were involved in the genesis and evolution of the mineralizing system. Overall, the measured $^{3}$He/$^{4}$He ratios plot between crustal radiogenic (3He/4He ~0.01 R_A) and mantle-derived (3He/4He > 6 R_A) end-members, reflecting a binary mixing, to varying extents, of mantle and crustal He along the flow path. Field relationships together with Pb isotope constraints indicate that the Touissit-Bou Beker MVT mineralization occurred epigenetically during Neogene time (Voirin 1965; Rajlich 1983; Bouabdellah et al. 2012), coincident with Neogene to Quaternary high-K, calc-alkaline to alkaline basaltic magmatism (Duggen et al. 2005; Lustrino and Wilson 2007). A genetic link between MVT mineralization in the Touissit-Bou Beker district and basaltic magmatism is therefore proposed.

The tectonic setting of the Touissit-Bou Beker district related to collision between the African and European plates (Bouabdellah et al. 2012), coupled with the structurally controlled emplacement of the district mineralization along major ENE-trending deep faults, would have favored the ascent of mantle-derived volatiles into the mineralized zones. This addition of heat to the upper crust also may have promoted regional-scale convective hydrothermal circulation. Indeed, increased heat flow related to thinning and extension of the lithosphere, in response to upwelling of the asthenosphere during Late Neogene time, would have promoted buoyancy-driven convection of a deep-seated, basement-equilibrated fluid that transiently stored chloride-complexed metal-rich brines. As proposed by Bouabdellah et al. (2015), mixing of (1) a Messinian downward-flowing, metal-depleted, shallow surface brine carrying bacteriogenic sulphur; and (2) an older, upward-flowing, high-temperature, deep-stored, rock-buffered metalliferous brine that interacted extensively with basement rocks may have triggered sulphide deposition.

Acknowledgements

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Table 1. Helium abundances (cm$^3$ STP/g) and isotopic ratios of fluid inclusions in sphalerite and galena from different stages of mineralization in Touissit, Bou Beker, and Beddiane deposits. Value for atmosphere is shown for reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Petrographic description and paragenetic position</th>
<th>$^{3}$He/4He (R_A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB$_1$</td>
<td>Massive fine-grained sphalerite from the early Zn-rich ore stage (Stage I)</td>
<td>5.36 ± 1.8</td>
</tr>
<tr>
<td>TB$_2$</td>
<td>Massive galena filling banded cm-sized vein from the Pb ore main-stage (Stage II)</td>
<td>4.52 ± 0.23</td>
</tr>
<tr>
<td>TB$_3$</td>
<td>Massive galena intergrown with iron-rich dolomite from the Pb ore main-stage (Stage II)</td>
<td>2.39 ± 0.12</td>
</tr>
<tr>
<td>TB$_4$</td>
<td>Octahedral galena encrusted on saddle dolomite from the cuboctahedral stage (Stage III)</td>
<td>0.51 ± 0.028</td>
</tr>
<tr>
<td>TB$_5$</td>
<td>Variously-colored banded sphalerite from the cuboctahedral stage (Stage III)</td>
<td>0.15 ± 0.11</td>
</tr>
<tr>
<td>TB$_6$</td>
<td>Brown octahedral sphalerite encrusted on saddle dolomite (Stage III)</td>
<td>0.00 ± 0.0028</td>
</tr>
<tr>
<td>TB$_7$</td>
<td>Octahedral galena growing up on pink saddle dolomite (Stage III)</td>
<td>0.00 ± 0.0029</td>
</tr>
<tr>
<td>Atmosphere</td>
<td></td>
<td>1.00 ± 0.0002</td>
</tr>
</tbody>
</table>
1574

References


Copper Mineralization in Adoudounian Cover of the Bou Azzer-El Graara (Anti Atlas, Morocco): Tectono-Stratigraphic Controls

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Abstract. Copper mineralization in sedimentary cover is well known in association with Pb and/or Zn in Sedex, Kupferschiefer, Mississippi Valley-Type, or Red bed deposits. In spite of great economic potential, the syngeneric versus epigenetic origin of widespread Cu occurrences in the Adoudounian sedimentary cover, in the Moroccan Anti Atlas, remains debated. Significant investigations that would provide critical information for mining exploration are lacking. Whatever their origin, these mineralizations do not correspond to classical sediment-hosted deposits, the ore being exclusively Cu concentrations in dolostone units. This study, based on field and microscopic observations, is focused on Cu mineralization hosted in the Adoudounian cover of the Bou Azzer-El Graara inlier. Two morphologic types of ore bodies exist. The first consists of stratabound lenses and the second type is vein networks along Variscan faults. Both types of mineralization have a stockwork texture and clearly postdate sedimentary fabrics, such as beddings and slumps; this suggests a common epigenetic origin for the both ore types. The proposed interpretation involves the upflow of Variscan fluid-driven interaction between a basement and its sedimentary cover.

Keywords. Copper mineralization, sedimentary cover, Anti Atlas, field relationships, morphology, texture.

1 Introduction

More than 200 copper occurrences in the Moroccan Anti-Atlas are hosted within the Neoproterozoic to Cambrian cover, often called A doudounian cover (Pouit 1966; Bouchta et al. 1977). The growing interest of mining companies for potential copper resources induces the need for a better understanding of these mineralizations. Ore bodies are localized at different stratigraphic levels within the cover and present different characteristics. Their origin remains in most cases poorly understood; a syngeneric model explaining all of the Cu mineralizations by a single event has never been considered. In counterpart, several different genetic interpretations of some unusual copper occurrences have been proposed: (i) Leblanc (1986) suggested that the A lous mineralization formed during the cooling of an ignimbrite; (ii) Concerning the Cu-occurrences in the dolostones units in the Adoudounian cover of “Tizert”, “Talat N’oumane”, “Tizirt,” and “A madouz,” whereas Pouit (1966), Bouchta et al. (1977), and Skacel (1993) considered that they were generated through a synsedimentary process, given the strong paleo-topographic control on ore deposition. Moreover, the Cu mineralizations hosted in the Neoproterozoic to Cambrian cover of the A nti-Atlas can be differentiated, according to morphology, as veins, disseminations, or stratabound bodies. So far, no relationship has been found among these different morphological types of orebodies (Pouit 1966; Skacel 1993). As a result, the syngeneric or epigenetic nature of such mineralization remains undetermined (Pouit 1966). The Bou A zzer-El Graara inlier contains numerous copper occurrences in A doudounian cover, in particular the Jbel Laassel deposit is currently being mined, highlighting the economic interest for these mineralizations. This study is based on field and microscopic observations. The different morphologies of major copper ores in the Bou A zzer-El Graara A doudounian cover are described and their potential tectono-stratigraphic controls are detailed. Then, new arguments are presented in order to link these different copper occurrences with one hydrothermal event.

2 Geological setting

The Bou A zzer-El Graara inlier is one of a series of Proterozoic windows, oriented NW-SE, which expose Panafri can formations in the central part of the A nti-Atlas (Choubert 1947). These formations are unconformably overlain by a thick Neoproterozoic to Cambrian volcano-sedimentary cover (Soulaimani et al. 2014) (Fig. 1). This cover can be divided into three formations, from bottom to top: (1) The Tiddiline Formation (~750 to 650 Ma) attributed to the “Saghro Group” (Thomas et al 2004); it is mainly unconformable on the Panarican substratum; (2) The Quarazate Group (~610 to 550 Ma), which rests in angular unconformity on the Tidiline Formation; (3) The terminal Neoproterozoic to Cambrian formation, often called “A doudounian,” consists of clastic and carbonate strata (Soulaimani et al. 2013).
This last formation is associated with a major marine transgression toward the southeast and can be subdivided into two groups: the Taroudannt Group, with Lower Dolostones and Lower Sandstones units, and the Tata Group, with Upper Dolostones and Upper Sandstones units (Choubert 1952; Boudda et al. 1979) (Fig. 2).

During the late Paleozoic compressional event, the PanAfrican basement structures were reactivated along the inlier’s borders. This deformation resulted in box-shaped folds distributed throughout the Bou Azzer-El Graara area, marked by large open synclines of Cambrian rocks (Soulaimani and Burkhard 2008). Upright detachment folds, from meters to decameters in scale, are common in the Lower Cambrian rocks and exhibit a predominant NW-SE trend with subordinate NE-SW structures (Soulaimani and Burkhard 2008).

3 Copper mineralization

3.1 Ore body

In the Bou Azzer-El Graara Adoudounian cover, two types of orebody morphologies can be distinguished, according to (i) the shape of the mineralized envelope at meter to kilometer scale, and (ii) the relation between this envelope and the geological features of the host rock: either stratabound or vein networks spatially associated with Variscan faults. The former ore type is exclusively located in Lower Dolostones units of the Taroudannt Group. It consists of two coarse-grained black dolostone beds separated by a micritic dolostone bed. This particular set of lithologies is localized in the lower part of Lower Dolostones (Fig. 2), and occurs continuously in the cover around the inlier, whether mineralized or not. Where present, the copper mineralization displays a stratabound geometry, with a thickness of ~1.5 to 4 m and a lateral extent of 2 m to more than 5 km (Fig. 3A), and a copper content of 0.4 to 2.5%. The most important ore bodies of this type are Tizi N’Mekraz, Oued R’Them, and Cha’a'b Lhamrat (Fig. 1).

The second ore type is present in both the Taroudannt and Tata Groups, throughout the Lower and Upper Dolostones (Fig. 2). It is exclusively associated with NW-SE-oriented, vertical to subvertical Variscan faults (Fig. 3B). On both sides of these faults, the cover presents meter to decimeter-scale folds with the same NW-SE-trending axes. These folds are concentrated in a more or less narrow band, named herein the “folding band.” The ore body is uniformly in contact with these faults; its lateral extension corresponds to the width of the “folding band.” On surface, the width is in the range of 2 to 200 m and the
lateral extent is 1 to 5 km. Depth extension is only known for the Jbel Laassel deposit, where it is at least 120 m. Copper contents are in the range of 0.3 to 3%. The most important ore bodies in the considered inlier are the Jbel Laassel deposit, the Amekssa and Assif N’Zaïd in the Upper Dolostones and the Jbel N’Zourk in the Lower Dolostones (Fig. 1).

Fig. 1. Simplified map of Morocco showing the location of the Bou Azzer El Graara area; Abbreviations: LD, Lower Dolostones; US, Upper Sandstones (see Fig. 2).

3.2 Texture and mineralogy

In the field, the copper mineralization of the two morphological types is essentially composed of sulphides: chalcocite and less commonly bornite, chalcopyrite, and pyrite, with associated malachite as a major mineral, subordinate chrysocolla, and rare azurite.

In both types of ore body, copper mineralization is exclusively present in quartz-dolomite veins that form a stockwork (Fig. 4). These veins cut sedimentary fabrics, like bedding and slumps. Vein abundance changes depending on the site, being lower in stratabound ore bodies than in vein network ones along Variscan faults.

At a microscopic scale, the texture of mineralization is similar for the two morphologic types, i.e., veins parallel or cut bedding but are uniformly connected to form a stockwork.

4 Discussion

From the textural point of view, the copper mineralization is present in the form of stockworks with the same ore and gangue mineralogy and the same order of magnitude copper content, whatever the morphologic type. These stockworks intersect all sedimentary fabrics. In consequence, these different types of mineralization can be considered epigenetic independent of the ore body morphology. As a whole, the reported observations suggest that all of the studied copper mineralization hosted in Aoudouinian dolostones may be cogenetic, i.e., related to a single mineralizing event, at the periphery of the Bou Azzar-El Graara inlier.

Fig. 3. Photographs: A, Stratabound ore body of Oued R’Them in Lower Dolostones; B, Vein network along Variscan fault of Amekssa in Upper Dolostones. Abbreviations: LD, Lower Dolostones; LS, Lower Sandstones; UD, Upper Dolostones; US, Upper Sandstones (see Fig. 2).

Fig. 4. Photographs: A, Stockwork of the Oued R’Them stratabound mineralization in Lower Dolostones; B, Stockwork of Jbel N’Zourk mineralization along Variscan fault in Lower Dolostones. Abbreviations: Bn, bornite; Cc, chalcocite; Ccp, chalcopyrite; Dol, dolomite; Ma, malachite; Qtz, quartz.

Soulaimani and Burkhard (2008) described Variscan kink bands with a cleavage occurring in the vicinity of Panafrian structures in the basement of the Bou Azzar-El Graara inlier. These authors attributed the folds to reactivation of Panafrian structures during Variscan compression. In the Aoudouinian cover, faults and folds are widely assigned to this Paleozoic compression, controlled by the movement of inherited basement structures (Leblanc 1972; Soulaimani 1997; Faïk et al. 2002; Soulaimani and Burkhard 2008). In the Bou Azzar-El Graara inlier, this deformation resulted in meter to decimeter folds, exhibiting NW-SE-trending axes with a subordinate NE-SW orientation (Soulaimani and Burkhard 2008). At Jbel Laassel, Amekssa, Assif N’Zaïd, and Jbel N’Zourk, the mineralization is spatially controlled by Variscan NW-SE faults and by NW-SE-oriented “folding bands.” Under such conditions, the formation of the second morphological type of mineralization took place, at the earliest, coeval with Variscan deformation. In addition, (i) the Cu mineralizations are localized in the Lower and Upper Dolostones, (ii) Variscan deformation in the Aoudouinian cover is controlled by the movement of structures inherited from the basement. It is thus possible to consider a fluid transfer process from the basement to the Aoudouinian cover. The latter interpretation is consistent with the Sm/Nd age of gangue carbonates (308 ± 31 Ma) and the U/Pb age of brannerite (310 ± 5 Ma), from a vein in the Bou Azzar Co-A’s district (Oberthür et al. 2009).

The determination of the age of the stratabound Cu mineralization in the lower dolostones is more problematic, however. Currently, we can only point out that the textural and paragenetic similarities between the two morphological types strongly suggest a similar Variscan age.

To conclude, this study presents new data that contribute to a better understanding of the genesis of copper mineralization in the Aoudouinian cover of the

Metallogeny of North and West Africa
Bou Azzer-El Graa district, and gives valuable information for mineral exploration in this region.

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A Cordilleran Zoning Model for the Polymetallic W-Au-Pb-Zn-Ag Tighza-Jbel Aouam District (Central Morocco): Contribution from New He-Ar and U-Th-Pb Data

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Abstract. The W-Au, Pb-Zn-Ag, and Sb-Ba polymetallic ores of the Tighza-Jbel Aouam (central Meseta, Morocco) have been considered zoned magmatic-hydrothermal deposits, hosted in Palaeozoic rocks surrounding late-Variscan granites. The spatial distribution of the deposits was interpreted as zoning around a supposed hidden batholith. New dating of zircon and monazite allow revision of this model. The Tighza-Jbel Aouam W-Au mineralization formed at 295-280 Ma and cuts granitic stocks dated at 320-300 Ma. It is related to a magmatic event only visible through a large hydrothermal biotic alteration halo, thus suggesting the presence of a hidden batholith. Based on the occurrence of large veins, stockworks, sheeted veins, and disseminations hosted in skarns, the W-Au deposit is considered similar to a porphyry-type deposit. The currently mined Pb-Zn-Ag ores developed during an epithermal magmatic-related episode dated at 254 ± 16 Ma; it is disconnected from the W-Au deposit. The polymetallic district of Tighza-Jbel Aouam thus represents a Cordilleran mineralizing style related to pulses of calc-alkaline magmatism. Late-Variscan and Permo-Triassic transpressive tectonics allowed localized magma emplacement and associated hydrothermal fluid circulation, and the formation of the polymetallic deposits.

Keywords. W-Au-Pb-Zn-Ag, fluid sources, He-Ar, U-Th-Pb, zoned polymetallic district, Moroccan Meseta.

1 Introduction

Many Pb-Zn-Ag-F deposits in Morocco as well as in Western Europe occur in veins that cut Palaeozoic rocks, late Variscan intrusive granites, and overlying Permo-Triassic to Jurassic sediments. In several occurrences, the spatial association of these veins with granites has been interpreted as proof of a genetic link between magmas and hydrothermal fluids, which produced the base-metal concentrations. By this model, the mineralizations are thus supposed to have an age of ca. 300 Ma.

Recent geochronological data have shown that some “Variscan” ore deposits from central Morocco are actually much younger (i.e., 205 ± 1 Ma for the El Hammam F deposit; Cheilletz et al. 2010). The genetic model of hydrothermal perigranitic Pb-Zn-Ag-F ore deposits in Morocco thus needs to be reconsidered, involving an update of the exploration strategy for these base and precious metals. In the Tighza-Jbel Aouam district (TJAD), fluid inclusion studies (Nerci 2006) previously suggested that the W-Au and Pb-Zn-Ag ores are associated with different types of fluids. This paper presents new He-Ar geochemical data for a better constraint on the sources of the mineralizing fluids. Furthermore, new geochronological investigations conducted on magmatic bodies (U/Pb on zircon) and hydrothermal mineralized Pb-Zn-Ag veins (Th/Pb on monazite) help to constrain the timing of the different magmatic and hydrothermal pulses in the TJAD (Tarrieu 2014) as already done for other deposits in Morocco (Levresse 2001; Pelletier et al. 2007).

2 Geological setting

2.1 Regional geology

The Moroccan Meseta domain corresponds to the southwesternmost segment of the European Variscan belt (Michard et al. 2008). The Tighza-Jbel Aouam district (TJAD) belongs to the eastern part of the Meseta domain that comprises Palaeozoic metasedimentary rocks cut by Variscan magmatic stocks and dikes (Fig. 1). Within the TJAD, mineralization is hosted in upper Visean limestone and schist, discordant on Ordovician siliceous schist and quartzite, Silurian graptolite-bearing black shale, and Devonian siliceous and marly limestone. These units are deformed into a succession of antiformal and synclines, SW-NE-trending, bordered by a major E-W
mega-shear corridor called the Tighza shear zone. All of these formations are metamorphosed to very low- to low-grade greenschist facies. They are intruded by numerous, nearly parallel SW-NE- trending microgranite and microgranodiorite dikes and five small stocks ranging along a N-S strike (Izougarza, Pitons de Tighza, Mispickel, Mine, K aolin; Fig. 1). These stocks have a high-K calc-alkaline affinity like most Variscan granites, testifying to a strongly enriched mantle component (Giuliani et al. 1987; Gasquet et al. 1996). The three southernmost stocks are surrounded and altered to various degrees by a large biotitic hydrothermal alteration halo associated with the W-Au mineralizing episode (Cheilletz 1984; Cheilletz and Isnard 1985). The gravimetric study conducted by El Dursi (2009) suggests that this hydrothermal alteration halo might be related to a hidden shallow intrusive pluton.

Figure 1. Geological map of the Tighza-Jbel Aouam polymetallic district, highlighting the mineralized veins. Mining activity focuses on the following veins: Signal, Structure 18, Sidi A hmed, and Ighrem Aousser.

2.2 Mineralizations

In the TJAD, three magmatic-hydrothermal systems have been identified (W-Au, Pb-Zn-Ag, and Sb-Ba) that together display a concentric base- and precious-metal zonation centred on the biotite hydrothermal alteration halo (A gard et al. 1958; Cheilletz 1984). The W-Au mineralization is concentrated in the vicinity of the outcropping stocks, cutting the Mine Granite. It formed first as skarns, then as large veins, stockworks and sheeted veins, and finally as disseminations (Cheilletz 1984; Nerci 2006). A mineralization sequence is observed from an early W-Mo assemblage (wolframite + scheelite + molybdenite) to a Bi-Te-Au-A s (with löllingite) assemblage, and finally a sulphide-rich assemblage (arsenopyrite + pyrrhotite) with minor Au (Nerci 2006). The main veins are parallel to the E-W Tighza dextral shear zone that formed under a transpressive tectonic regime.

The Pb-Zn-Ag mineralization occurs within several large veins with N25 to N75°E orientations that commonly present a "Y" shape, suggesting vein opening in a sinistral conjugate strike-slip system (Cheilletz 1984; Fig. 1) related to the Tighza shear zone. It is a sulphide-rich assemblage (galena + sphalerite) associated with a carbonate ± quartz gangue. The paragenetic sequence is divided into 4 stages:

- **S1** is uniformly barren and contains a siderite + quartz assemblage.
- **S2** is the first mineralized sequence, having a galena ± sphalerite assemblage associated either with akerite (Sidi A hmed and Ighrem Aousser, SA-1A veins) or calcite ± ankerite ± siderite ± red chalcedony (Signal vein).
- **S3** is also mineralized with a galena ± sphalerite assemblage, mainly associated with siderite (and quartz in SA-1A vein and rare barite in Signal vein).
- **S4** is the latest sequence is barren and contains a calcite + quartz + pyrite assemblage (with some barite in Signal vein).

Gangue carbonates contain numerous µm-size inclusions of monazite and xenotime that are strongly altered to synchysite, thus enhancing the REE content of the carbonates (ΣREE up to 4000 ppm in some samples; Tarrieu 2014).

The Sb-Ba mineralization has only been documented by A gar d et al. (1958). It occurs as local lenses of stibnite ± pyrite ± chalcopyrite.

3 Relative chronology

Field observations allow the establishment of a relative chronology among the three main mineralization events and the magmatic pulses. Because the Sb-Ba mineralization lacks spatial relationships with the W-Au or the Pb-Zn-Ag occurrences, its timing remains unclear. However, A gard et al. (1958) suggested that the Pb-Zn-Ag veins postdate the Sb-Ba mineralization, based on other evidence elsewhere in Morocco. These authors also noted that the Sb-Ba veins cut some granitic dikes.

The W-Au veins cut the outcropping magmatic stocks, but they are older and are displaced by the Pb-Zn-Ag mineralization (Fig. 2). As described above, the W-Au mineralization is associated with the biotite-rich alteration halo affecting the stocks (Fig. 1), and is thus contemporaneous with a hidden magmatic event proposed by El Dursi (2009). Dike emplacement took place between the two main hydrothermal events as some of them cut the W-Au mineralization, and others are displaced by the Pb-Zn-Ag deposits.

From the above observations, the following chronology is proposed: (1) dike emplacement, (2) Sb-Ba veins, (3) emplacement of the currently outcropping stocks, (4) W-Au mineralization associated with a hidden pluton, (5) dike emplacement, and (6) Pb-Zn-Ag mineralization. The magmatic activity might have
2.2 Mineralizations

The Tighza-Jbel Aouam shear zone (TJAD) hosts a mineral deposit that is associated with a late Variscan/late-Variscan granite emplacement and Permo-Triassic volcanism related to rifting during formation of the Central Atlantic Magmatic Province (Gasquet et al. 1996; Verati et al. 2007).

From the above observations, the following chronology among the three main mineralization events can be distinguished: (1) dike emplacement, (2) Sb-Ba mineralization, (3) Pb-Zn-Ag veins postdate the Sb-Ba mineralization, (4) dike emplacement, and (5) Pb-Zn-Ag ore mineralization (structure 18).

In the TJAD, three magmatic-hydrothermal systems have been identified (W-Au, Pb-Zn-Ag, and Sb-Ba) that together display a concentric base- and precious-metal mineralizing episode (Cheilletz 1984; Cheilletz and Isnard 1985). The gravimetric study conducted by El Dursi (2009) suggests that this hydrothermal alteration halo might be related to a hidden shallow intrusive pluton.

The late Variscan/late-Variscan granite emplacement and Permo-Triassic volcanism related to rifting during formation of the Central Atlantic Magmatic Province (Gasquet et al. 1996; Verati et al. 2007). Metallogeny of North and West Africa 1581

Figure 2. Underground field photograph showing the Pb-Zn-Ag veins cutting and displacing the W-Au mineralization (structure 18).

4 Fluid sources

In order to give insights into the mineralizing fluid sources, He-Ar analyses were performed on both the W-Au and the Pb-Zn-Ag ores.

The W-Au and Pb-Zn-Ag mineralization both have Ar isotopic values ranging between 299 and 328, which is consistent with meteoric Ar \( (^{40}\text{Ar})/^{36}\text{Ar} = 295.5; \) Fig. 3.

The Pb-Zn-Ag ore has a very low \(^{3}\text{He}/^{4}\text{He} \) signature (0.01-0.10) that is characteristic of a crustal fluid (Fig. 3). In contrast, the W-Au ore has a higher \(^{3}\text{He}/^{4}\text{He} \) ratio, ranging from 1.0 to 1.8, the latter suggesting a small mantle component.

As suggested previously by Pb isotope and fluid inclusions studies (Nerci 2006; Tarrieu et al. 2011), the Pb-Zn-Ag mineralizing fluid resulted from mixing of meteoric and crustal fluids, whereas the W-Au mineralizing fluid derived from the mixing of meteoric, crustal, and mantle fluids. The W-Au and the Pb-Zn-Ag deposits are thus clearly unrelated genetically.

5 U/Pb and Th/Pb geochronological data

Zircons from magmatic rocks contain numerous and complex growth zones that are related to magmatic and/or later hydrothermal events. In situ U/Pb dating of such zircons thus allows dating of both types of events (e.g., Pelleter et al. 2007). As shown in Figure 4A, zircons from the TJAD granitic stocks and dikes show such zoning, suggesting that they record several magmatic and hydrothermal events. Some grains also have an inherited core (ages up to 420 Ma; Fig. 4A).

With the exception of some inherited cores and two very young dates, all individual ages are 320 to 240 Ma with a polymodal distribution (Fig. 4C). Three main periods can be distinguished: 320-300 Ma, 300-280 Ma, and 280-240 Ma. These periods are well correlated with intercept ages obtained for the stocks and one dike. The two older magmatic periods are well documented throughout Morocco, but the 280-240 Ma interval has only been evidenced on a single microdioritic dyke from the Jebilet massif, using the K-Ar chronometer on kaersutite (Gasquet et al. 1996). At a regional scale, this late magmatic pulse might represent the link between Variscan/late-Variscan granite emplacement and Permo-Triassic volcanism related to rifting during formation of the Central Atlantic Magmatic Province (Gasquet et al. 1996; Verati et al. 2007).

Figure 3. He and Ar isotopic compositions of W-Au and Pb-Zn-Ag ore minerals. Mantle, crustal, and meteoric signatures are from Burnard et al. (1999) and references therein.

Figure 4. A. SEM image of a zircon grain showing an inherited core and multiple growth zones. B. SEM image of a dated monazite hosted in S4 calcite. C. Synthesis of all ages obtained for both magmatism and hydrothermalism in the TJAD (this study and literature data).

Round 3: Field observations allow the establishment of a relative chronology among the three main mineralization events. Some grains also have an inherited core (ages up to 420 Ma; Fig. 4A).
Two 10-15 μm-sized monazite crystals from the Pb-Zn-Ag gangue carbonates were large enough to allow LA-ICPMS Th/Pb dating (Gasquet et al. 2010; Fig. 4B). These monazite grains give ages of 254 ± 16 Ma and 257 ± 48 Ma. The former, better-defined, age is assumed to date the Pb-Zn-Ag mineralizing event, which is contemporaneous with the youngest magmatic pulse (dikes; Fig. 4C).

6 Discussion and conclusion

The Pb-Zn-Ag mineralization of the Tighza-Jbel Aouam district has been dated for the first time at 254 ± 16 Ma. Such a young age confirms field evidence and geochemical data, and indicates that the Pb-Zn-Ag event is not connected with the W-Au occurrences as suggested previously. The polymatic Tighza-Jbel Aouam district thus developed during multiple injections of Cordilleran-type, calc-alkaline intrusives that produced hydrothermal pulses, each of which was associated with distinctive stages. The two main mineralizing episodes, W-Au then Pb-Zn-Ag, therefore could be related to two successively telescoped porphyry- then epithermal-style environments. This model leading to the base and precious metal zonation pattern in a polymatic district has also been encountered in other giant districts (e.g., Morococha in central Peru; Catchpole 2011; Catchpole et al. 2015). In the TJAD, fluid flow and related polymatic mineralization were generated during a late-Variscan to Perno-Triasic transpressional regime (Michard et al. 2008), which favored emplacement of mantle- and crustally derived magmas, together with mixing of fluids of diverse origins. Fluid and magma emplacement were channeled by the Tighza fault, which played a major role in the district in localization and zonation of the polymatic mineralization.

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Abstract. A two-stage, knowledge-driven, Mamdani-type fuzzy inference system (FIS) is implemented to model the orogenic gold prospectivity in the Paleoproterozoic Kumasi Basin, Ghana, West Africa. The key components of the mineral system were modelled in the first stage, and their outputs were combined using a conjunction operator in the second stage in order to derive a prospectivity map. The model captured the linguistic reasoning of exploration geologists in the form of fuzzy if-then rules and objective mathematical functions, rather than in the form of explicit class weights and map weights as in traditional fuzzy models. The high-prospectivity areas on the map are elongate features that are spatially coincident with areas of structural complexity which possibly were derived from reactivation of NE-SW-striking D2 thrust faults and subsidiary structures during D4, implying a strong structural control on gold mineralization. The model effectively captured 99% of the known gold deposits and the main mineralised trends. The application demonstrates the efficacy of an FIS in capturing the linguistic reasoning of exploration geologists. In spite of using a large number of variables, the curse of dimensionality is precluded because no training data are required for parameter estimation.

Keywords. Kumasi Basin, Orogenic gold, Mineral prospectivity modelling, Fuzzy inference system (FIS)

1 Introduction

The Kumasi Basin located in the south western part of Ghana forms a part of the West African Craton (Fig. 1). The structural and geodynamic evolution of the Kumasi Basin during the Paleoproterozoic Eburnean orogeny forms a critical control over gold mineralization in the Kumasi Basin. The work presented in this paper, commissioned by Asanko Gold Inc., aims at understanding the geological frame work and gold metallogeny of the entire Kumasi Basin for finding new exploration targets for the company. The study involved developing an FIS-based prospectivity model for orogenic gold mineralization in the Kumasi Basin by thoroughly conceptualizing the processes involved in gold mineralization in the Kumasi Basin, creating a genetic model using the mineral systems approach, evaluating every aspect of each of the orogenic-gold-mineral-system component, and analysing its influence on localization of gold deposits.

![Figure 1. Location of the study area: Kumasi Basin in Ghana, West Africa (modified after Jessell et al. 2012).](Image)
In the subsequent sections we describe the geological setting of the Kumasi Basin, the orogenic gold mineral systems model, and details of the FIS-based model used in the gold prospectivity modelling. We then describe and discuss the results. The prospectivity model was developed for the entire Kumasi Basin, but for confidentiality reasons only those results are reported in this contribution that fall within Asanko’s concession area. Follow up exploration activities are planned be undertaken by the company in the areas identified as highly prospective by the model.

2 Geological setting

The Kumasi Basin is located between intensely metamorphosed terranes of the Ashanti Belt in the SE and the Sefwi-Bibiani Belt in the NW. The basin is bounded by trans-lithospheric basin-forming faults, namely, Bibiani Fault and K etesso Fault along the western margin, and the Ashanti Fault along the eastern margin (Essell et al. 2012; Perrouty et al. 2012). It evolved from a foreland basin into a back arc basin and was subducted under active volcanic arcs towards both eastern and western margins during the basin inversion phase that occurred during the Eburnean Orogeny, which commenced at around 2.13 Ga and continued up to 1.98 Ga (Feybesse et al. 1990). The entire sequence was uplifted and eroded during the Eburnean tectono-thermal event at around 2.13 Ga and continued up to 1.98 Ga (Feybesse et al. 2006). The Eburnean Orogeny played a critical role in orogenic gold mineralization in the Kumasi Basin.

Lithostratigraphically, the Kumasi Basin comprises early Proterozoic Birimian Supergroup overlain by the Tarkwaian Group, both of which were later deformed during the Eburnean Orogeny. The Birimian Supergroup contains linear and parallel belts of metavolcanic rocks and the intervening isoclinally folded, younger sedimentary sequences (Leube et al. 1990). The Birimian volcanic and sedimentary facies were intruded by the belt granitoids and the basin granitoids, respectively (Leube et al. 1990). The entire sequence was uplifted and eroded during the Eburnean tectono-thermal event at around 2.10-2.09 Ga (Leube et al. 1990). The Birimian Supergroup rocks are overlain by clastic sedimentary rocks of the Tarkwaian group which are derived from the erosion of the Birimian Supergroup rocks (Leube et al., 1990). Contemporaneous with the Tarkwaian sedimentation was the Eburnean Orogeny which involved emplacement of granitoid rocks known as the Eburnean Plutonic Suite into the Birimian Supergroup and the Tarkwaian group.

3 Orogenic gold mineral systems in the Kumasi Basin

A conceptual genetic model of orogenic gold mineral systems was developed to understand and systematically analyse various processes involved in the formation and localization of gold deposits in the Kumasi Basin. The matrix shown in Table 1 summarizes the critical components of the gold mineral system in the Kumasi Basin, their respective targeting criteria, and the details of the derivative predictor maps. The predictor maps were used in the FIS to model the critical mineralization processes by proxy.

4 The gold prospectivity model

A Mandani-type FIS-based prospectivity model was used in this study. The model is described and explained in detail by Porwal et al. (2014). In brief, the model captured the linguistic reasoning of exploration geologists in the form of fuzzy if-then rules and objective mathematical functions, rather than in the form of explicit class weights and map weights as in traditional fuzzy models. In the present work, we used a two-stage fuzzy model (Fig. 2).

In the first stage, individual FIS were designed for modelling each of the key components, namely, pathways, physical traps and chemical traps (Table 2). The source component was ignored because the broad spatial distribution of the known gold deposits all over Ghana, and the similarity of their morphology and timing point towards the presence of a broad, relatively homogenous, source rather than point sources like individual plutons or batholiths as in the case of, for example, a porphyry system. In the second stage, the outputs of each of the above FIS were combined using a conjunction (product) operator (Table 2).

The first stage FIS outputs three intermediate maps showing the prospectivity for each of the mineral system component, viz. pathways, physical traps and chemical traps. The second stage integrates the above outputs using a conjunction operator to obtain the final mineral prospectivity map for orogenic gold in the study area (Fig. 3). A cumulative area fuzzy favourability plot (CAFF, Porwal et al. 2003) is used to reclassify the output map.

![Figure 2. FIS-based prospectivity modelling flow chart.](image)

Since the spatial distribution of the known deposits was not used at all in developing the model, we evaluated the performance of the model based on its efficiency in predicting the known deposits. The model captures most of the known mineral deposits present in the study area (Fig. 3). Quantitatively, 99% of the known mineral deposits are captured by the model in high-prospectivity and moderate-prospectivity areas that occupy 31% of the study area. Only 1% of the known deposits fall in the low-prospectivity areas.

5 Discussion and conclusions

The method implemented in this paper for orogenic gold prospectivity modelling of the Kumasi basin comprises first formulating a genetic model to conceptualize the entire process of orogenic gold mineralization in the study area to identify key controls on mineralization and then discerning spatial proxies of these controls to develop an FIS. The consequent prospectivity model captures the
mineralization processes rather than just focussing on the features associated with mineral deposits and statistical measures. Prospectivity modelling is implemented without any regard to the existing mineral deposits and hence it is not biased by the attributes of already discovered deposits. If the processes and components driving the targeted mineral system are correctly modelled and incorporated in an FIS, then it should be able to predict the known deposits very well.

Figure 3. FIS-based orogenic gold prospectivity map for Kumasi Basin (results are clipped to the Asanko Gold Inc.'s concession area due to confidentiality reasons).

The output prospectivity map shows a strong spatial association between existing deposits and the structural trends of mineralization identified by the model. These trends in the distribution of the known deposits are established by constructing Fry plots and rose diagrams. The Fry plot exhibits a dominant NE-SW trend, which is in agreement with the structural trends identified in the genetic model. The rose diagrams of the Fry translations are used to identify the anisotropy in the distribution of points and to recognize mineralization trends and controls at different scales. At the deposit scale, a broadly random distribution of points is observed, with spikes in the NE-SW, NW-SE and NNW-SSE directions. At the camp scale the trend becomes prominently NE-SW, with small spikes along NW-SE and NNW-SSE directions. At the district scale, the trend persists along NE-SW direction. This prominent NE-SW trend is related to the D2 thrust faults, which seem to exhibit major influence on mineralization. The smaller spikes along NW-SE and approximately at NNW-SSE directions are interpreted to be associated with the flexures caused due to sinistral strike-slip faults generated by reactivation of the D2 thrusts during the D4 deformation event. It is notable that at all scales distinct trends are observed along NE-SW, NW-SE and approximately at NNW-SSE directions. The only difference is in the length of the spikes. Thus it can be inferred that at the district scale the NE-SW trends dominate, hence at this scale of prospectivity modeling mineralization is strongly controlled by the D2 thrust faults. However on the deposit scale, influences of the splay, jogs and bends along D2 thrust faults associated to the D4 deformation event becomes more discernible as evidenced by the trends along NW-SE and approximately at NNW-SSE directions.

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References


Table 1. Orogenic gold mineral systems matrix for Kumasi Basin.

<table>
<thead>
<tr>
<th>Component</th>
<th>Targeting Criteria</th>
<th>Primary Data</th>
<th>Predictor Maps</th>
<th>Rationale</th>
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</thead>
<tbody>
<tr>
<td>Source of energy</td>
<td>Magma/crust, metamorphism</td>
<td>Not available</td>
<td>None</td>
<td>For regional scale prospectivity modelling sources of energy, fluids, ligands and metals are assumed to be present as evidenced from the fact that many economically viable gold deposits have been discovered in the study region.</td>
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<tr>
<td>Source of fluids</td>
<td>Magma/crust, metamorphism</td>
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<td>None</td>
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<tr>
<td>Source of ligands</td>
<td>S from continental crustal rocks, S from pre-existing pyrite and sulphate deposits</td>
<td>Not available</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Source of metals</td>
<td>Crustal rocks</td>
<td>Not available</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Pathways</td>
<td>Crustal scale structures: D2 thrust faults</td>
<td>Geophysical data (electromagnetics, magnetics and radiometrics).</td>
<td>Proximity to D2 thrust faults</td>
<td>D2 thrust faults are fundamental (basin forming) faults, reactivated during basin inversion in a NW-SE trending compression regime. Hence favourable pathways for fluid migration. Indicate presence of zones of silicification due to hydrothermal alteration; these ridges indicate passage of hydrothermal fluids.</td>
</tr>
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<td></td>
<td>Topographic ridges</td>
<td>SRTM DEM</td>
<td>Proximity to ridges with elevations 30-50m greater than the average elevation and trending along D2 thrust faults</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lithological contacts weighted by competence contrast density</td>
<td>Geological map</td>
<td>Density estimation of competence contrast values</td>
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<tr>
<td>Physical traps</td>
<td>Flexures along D2 thrust faults</td>
<td>Geophysical data (electromagnetics, magnetics and radiometrics).</td>
<td>Proximity to flexures along D2 thrust faults</td>
<td>NE-SW trending thrust faults were reactivated as sinistral strike-slip faults during D4-D5 deformation event. Flexures along these created pressure shadow region which are domains of high permeability and fluid flux (suction) and where the sudden release of pressure causes Au precipitation. A long contacts of incompetent and competent rocks, there is change from ductile to brittle deformation; Thus spaces are created due to formation of fractures, dilation jogs along these contacts accompanied by a sporadic release of pressure. This causes volatiles to escape and Au to precipitate.</td>
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<td></td>
<td>Lithological contacts weighted by reactivity gradients</td>
<td>Geological map</td>
<td>Density estimation of reactivity contrast values</td>
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<tr>
<td>Chemical traps</td>
<td>Fe-rich Paleoproterozoic rocks</td>
<td>Magnetic and electromagnetic data</td>
<td>Proximity to Fe-rich Paleoproterozoic rocks</td>
<td>Fe-rich rocks react with soluble gold complexes in the fluids, leading to their destabilization and precipitation of gold.</td>
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<td></td>
<td>Lithological contacts weighted by reactivity gradients</td>
<td>Geological map</td>
<td>Density estimation of reactivity contrast values</td>
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Table 2: FIS for modelling the prospectivity of pathways, physical traps and chemical traps in the Kumasi Basin (only a few rules are shown for illustration).

<table>
<thead>
<tr>
<th>Premise (IF) Part</th>
<th>Consequent (THEN) Part</th>
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<tr>
<td>Pathways</td>
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<tr>
<td>01. IF D2 Thrust is Proximal AND Topographic Ridge is Proximal</td>
<td>THEN Pathways Prospectivity is Very High</td>
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<tr>
<td>02. IF D2 Thrust is Distal AND Topographic Ridge is Distal</td>
<td>THEN Pathways Prospectivity is Very Low</td>
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<td>Physical Traps</td>
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<td>03. IF Competence Contrast Density is High AND D2 Flexures are Proximal</td>
<td>THEN Physical Traps Prospectivity is Very High</td>
</tr>
<tr>
<td>04. IF Competence Contrast Density is Low AND D2 Flexures are Distal</td>
<td>THEN Physical Traps Prospectivity is Very Low</td>
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<td>Chemical Traps</td>
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<tr>
<td>05. IF Fe-Rich Rocks are Distal AND Reactivity Contrast Density is Low</td>
<td>THEN Chemical Traps Prospectivity is Very Low</td>
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<td>06. IF Fe-Rich Rocks are Proximal AND Reactivity Contrast Density is High</td>
<td>THEN Chemical Traps Prospectivity is Very High</td>
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Craton-Scale Lithostratigraphic Correlation as an Insight for the Geodynamic Evolution of the SWAC

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Abstract. The Paleoproterozoic Baoule-Mossi Domain within the South West African Craton is one of the most heavily mineral endowed regions in the world. However the geodynamic framework of this unique endowment is poorly constrained. The evolution of the craton can be mapped out through detailed analysis of volcanic and sedimentary successions, which are intimately linked to geodynamic processes. Six major lithostratigraphic cycles have been identified and correlated across the Baoule-Mossi Domain: the Lower Birimian Cycle One (ca. 2300-2180 Ma), the Lower Birimian Cycle Two (ca. 2160-2150 Ma), the Upper Birimian Cycle One (ca. 2150-2140 Ma), the Upper Birimian Cycle Two (ca.2140-2115 Ma), the Tarkwaian Cycle (ca. 2115-2095 Ma) and the Bandamian Volcanics (ca. 2100-2070 Ma). These cycles can be linked to specific geodynamic settings providing additional understanding of the Birimian/Paleoproterozoic Baoule-Mossi Domain global geodynamic evolution.

Keywords. Lithostratigraphic, Evolution, Geodynamic, Craton Scale, South West Africa.

1 Introduction

The South West African Craton (SWAC) is the host to large mineral resources including, but not limited to, Au, Fe, U and Al. Our ability to unravel the processes at time of mineralisation strongly relies on our ability to decipher the lithostratigraphic record. Despite numerous studies of the SWAC the regional scale, the lithostratigraphic sequence remains largely unconstrained (Abouchami et al. 1990). This has led to uncertainty over the nature and timing of the geodynamics at the time of mineralisation.

Similar to most Precambrian Terranes, the SWAC exhibits a protracted tectonic evolution of which only the latest structural increment is preserved. However, an insight into the early stages the SWAC formation may be gathered through careful lithostratigraphic and reconstructions. Lithostratigraphic successions including mafic and ultramafic volcanic rocks, intermediate felsic volcanic rocks and sedimentary basins often present a cyclic nature that can be linked to tectonic events (Barnes and Van Kranendonk 2014). On the basis of a lithostratigraphic compilation, it is therefore possible to assess the geodynamic framework at the time of deposition of the supracrustal cover. Work of this nature has been influential in resolving the tectonic evolution of Archean Terranes such as the Yilgarn Craton in Western Australia (Squire et al. 2010) and the Archean Abitibi Belt in Canada (Weller et al. 1994).

This paper presents the first integrated stratigraphic study of the SWAC. This lithostratigraphic compilation and correlation provides an insight into the geodynamic evolution that occurred during the Birimian/Eburnean period and that underpins the SWAC world-class mineral endowment.

2 Methods

This lithostratigraphic compilation is the product of three years of research compiling historic data together with lithological, geochemical and geochronological data acquisition in Ghana, Burkina Faso, Côte d’Ivoire, Mali, Guinea and Senegal. Supracrustal rocks have metamorphic assemblages ranging from lower greenschist to granulite facies. For simplicity the meta-prefix has been removed.

3 Geological setting

The SWAC refers to the southern portion of the West African Craton, consisting of the Archean Kenema-Man Domain (Boher et al. 1992) juxtaposed against the Birimian Baoule-Mossi Domain (Bonhomme 1962). The Archean Kenema-Man Domain spans the borders of Liberia, Guinea and Sierra Leone and is subdivided into three complexes; Pre-Liberian (ca. 3540-3050 Ma), Liberian (ca. 2900-2800 Ma) and the BIF Successions (ca. 2871-2615 Ma) (Egal et al. 2002). The Birimian Baoule-Mossi Domain, which is the focus of this paper, consists of volcanic, sedimentary and granitic rocks (Fig 1). The fragmented nature of the supracrustal rocks within voluminous granitoid complexes has resulted in a varied and complex naming convention. We have revised the lithostratigraphic column for the SWAC into belts, basins and intrusive complexes, following the pre-existing nomenclature set out by (Baratoux et al. 2011).

3.1 Birimian Baoule-Mossi Domain

The Baoule-Mossi Domain stretches from NE Burkina Faso in the east to the Kidougou-Kenieba Inlier on the Mali-Senegal border in the west. The domain consists of a series of volcano-sedimentary belts deposited between ca. 2250-1980 Ma. This supracrustal sequence consists
of thick mafic sequences of tholeiitic basalt, dolerite and gabbro intercalated with intermediate-felsic to calc-alkaline volcanics and immature volcanic derived sediments. These are over lain by detrital sedimentary units; turbidites, mudstones and carbonates in a series of sedimentary basins. The last of these sedimentary basins is the Tarkwa Group (Kitson 1928), a series of polymictic conglomerates, sandstones and shale (Davis et al. 1994). The Tarkwa Group is the youngest unit within the supracrustal succession (Pigois et al. 2003). Pre-, syn- and post-kinematic intrusive complexes have intruded these rocks. The tectonic events that deformed these supracrustal rocks and intrusive complexes occurred between ca. 2200 and 2000 Ma and is referred to as the Eburnean Orogeny (Bonhomme et al. 1962). This resulted in the inversion of supracrustal rocks, and their juxtaposition with the Kenema-Man Domain.

The entire SWAC has been intruded by at least three phases of Proterozoic or younger mafic dolerite dykes and sills. These cut all Birimian lithostratigraphic sequences (Jessel et al. 2015). The youngest rocks observed in the region are a series of sub-horizontal sandstones, dolomites and limestones. These unconformably overlie the Birimian supracrustal rocks and are Cambrian to Silurian in age (Trompette 1973).

Figure 1. Simplified geological map of the SWAC showing the location of the Archean Kenema-Man Domain and the Birimian Baoule-Mossi Domain (modified after M'lesi et al. 2004).

4 Lithostratigraphic Cycles

Six major stratigraphic groups can be correlated across the SWAC. These include the Lower Birimian Group – Cycle One, Lower Birimian Group – Cycle Two, the Upper Birimian Group – Cycle One, Upper Birimian Group – Cycle Two, the Tarkwa Group and the Bammain Volcanic Group.

4.1 Lower Birimian Group – Cycle One (ca. 2300-2180 Ma)

The Lower Birimina Group – Cycle One forms the base of the SWAC lithostratigraphic sequence and consists of thick sequences of spatially extensive basaltic lavas, gabbros and pyroxenites intercalated with bimodal intermediate andesitic – ryholitic volcanics and rare granitoids. Mafic rocks appear to be consistently of tholeiitic composition, although discreet, and spatially restrictive mafic and ultramafic rocks of calc-alkaline composition have been recognised e.g. Boromo Belt, Burkina Faso. In Burkina Faso the Lower Birimian Group is dated at 2273±19 Ma (Sounaille et al. 2008) and intruded by granites dated at 2253±15 Ma (Tshibubudze et al. 2013). The bimodal extrusive volcanism has ages ranging from ca. 2250, 2200 and 2220 Ma (Lahondere et al. 2002). The geochronological record suggests that the Lower Birimian Group emplaced continuously between ca. 2280 Ma and 2180 Ma.

4.2 Lower Birimian Group – Cycle Two (ca. 2180-2150 Ma)

The Lower Birimian Group - Cycle Two is conformable with the earlier group, but marks the disappearance of tholeiitic basaltic volcanism across the craton, and is associated with a major phase of calc-alkaline volcanism. The calc-alkaline volcanic sequence consists of andesite, dacite and rhyolitic lavas, pyroclastic flows and tuffs, which are locally reworked and intercalated with volcanoclastic sediments. This phase correlates with granitc rocks of similar composition in the eastern part of the Baoule-Mossi Domain. This Group was dated in Burkina Faso and Ghana at between ca. 2180 and 2150 Ma (Bruguier and Baratoux 2013; Castaing et al. 2003).
4.3 Upper Birimian Group – Cycle One (ca. 2150 – 2140 Ma)

Unconformably overlying the Lower Birimian Group, the Upper Birimian Group - Cycle One represents a sharp, regionally extensive transition from the calc-alkaline succession of the Lower Birimian Group to the deposition of volcaniclastic sediments. The base of this cycle consists of volcanic derived polymictic conglomerates intercalated with feldspathic sandstones and occasional andesite flows, shales and chemical sediments. The top of the group has a decrease in volcanic input. Direct U-Pb dating of andesitic flows intercalated within the volcaniclastics returned an age of 2142±2 Ma. Sefwi Belt, Ghana (Adadey et al. 2009) whereas, U-Pb detrital zircon ages yield a maximum depositional age of ca. 2160 to 2150 Ma e.g. Yanfolila Belt, Mali (Davis UnPub). The geochronological data suggest the emplacement of the Lower Birimian Group - Cycle One was between ca. 2150 to 2140 Ma.

4.4 Upper Birimian Group – Cycle Two (ca. 2140-2115 Ma)

The Upper Birimian Group – Cycle Two disconformably overlies older the Upper Birimian Group. It is represented by a series of large clastic sedimentary successions that dominate the geological map of the Baoule-Mossi Domain e.g., the Kumasi, Comoë-Sunyani and Siguiru Basins. They are largely composed of variably reworked greywacke, shale, chemical sediments (carbonaceous shales and graphite) and spatially restricted carbonate horizons and formations. U-Pb detrital zircon ages indicate a maximum age of deposition of ca. 2140 to 2125 Ma e.g Bruguier and Baratoux 2013. The existing data suggest that the Upper Birimian group – Cycle Two was emplaced between ca. 2140 and 2115Ma. The upper limit is constrained by the deposition of the onset of deposition of the Tarkwa Group at ca. 2115 Ma.

4.5 Tarkwa Group (ca. 2115 – 2095 Ma)

The Tarkwaian sediments are a group of spatially restricted, but regionally extensive polymictic conglomerates, coarse well bedded sandstones and shale that unconformably overlie the Birimian volcanics and clastic sedimentary sequences in narrow, elongate basins that are parallel to volcanic belts. The contact observed with the Birimian Group is typically faulted. The composition of the basal conglomeratic sequence is highly variable, reflecting local source, and in places can be subdivided into two successions. Diorite intrusives emplaced into the sequence at Tarkwa have a U-Pb age of 2097±2 Ma (Oberthur et al. 1998) constraining an upper age limit to deposition. U-Pb ages from detrital zircons yield a range of maximum depositional ages from ca. 2115 to 2095 Ma, with a full range of inherited zircons extending back to ca. 3550 Ma, (Lebrun et al. 2015; Pigois et al. 2003). The Tarkwaian Group deposition occurred between ca. 2115 - 2095 Ma.

4.6 Bandamian Calc-Alkaline Volcanic Group (ca. 2100-2070 Ma)

Late Calc-Alkaline volcanics rocks, termed the Bandamian (Hirdes et al. 1996) are a series of intermediate to felsic calc-alkaline volcanic and magmatic units that are spatially restricted along the Kenema-Man – Baoule-Mossi Domain boundary in Guinea (Kinero Volcanic Belt) (Thiébont 1989) and along the Sengal-Mali Shear Zone, within the Kedougou-Kenieba Inlier (Falcone Volcanic Belt) (Lahondere et al. 2002). These volcanics consist of dacitic to andesitic lavas (Bassot 1987) intercalated with ryholitic flows and tuffs (Hirdes and Davis 2002). These on-lap the Birimian sediments of the Siguiru and Kofi Formations (Milési et al. 1989). Direct U-Pb and Pb-Pb dating of andesitic and ryholitic flows yields between 2093±2 Ma (Freybisse et al. 1999) and 2070±10 Ma (Calvez et al. 1990).

4.7 Intrusives

A series of ultramafic-mafic intrusive complexes are recognised across the craton and are poorly constrained in time and space, however the dolerite dykes and sills have been constrained to two phases; ca. 2105 – 2100 Ma and ca. 2130 – 2115 Ma (Davis UnPub; Adadey et al. 2009). Felsic intrusive complexes are also ubiquitous in the Baoule-Mossi Domain with a recent compilation produced by (Parra-Avila 2015).

5 Discussion and conclusions

The lithostratigraphic synthesis of the SWAC lithostratigraphic record between ca. 2300 – 2100 Ma can be correlated across the entire Baoule-Mossi Domain. This may suggests that the geodynamic process acting upon the Baoule-Mossi Domain between 2300 – 2100 Ma was uniform across the domain. Within this time period, major breaks in the lithostratigraphy are observed to occur at ca. 2180, 2150, 2115 and 2100 Ma. The switch at ca. 2180 Ma represents the first major change, with the cessation of tholeiitic to calc-alkaline volcanism. Basalts are replaced on a craton scale by intermediate-felsic extrusive lavas and pyroclastic deposits; this is interpreted to be the beginning of convergent geodynamic setting and amalgamation of arc-like terranes. The second major event recorded in the lithostratigraphic pile is associated with the cessation of volcanism at ca. 2150 Ma, and the onset of large-scale sedimentation. These sedimentary basins display basal reworked volcanic material grading into thick sequences of greywacke at ca. 2130 Ma. This shutdown of volcanism and coeval detrital sedimentation indicates substantial uplift of the Baoule-Mossi Domain, possibly following final arc amalgamation and associated development of foreland sedimentary basin. The third major event across the craton is the deposition of the Tarkwa Group at ca. 2115 – 2097 Ma into narrow elongate basins. The short depositional window is indicative of a change in the regional geodynamics. The presence of Archean detrital zircons and clasts in the Tarkwa Group that can be directly to the Archean Kenema-Man domain, indicates that the Baoule-Mossi
domain was juxtaposed against the Archaean domain by ca. 2115 Ma, and the craton was subsequently exposed/uplifted. After ca. 2100 Ma new lithospheric-graphic components appear to solely develop on the western margin of the craton. This resurgence and shift in volcanism to the western Baoule-Mossi domain represents a fourth major event, but is diachronous.

Acknowledgements

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High-K to Shoshonitic Magmatism across the Northern Archean Kéména Man Margin (Guinea): Implications for the Eburnean Orogenic Gold Mineralizations

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Abstract. The Baoulé-Mossi Paleoproterozoic domain is known for its world-class orogenic gold deposits formed during the Eburnean orogeny between ca. 2.15 and 2.07 Ga. As part of the orogenic cycle, a suite of mafic and felsic potassic intrusive rocks was emplaced between ca. 2.10 to 2.08 Ga along the Paleoproterozoic margin of the Archean Kéména Man craton in Guinea. These high-K to shoshonitic intrusive rocks are characterized by (i) enrichment in LILE and LREE, (ii) strong Pb spikes and (iii) depletion in Ta-Nb-Ti. These features could suggest that the mantle source was metasomatized by Pre-Eburnean subduction. Two different Hf model ages were obtained for these Paleoproterozoic shoshonitic rocks suggesting two distinct sources involving crust extraction from the depleted mantle at ca. 2.7-2.4 Ga and at ca. 3.7-3.2 Ga. We envisage that these shoshonitic magmas derived by partial melting of metasomatized lherzolitic mantle in response to lithospheric delamination after the Paleoproterozoic Baoulé-Mossi/Archean Kéména Man collision during the late Eburnean orogeny. We propose that this reworking magmatic event at ca. 2.10-2.08 Ga could have remelted residual Au-rich cumulates left in the deep lithosphere by arc magmatism and be responsible for large-scale fluid migration related to late orogenic gold mineralizations in the Baoulé-Mossi domain.

Keywords. Eburnean orogeny, delamination, potassic magmatism, gold mineralizations

1 Introduction

The West African Craton hosts a number of world-class orogenic gold deposits formed during a narrow time window toward the late stages of the Eburnean orogeny between ca. 2.15 and 2.07 Ga (Milesi et al. 1992; Oberthür et al. 1998; Goldfarb et al. 2001; Feybesse et al. 2006; Béziat et al. 2008; Fig. 1a). Deposit-scale studies conducted over the past decade traditionally investigated the metallogenic characteristics of the deposits including its mineral and structural habit, the timing of gold deposition and evaluate possible metal sources (Milesi et al. 1992; Béziat et al. 2008). Traditionally, two plausible sources for mineralising fluid were suggested: (i) metamorphic rocks or (ii) felsic-intermediate magmas (Lawrence et al. 2013). Regardless of these deposit scale characteristics, the geodynamic engine empowering the mineralisation across the Baoulé-Mossi domain remains uncertain. In this study, we apply the mineral system concept whereby gold deposits are viewed as small-expression of orogen- to lithosphere-scale processes (Bierlein et al. 2006; Groves and Bierlein 2007; McCuaig et al. 2014 and references therein). We present complementary geochemical whole-rock data and U-Pb coupled to Lu-Hf isotope analyses on zircon from plutonic rocks sampled along the Paleoproterozoic margin of the Archean Kéména Man domain in Guinea. This approach allows to unravel the processes controlling crust production, reworking and accretion, which in turns may have been critical geodynamic elements for the exceptional gold endowment of the Paleoproterozoic Baoulé-Mossi crust.

2 Geological setting

The West African Craton includes two principal Precambrian domains: the Réguibat Rise to the North and the Leo-Man Rise to the South (Rocci 1965). The Leo-Man Rise is composed by an Archean cratonic nucleus in the southwest, the so-called Kéména-Man domain, surrounded by some Paleoproterozoic belts in the north and east defining the Baoulé-Mossi domain (Feybesse and Milesi 1994; Fig. 1). The Baoulé-Mossi domain consists of low-grade Birimian greenstone belts intruded by Tonalite-Trondjemite-Granodiorite (TTG) suites and granitoids (Baratoux et al. 2011 and references therein). Based on petrography, geochemistry, geochronology and airborne magnetic Baratoux et al. (2011) and radiometric signatures (M etaka et al. 2011), the plutonic rocks of the Baoulé-Mossi domain can be divided into three groups. The first magmatic episode is characterized by calc-alkaline biotite-amphibole bearing TTG suites dated from ca. 2.25 to 2.12 Ga. The second episode is represented by calc-alkaline K-feldspar-biotite bearing granodiorite-granite intrusions dated between ca. 2.12 and 2.09 Ga. Both M E1 and M E2 magmatic events represent a major period of crustal growth. The third episode is dominated by potassic K-feldspar bearing granites and restricted to late orogenic stages between ca. 2.11 and 2.07 Ga. Following the main period of magmatic accretion of the juvenile crust between ca. 2.20 and 2.15 Ga (Feybesse et al. 2006), the Baoulé-Mossi Paleoproterozoic crust was deformed during the Eburnean orogeny from ca. 2.15 to 2.07 Ga (Bonhomme 1962).
Several weakly foliated and unfoliated plutonic samples were collected for geochemical (whole-rock by ICP-AES and ICP-MS), geochronological (U-Pb by LA-ICP-MS) and isotopic (Lu-Hf by MC-LA-ICP-MS) analyses.

4 Results

4.1 Whole-rock geochemistry

The plutonic rocks from the Baoulé-Mossi domain plot in the Q-A-P normative classification diagram in the quartz monzodiorite (55.70<SiO₂<64.60 wt.%) and monzogranite (71.60<SiO₂<73.70 wt.%) fields. Quartz monzodiorites show high-K calc-alkaline affinities. They present high-K calc-alkaline to shoshonitic affinities. In primitive mantle-normalized spidergram, both quartz monzodiorite and monzogranite display negative Nb-Ta, P and Ti and strongly positive Pb anomalies. Negative Eu anomalies are steeper for monzogranites. They are enriched in LILE and LREE and present high Rb/Sr (0.1-1.5) and low Ce/Pb (3.16-10.88) ratios. In the Kéména-Man domain, plutonic rocks plot in the granodiorite field (73.00<SiO₂<74.40 wt.%). These granodiorites present poor ferro-magnesian elements (Fe₂O₃T + MgO + TiO₂ < 1.5) and low Ce/Pb (3.16-10.88) ratios. In the Kéména-Man domain, plutonic rocks plot in the granodiorite field (73.00<SiO₂<74.40 wt.%). These granodiorites present poor ferro-magnesian elements (Fe₂O₃T + MgO + TiO₂ < 2.90 wt.%) and high Na₂O (3.91-4.89 wt.%) contents and exhibit medium- to high-K calc-alkaline affinities. In primitive mantle-normalized spidergram, these samples show Na-Ta and Ti anomalies but no Sr nor Eu anomalies.

4.2 Zircon U-Pb dating and Hf isotope

Six samples were collected in the Baoulé-Mossi domain for U-Pb dating and Hf isotopic analyses including two quartz monzodiorites (JD035 & JD071) and four monzogranites (JD018, JD019, JD033 & JD034). The quartz monzodiorites were dated at 2093±4 Ma and 2096±6 Ma whereas the monzo-granites returned younger U-Pb ages ranging from 2098±9 to 2082±6 Ma. Two monzogranite samples JD033 and JD034 present inherited zircon grains with U-Pb ages ranging from ca. 3.7 to 2.8 Ga. Considering only Paleoproterozoic U-Pb ages, all these samples display two distinct groups in the (176Hf/177Hf) versus 207Pb/206Pb age (with degree of concordance > 98%) diagrams (Fig. 2). One cluster (JD018, JD019 & JD071) is characterized by higher (176Hf/177Hf) ratios versus 207Pb/206Pb age (with degree of concordance > 98%) diagrams (Fig. 2). The second cluster (JD033, JD034 & JD035) is characterized by lower (176Hf/177Hf) ratios ranging from 0.281373 to 0.281547 and calculated εHf, ranging from -2.38 to 4.05. The second cluster (JD033, JD034 & JD035) is characterized by lower (176Hf/177Hf) ratios ranging from 0.281002 to 0.281163 and calculated εHf, ranging from -16.61 to -9.31. The Archean inherited zircon grains (JD033 & JD034) present (176Hf/177Hf) ratios ranging from 0.280245 to 0.280848 and calculated εHf, ranging from -10.94 to -2.11. In the Kéména-Man domain, the Archean inherited zircon grains (JD033 & JD034) present (176Hf/177Hf) ratios ranging from 0.280640 to 0.280878, from 0.280700 to 0.280754 and from 0.280821 to 0.280866 with calculated εHf, ranging from -19.49 to 1.47, from -7.06 to -1.17 and from -3.99 to -2.46 (Fig. 2).

3 Methods

A geological transect across the transition from the Archean Kéména-Man nucleus to the Paleoproterozoic Baoulé-Mossi domain was conducted in 2013 (Fig. 1b).
5 Discussion

5.1 Reworking versus juvenile growth of the Birimian Paleoproterozoic crust

Results of U-Pb dating of magmatic zircon grains demonstrate that a period of magmatic activity was continuous between ca. 2.10 and 2.08 Ga in the Baoulé-Mossi Paleoproterozoic province of north-eastern Guinea (Fig. 1). These results are in good agreement with previous U-Pb ages ranging from 2.09 to 2.07 Ga obtained on magmatic zircon (Egal et al. 2002). These Paleoproterozoic intrusive rocks present clearly two different Hf signatures suggesting two different sources. This suggestion is also supported by geochemical data. Samples with high ($^{176}$Hf/$^{177}$Hf)$_\text{t}$ ratio are characterized by high K$_2$O and Rb contents and vice versa. Paleoproterozoic zircon grains which have more radiogenic Hf signatures show mostly super-chondritic $\varepsilon$Hf($^{2L1}$, Ga) values with calculated TDM model ages ranging from ca. 2.7 to 2.4 Ga. These results suggest that the northernmost magmatic rocks of Guinea belong to a juvenile crust extracted from a depleted mantle source (but later enriched maybe in volcanic arc context), with no significant reworking of Archean crust. In contrast, Paleoproterozoic zircon grains which have less radiogenic Hf signatures show sub-chondritic $\varepsilon$Hf($^{2L1}$, Ga) values with calculated TDM model ages ranging from ca. 3.7 to 3.2 Ga. Thus, these data support that the southern magmatic rocks are formed by reworking of a pre-existing Archean crust. This interpretation is also evidenced by the presence of inherited Archean zircon grains in the southernmost monzogranites.

The monzogranites were interpreted in the past as produced above a subduction zone, sharing geochemical analogies with the magmatic suites of recent active margins (Egal et al. 2002). However, geochemical characteristics of these rocks do not match all features of adakites (Martin et al. 2005). The combination of high contents of the incompatible elements Rb-Th-U-K-Pb-LREE, Nb-Ta-Ti depletion and low Ce/Pb suggest that an enriched component (enriched mantle source or crustal contamination) was involved in the genesis of these plutonic rocks. Accordingly, we propose that the potassic intrusive rocks may be derived by partial melting of a metasomatized lithospheric mantle and/or related to crustal contamination. The high Rb/Sr ratios suggest the presence of philogipite in the source region. When coupled with the coincident Pb spikes and Nb-Ta-Ti negative anomalies the geochemical signature of the monzogranites point towards an enriched mantle source. We therefore propose that this magmatic activity is related to post-subduction arc contraction caused by collision leading delamination of the subcontinental lithospheric mantle (Fig. 3). This collision involved juvenile Paleoproterozoic arc terranes, known as the Baoulé-Mossi domain, accreted to an Archean block, known as the Kénéma-Man craton. A possible crustal contamination during magma ascent is illustrated by the presence of inherited Archean zircon grains for the southernmost monzo-granites. Archean crust is clearly expressed in the south with the presence of TTG granitoids dated at ca. 3.09 Ga (Leonian cycle) and ca. 2.88 Ga (Liberian cycle) (Thiéblemont et al. 2004) and presented TDM model ages ranging from ca. 3.5 to 3.4 Ga. Other scenarios as slab break-off also described during late- to post-collisional periods could explain the high-K to shoshonitic affinities of these granitoids but fail to explain their large lateral spatial extent, across hundreds of kilometres.

5.2 Implications for gold mineral system

Ore-forming processes involve the concomitant development of several critical elements including a favorable lithosphere architecture, transient geodynamic framework, metal fertility and preservation of primary depositional zone (McCuaig et al. 2014 and references therein). As proposed by Bierlein et al. (2006), it is suggested that the thickness of Subcontinental Lithospheric Mantle (SCLM) at the time of gold mineralization controls the potential for giant gold deposits: the thinner the SCLM, the greater the potential for high heat flux from asthenospheric upwelling. In this study, we propose a post-collisional delamination of a juvenile and non-stabilized lithospheric mantle offers a possible transient geodynamic process that may have been critical to the formation of ore deposit in the West African Craton.

In this interpretation the late potassic magmatism bloom that occurs between ca. 2.10 and 2.08 Ga is seen as a critical magmatic even driving large-scale fluid and metal migration. Post-collisional potassic magmatism produced through the remelting of previously subduction-modified arc lithosphere has recently been demonstrated as a fertile source for epithermal Au deposits are the (Richards 2009). Indeed, metasomatized mantle lithosphere or hydrous lower crustal cumulates residual from first stage arc magmatism are rich in sulfides and thus represent a fertile source for hydrous Au-rich magmas in post-subduction context (Richards 2009).

Metallogeny of North and West Africa 1593
Figure 3. Post-collisional lithospheric mantle delamination model between ca. 2.10 and 2.07 Ga.

6 Conclusion

The transition from the Paleoproterozoic Baoulé-Mossi belts to the Archean Kéméné-M an domain in Guinea is intruded by late weakly to unfoliated high-K to shoshonitic intrusive rocks dated between ca. 2.10 and 2.08 Ga. This transition from juvenile to old domains is supported by the different Hf signatures. Indeed, one generation of potassic intrusive rocks is characterized by positive \( \varepsilon_{Hf} \) (2.1 Ga) values and Hf model ages between ca. 2.7 and 2.4 Ga, age of the extraction of the crust from a depleted mantle. The second generation of potassic intrusive rocks present negative \( \varepsilon_{Hf} \) (2.1 Ga) and Hf model ages between ca. 3.7 and 3.2 Ga. The presence of inherited Archean zircon grains in this second generation of intrusive rocks is also consistent with the reworking of an old Archean crust. The scenario of a collision during the late Eburnean orogeny leading to the mantle lithosphere delamination allows two explain both Hf signatures and the geochemical affinity of these potassic intrusive rocks. A previous subduction period is invoked to explain the presence of a metasomatized mantle. Post-subduction magmas remelting Au-rich residual sulfide left in the deep lithosphere by arc magmatism are also responsible of large-scale fluid migration. This tectonothermal event is proposed as a possible engine empowering late orogenic gold mineralizations in the Baoulé-Mossi domain.

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Mineralogical and Structural Evolution of Vein Mineralization in the Zgounder Ore Deposit (Central Anti-Atlas, Morocco)

Abstract. The Zgounder ore deposit is hosted in Neoproterozoic volcano-sedimentary series. The mineralization is dominated by native silver with few silver sulfosalts (acanthite, pearceite), and base-metal sulfides. Both arsenic content in arsenopyrite and homogenization temperatures of fluid inclusions indicate initial conditions of high temperature. Similarities are obvious with the neighbouring silver ore deposit of Imiter and lead to consider Zgounder as another example of Neoproterozoic epithermal deposit in the Anti-Atlas of Morocco, a region that appears more and more as a silver metallogenic province.

Keywords. Silver, Zgounder, Imiter, veins, Late-Neoproterozoic, Morocco

1 Introduction

The Zgounder ore deposit was recognized and has been operated since Antiquity. The Zgounder silver deposit was mined from 1955 and is currently closed in 1990 but has extensive reserves and has then be the subject of recent investigations from the Fifties to the Present. The deposit is located on the topographic sheet Talliwine 1/100 000 in the Taroudant province about 150 km south of Marrakech, 210 km to the east of the city of Agadir and a few kilometers from the village of Askaoun (Figure 1).

It is located in the western part of the Central Anti-Atlas on the western flank of the Precambrian massif Siroua.

In the last decade, the Maya gold and silver group resumed exploitation and exploration in the area and drilled several boreholes. This study is based on the description of these boreholes on petrographic and mineralogical description of the numerous samples collected in the drill cores. New data on the polymetallic mineralization of the ore deposit the Zgounder mining, particularly the assemblage dominated by Ag mineralization are presented.

2 Geological setting and mineralization

The Zgounder deposit is located in the western part of the Central Anti-Atlas, on the western flank of the Precambrian Siroua massif (Figure 1), which occupies a special position between two major geodynamic structural domains:

(i) a northern area, attached to Pan-African and affected by collapses structures;

(ii) a meridional and Eburnean area belonging to a stable west African craton.

Figure 1. Synthetic Geologic presentation of Precambrian belt of Anti-Atlas (after Choubert 1963).
The Zgouber deposit is the oldest and the most famous silver deposit in Morocco after Imiter. The mineralization is hosted by metavolcano-sedimentary formation (Zgounder formation) of Neoproterozoic age, which overlie an andesitic basement. (Figure 2).

This formation is bordered to the west by the granodiorite of Askawn, and in the east by a volcano-clastic Ediacarian material. It is on the edge of the Pan-African suture zone recovered in monotone (Asladay 1977) in EW direction with a general discharge south. From north to south, we found the following formations:

1) blue formation at the base: made of sandstone, greywacke and siltstones, it ends with a level orange rhyolite;
2) brown formation made of sandstone micaceous schists and levels of breccias and pelites at the top of this formation has introduced a doleritic dyke;
3) black formation: it begins with a volcanic complex (ignimbrite breccias rhyolites ...), which is the roof of the mineralized facies at the top of the brown formation.

The mineralization is formed by native silver, pyrite, chalcopyrite, sphalerite, galena, with Ag-Sb-Pb sulfosalts and argentite that have been precipitated during successive mineralizing fluid circulations.

3 Processing TM images of the district of Zgounder

Compared to the regional geological map and field study of Zgounder area, we observed the alteration halo oriented EW at the Neoproterozoic units in the Wadis. To the east, the mineralization is stopped by a rhyolitic injection. Somewhere, the contact between rhyolite and enclosing units, is mineralized on native silver Fig. 4.
4 Tectonic setting

The structuring of the Zgounder region is related to the final phase of the Pan-African orogeny B2 affecting the upper Proterozoic courses of Anti-Atlas (Leblanc 1975). This phase, characterized by a low intensity and brittle deformation, materialized in the region by faults and fracturation of Precambrian formations where the dolerite rhyolite dykes are mainly oriented E-W.

Silver deposit of Zgounder shales are affected by many different types of faults that form zones of shredding.

In the area, the general structure is monocline oriented EW. The terranes are affected by flexures and directional NE or NEN folds.

5 Discussion

It can be concluded that there is an establishment of a zonation from East to West in the deposit Zgounder (Figure 5).

5.1 Eastern zone

In the east of the Zgounder silver deposit, chlorite and sericite schists are generally east-west and dips ranging from 60° to 80° south. At the far east, the schistose units thins and closes at its tectonic contact with the rhyolites. In this region, dolerite sills are not observed. Also, the tectonic and hydrothermal grinding structures are less developed or invisible (back filled with waste rock piles), so the mineralization is visible only in the contact between rhyolite and blach shales. It is represented generally by some sphalerite, galena and pyrite. This contact can be the subject of exploration core sampling to seek extension of this mineralization downstream.

5.2 Central zone

This is the most important area of the deposit. The direction of the shale is generally E-W dipping 60° to 70° south, but local inverse dips (to the N) can often be
seen in northern trough body next to Talat N’ouna, this dip becomes stronger and even reaches the vertical in some cases this is due to a great EW fault at this talweg.

5.3 Western zone

In the west direction of shale is almost constant N 75° to N 80° with a dip that varies to the South, but with local vice versa, especially in the vicinity of faults. The contact between shales and ignimbrites -rhyolites is normal. Heading towards the far west, the dolerite sill thins and then closes.

Tectonically, the West zone is affected by multidirectional faults of different types (strike-slip, normal faults ...) that often develop more grinding zones at least broad. A fault N 85 and dipping 75°S and quartz filling and oxides can be sampled systematically for analysis of gold (Au). On may also encounter folds axial plane N 45 to N 50°. The mineralization on the surface decreases in the shales. Rare outcrop encountered pyrite and arsenopyrite especially on the banks of Zgounder’s Wadi.

6 Conclusion

Similarities are obvious with the neighbouring silver ore deposit of Imiter (Popov et al. 1986; Tuduri 2005; Gasquet et al. 2005; Levensse 2001) and lead to consider Zgounder as another example of Neoproterozoic epithermal deposit in the Anti-Atlas of Morocco, a region that appears more and more as a silver metallogenic province.

References

Gold in Co-Ni ore from Bou Azzer El Graara (Central Anti-Atlas, Morocco): Mineralogy and Structural Control

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Abstract. The cobaltiferous mineralization in Bou Azzer occurs in the form of lodes and pockets at the contact of serpentinite and felsic rocks, mainly Co-Ni-Fe arsenides, sulpharsenides, sulphides, brannerite-uraninite, bismuth, and gold. Whole-rock analyses of ore samples show that gold is irregularly distributed in the ores (0.1-65 g/t Au). Maximum contents of Ag, Pt, and Pd are 338 g/t Au, 43 ppb Pt, and 17 ppb Pd. Gold correlates positively with Ag, Co, Ni, and Cu. In Co-rich ore, gold content ranges from 3 to 49 g/t, whereas the other arsenides contain only 0.5-2 g/t Au. Both in the ore of western and eastern part of the district, gold is well expressed, native gold (2-50 μm) occurs, with decreasing abundance, in: skutterudite, cobaltite, gersdorffite, chalcopryte, rammelsbergite, and molybdenite-brannnerite. In the eastern part (Ait-Ahmame); abundant free grains of gold are occur outside the Co-rich zone, disseminated in listvenite; this gold is probably related to late Hercynian mineralization along fracture zones associated with sulphide and hydroxide minerals (mainly annabergite-heterogenite). EPMA analyses indicate that gold ranges in composition from 40-92 wt. % Au, 9-57 wt. % Ag, and up to 2.28 wt. % Hg. Individual gold grains typically are chemically homogeneous, and two populations are recognized: native gold and electrum.

Keywords. Bou Azzer, gold, Co-Ni-Fe arsenides, sulpharsenide and sulphide mineralization.

1 Introduction

The cobalt deposits of Bou Azzer district, located about 140 km SW of Ouarzazate, are associated with the Precambrian greenstone belt along the southern Atlasic fault in the Bou Azzer-El Graara inlier. This inlier contains more than 100 deposits of Co-arsenides, such as Michoui in the west to Ait Ahamne in the east (Fig. 1); it is well known for these types of deposits with gold as an important by-product, and also for podiform chromitites, and the mined-out Bleida copper deposit.

The Co-As ores have been mined since 1930 and have yielded approximately 70,000 t of Co and about 5 t of gold. Currently, the CTT/M anam has an annual production capacity of 2500 t of Co, 10,000 t of As, 300 t of Ni, and 250 kg of Au. In the present paper, we present new data on (i) the mineral chemistry of the Co-Ni ores, and (ii) the chemistry of gold minerals identified in the ore from different deposits of the Bou Azzer ophiolite.

2 Geological context

The Bou Azzer-El Grâara inlier corresponds to a Variscan structure that extends along the foothills of the Anti-Atlas Mountains. The Precambrian basement domain has two main subdivisions:

1- A metamorphic supergroup that includes: (i) orthogneiss and metagabbro in the south (Iigrane, Tazizaourop, Oumillii, and Bou Azzer), formerly described as Paleoproterozoic (Leblanc 1975), and whose the protolith is dated to ca. 750 Ma (Lemos et al. 2006); (ii) sedimentary rocks of the Neoproterozoic platform on the northern margin of the West African craton, which is associated with the copper-sulphides mineralization of Bleida; (iii) volcano-sedimentary rocks “Tichibanine-Bengad” that have a well-established arc affinity (Leblanc 1975; Bodinier et al. 1984); and (iv) the ophiolitic complex of Bou Azzer, which although incomplete and strongly dismembered, contains all units of an ophiolite suite. These units are entirely metamorphic and intruded by diorites dated at ca. 650 Ma (Inglis et al. 2005).

The cobalt mineralizations at Bou Azzer is spatially and genetically associated with serpentinites, resulting from the combination of hydrothermal fluids and a leaching of some cobalt and nickel from the serpentinites (Maacha 2011).

2- A non-metamorphic supergroup, which is major discordance with the Panafican substrate, includes: (i) The clastic series of the Tidilline Group, folded during late Panafican orogeny along major faults; and (ii) the pyroclastic lava and volcaniclastic sediments of the Ouarzazate Group that rest in angular unconformity on the Tidilline Group.

3 District metallogeny

The Bou Azzer inlier contains more than 100 cobalt arsenide ore bodies (Fig. 1). Their morphology depends largely on the rheology and structure of the host rocks. During our field work (underground and surface), the analysis of data from this field work has enabled us to produce a new classification model, in which we distinguish six types of orebodies:

Metallogeny of North and West Africa 1599
Panafrican alteration of the serpentine, constitutes the discordant contact between serpentinites and felsic rocks. These bodies are generally in the form of columns oriented ENE, and localized along the tectonic contact between the serpentinites and quartz diorite rocks. These ore bodies are of large dimension with thicknesses exceeding 10 m and extents at depth of more than 700 m. The listwenites (quartz-carbonate gange), which are products of early alteration of the serpentinite, are the main lithological control of the mineralization.

b- The Meshou deposit: this type includes all veins of second order whose orientation varies between NW and NE. They are hosted by diorite not far from massifs of the serpentinites, in the form of extensional veins. Lateral extents average 30 m, with an average depth of 200 m and limited thickness of 1 m.

c- The Tamdrost type: this style of mineralization includes extensional veins, transtensional veins, and fault-hosted massive bodies. They are associated with the discordant contact between serpentinites and felsic volcanic rocks of the Ouarzazate Group. The “carapace of Ambed,” which is product of exogenous late Panafican alteration of the serpentine, constitutes the main exploration guide for this type of mineralization, including for the flat-lying bodies commonly termed “amas.” The mineralization extends on an extension beyond 300 m and 50 m wide. Mineralization of this type is particularly rich in nickel. The oblique veins hosted by the felsic volcanic rocks are characterized by pervasive hydraulic fracturing.

d- The Aghbar deposit: this type is localized by doming of the serpentinite owing to its rheology. Mineralization is focused on the flanks of the diapir related to synchronous fracturing. The average thickness is 10 m with a depth of 400 m. The altered serpentinite hosting the arsenides is similar to that of the Tamdrost type. The “carapace d’Ambed” is the main lithological control on the mineralization where fracturing and dissolution processes played a major role in governing the size of the deposits.

4 Analytical techniques

Samples from surface, drill core, and underground workings in operating mines (up -420 m depth) were analyzed by Actlabs, Canada, using ICP-OEM and NIS fire assay-INAA methods. At the BGR, light and scanning electron microscopy (SEM), whole-rock XRF and electron microprobe analysis (EPMA) of selected minerals were performed. Gold and all mineral phases were analyzed using a CAMECA SX100 electron microprobe at the Federal Institute for Geosciences and Natural Resources, Hannover, Germany (BGR); operating conditions were 20 kV accelerating voltage and 30 nA beam current. Counting times were 10 s or 20 s for all elements. The following X-ray lines and standards were used: Os_Mα, Ir_Lα, Pt_Lα, Au_Lα, Ru_Lα, Rh_Lα, Pd_Lα/Lβ, Ag_Lβ, Fe_Kα, Co_Kα, Ni_Kα, Cu_Kα, Se_Lα, Te_Lα, Bi_Mα, Sn_Lα, and Sb_Lα (metals), Pd_Lα/Lβ (synthetic PdS), S_Kα (synthetic Pt0.7Pd0.3S, PdS, and pyrite), As_Lα (synthetic GaAs). Raw data were corrected using the PAP program supplied by CAMECA. Additional corrections were performed for enhancement of data for
Rh, Pd, Ag, Cu, As, and Sb using secondary lines. Detection limits of the analyzed elements are on the order of 0.1 wt. %.

5 Ore chemistry and mineralogy

Field work and microscopic investigation show that the ores have been very strongly tectonized and display several phases of cataclasis and crystallization, resulting in the formation of complex breccias and banded mylonites. Ore minerals are disseminated to massive. The main assemblages identified in this work contain [Co-Ni-Fe] tri-arsenides, di-arsenides, monoarsenides, sulpharsenides, selenides, sulphides, sulphasalts, various oxides, and native elements dominated by gold and bismuth.

Gold: Gold grains up to 50 µm are present in association with the Co-Ni-Fe and Cu mineral phases. Gold is an important by-product of mining in the Bou Azzer district and has been the focus of numerous previous investigations (Leblanc and Fischer 1990; En-Naciri 1995; El Ghorfi et al. 2005; Amed et al. 2009).

Gold is commonly homogenous and occurs in different specific forms: (i) open-space fillings in fragments and cracks in skutterudite; (ii) in cobaltite and rammelsbergite and as intergrowths with chalcopyrite, digenite, hematite, calcite, and quartz (Fig. 3-E and F); (iii) fine-grained (<50 µm), inclusions within primary Ni-rich phases (nicolette, skutterudite-I; Fig. 3-A, C and D), or in later-formed Co- and Ni-rich minerals, and (iv) comparatively large crystals (up to 1 mm) in the chlorite-carbonate matrix associated with molybdenite, oxides, and hydroxides.


Nicolette typically contains inclusions of gold and occurs in various forms: as inclusions within skutterudite-I, and in the contact between rammelsbergite and gersdorffite or completely enclosed in rammelsbergite.

Rammelsbergite forms inclusions in, or is associated with, gersdorffite. Among 51 analyses obtained, some grains show a composition close to the theoretical formula [NiAs2] with a Ni/As ratio varying between 0.48 and 0.53 wt. %.

Löllingite: EPMA analysis reveals the existence of three compositional types: (i) Ni-rich löllingite, which commonly forms inclusions in niccolite within zoned skutterudite, and has an average composition of [(Fe0.60Ni0.28Co0.07)] A5.96S0.08; textural relationships and chemistry show that this mineral is related to an early stage in the paragenesis; (ii) Co-rich löllingite, occurring in the matrix in association with safflorite and locally replaces skutterudite in growth zones, the average composition being [(Fe0.71Co0.26N1.008) A5.94S0.05]; and (iii) löllingite (ss) which forms fibrous rosettes, isolated in the matrix, which show clear zoning, including an iron rich-center; its composition is relatively uniform [(Fe0.96Co0.033 Ni0.01)A5.88S0.11] and approaches the theoretical formula of FeAs2.

Safflorite: EPMA analyses (n = 21) performed on safflorite reveal the existence of two types: (i) one having an average composition of (Co0.78Ni0.08Fe0.15) A5.95S0.05, which forms inclusions in skutterudite or is isolated in the quartz-carbonate matrix as zoned aggregates of safflorite-löllingite; and (ii) a second type with a composition of (Co0.69Ni0.007Fe0.28) A5.95S0.05; this type of safflorite uniformly shows a chemical zoning of cobalt and iron. Zoned crystals display either an enriched center in löllingite-safflorite or, most commonly, a center of safflorite surrounded by alternating thin lamellae of löllingite and safflorite.

Skutterudite: This is the predominant cobaltiferous mineral, represented by massive or disseminated crystals up to ~5mm in size, or in aggregates distributed in the quartz-carbonate gangue. EPMA analyses (n = 137) reveal two generations: (i) Skutterudite-I or Ni-rich Skutterudite, commonly with inclusions of electrum or gold, is characterized by relatively high Ni contents with the average composition of (Co0.63Ni0.17Fe0.08) A5.88S0.06; and (ii) Skutterudite-2, with native gold inclusions (Fig. 3-C), is relatively rich in cobalt and has a wide range of compositions from (Co0.79Ni0.09Fe0.011) A5.95S0.05 to (Co0.84Ni0.08Fe0.08) A5.90S0.05.

Gersdorffite: this mineral occurs in association with nicolette, chalcopyrite, and cobaltite, with an average chemical formula of (Ni0.72Fe0.28Co0.06) A5.98S0.02. Cobaltite: commonly contains inclusions of native gold. It is associated with safflorite-löllingite, and rarely with skutterudite bands. The average chemical composition is: (Co0.78Ni0.16Fe0.05) A5.95S0.08 with a AS/S ratio of all the analyzed cobaltite of 2.43.

Sulphides are dominated by chalcopyrite, digenite, covellite, molybdenite, pyrite, sphalerite, and bismuthinite (Bi3S5). Sulphosalts include tetrahedrite [(Cu, Fe)2(Sb, Se)3] and clausthalite (PbSe). Bismuth is exceptionally associated with bismuthinite. Oxides are chromite, magnetite, rutile, anatase, annabergite, heterogenite, erythrite, brannerite [(U, Ca, Y, Ce) (Ti, Fe)3O6] and uraninite (UO2).

6 Discussion

The Bou Azzer cobalt deposits consist of cobalt (Ni-Fe) arsenides with accessory sulpharsenides, Cu-sulfides, molybdenite, brannerite-uraninite, and gold in a quartz-carbonate gangue. Carbonates and brannerite that coexist with molybdenite yield, respectively, ages of 308 ± 31
M a (Sm-Nd) and 302 ± 9 M a (U-Pb). These new ages suggest that the principal Co-Ni-As-(Au) mineralization at Bou Azer, occupying the main ore-bearing structures, formed during the Hercynian orogeny (Oberthür et al. 2009). Field studies show that the ore is mainly controlled by tectonic structures within the trend N40°E to N120°E (Fig. 2), and has undergone several phases of brecciation and recrystallization related to late Pan-African and Hercynian deformations. Important hydrothermal remobilization occurred mainly along the northern border of the Bou Azer district and produced the varying shapes of the orebodies: lodes, veins, stockworks, complex shells, and flat lenses (Fig. 1 and 2). Gold that is evidently associated with cobalt (Ni-Fe) arsenides probably precipitated with the cobalt during the first stages of mineralization. It is mentioned that the arsenides are the main source rock for gold, as are the ultramafic rocks for most Archean gold deposits (e.g., Kerrich et al. 1981). The gold content of the Bou Azer arsenides is very low (<15 ppb). The Bou Azer quartz-carbonate rocks have 0.01 to 8 g/t Au. This type of gold in carbonized ultramafic rocks is known in Archean greenstone belts and in many ophiolite complexes (Leblanc and Fisher 1990); the resulting quartz-carbonate rocks correspond to listwanenite (Plosko 1963), and are considered as important gold target for exploration in studied area. Gold may have been leached from the serpentinites by CO2-rich fluids and taken into solution in the form of A s-A u complexes. At the contact of the carbonized rocks, the A s-A u complexes precipitated these metals together with cobalt arsenides (Leblanc and Fisher 1990).

During this work, we have demonstrated the mineralogical expression of gold in Bou Azer ore deposits. Results reveal the presence of five types of gold occurrence (Fig. 3): (i) microscopic primary inclusions within niccolite; (ii) small rounded inclusions within skutterudite-I; (iii) larger inclusions in skutterudite-II, rammelsbergite, cobaltite, and chalcocypirite; (iv) open-space fillings mainly in skutterudite associated with chalcocypirite and digenite; and (v) large millimeter-size grains in a carbonate matrix associated with molybdenite and brannerite.

The composition of the gold grains is relatively different in various ore types (Fig. 4), being higher in A g in the first (i) than in the last (v). There is a general inverse correlation between A u and A g contents in gold analyses. The A u contents of the first type (i) of gold show a wide range from 10 to 45 at. %, with A g contents varying from 55 to 90 at. %. The gold contents of the second type (iii) to (v)) range from 53 to 79 at. %, with A g contents varying from 20 to 46 at. %, and up to 2.28 wt. % Hg, with detectable amounts of Bi and S. The free gold grains associated with oxide minerals (mainly annabergite) in the carbonate matrix vary in A u content from 93.0 to 98.7 at. %; A g contents of this type of gold range from 6.7 to 1.2 at. %.

Finally, our new mineralogical analyses provide an aim to assessing the gold potential of specific sector in the Bou Azer district, and may be of interest for improved understanding of the mineralogical expressions of the gold.

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Microstructural and Textual Evidence for Protracted Polymetallic Sulphide Mineralization in the Jebilet Massif (Variscan Belt of Morocco)

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Abstract. Microstructural and textual relationships among pyrrhotite, pyrite, and deformation/metamorphism in several Cu ± Zn ± Pb deposits of the Jebilet massif indicate a protracted period of polymetallic sulphide mineralization. Pyrrhotite is generally deformed and could result from remobilization of primary syngenetic pyrrhotite. However, at least part of the pyrrhotite mineralization is syntectonic, formed by direct crystallization from a syntectonic metamorphic fluid. Pyrite is generally encountered as (i) primary syn- to late tectonic pyrite formed by direct crystallization from a syn- metamorphic fluid and late to post-metamorphic mineralizing fluid, and (ii) secondary late to post-metamorphic pyrite formed by dissolution of the pre-existing pyrrhotite by late to post-metamorphic fluids. Primary syngenetic pyrite has not been observed, nor does it transform to pyrrhotite during prograde metamorphism.

Keywords. Pyrrhotite, Pyrite, Metamorphism, Massive sulphide deposits, Morocco.

1 Introduction

The central part of the Jebilet massif of northern Morocco comprises Carboniferous sedimentary rocks, deformed and metamorphosed to low grades during the Variscan, and hosts a significant polymetallic massive sulphide mineralization (see overview by Lusty et al., this volume) together with numerous syntectonic intrusions. The abundance of pyrrhotite and the rarity of pyrite is a conspicuous feature of the Jebilet massive sulphide deposits, and make the Moroccan massive sulphide deposits rather unusual (Marcoux et al. 2008, Moreno et al. 2008). The origin of these sulphide minerals (i.e., primary or metamorphic) in the Jebilet massive sulphides is uncertain. Study of the detailed textural relationships of the sulphides is very important to understand the genesis of these deposits. There are three options for the genesis of pyrrhotite and pyrite, which could be: (i) synsedimentary or diagenetic. In such a case these sulphides are pre-tectonic and the massive sulphide deposits are either VMS or SEDEX deposits; (ii) secondary, i.e., these sulphides formed at the expense of other pre-existing S- bearing minerals (e.g. pyrrhotite replacing pyrite during prograde metamorphism). In such a case the massive sulphide deposits represent VMS or SEDEX mineralization remobilized during regional deformation and metamorphism; (iii) metamorphic, i.e., pyrrhotite and pyrite crystallized directly from a mineralizing metamorphic fluid. In this case, the massive sulphide deposits are syn-metamorphic in origin, and fluids emanating from the contemporaneous syntectonic magmatic intrusions may also be involved in the genesis of the deposits.

To address this uncertainty we have examined the microstructural relationships among pyrrhotite, pyrite, and deformation and metamorphism in several deposits of the Jebilet massif.

2 Geological setting

The massive sulphide deposits of the Variscan fold belt of Morocco are present in the Jebilet massif and its southern extension (the Guemassa outcrops; see overview by Lusty et al., this volume). In the Jebilet massif, they are located in a central unit which is separated from the eastern and the western units by a wrench fault and a thrust-wrench shear zone, respectively (Fig. 1). The deposits are hosted by Upper Visean (Middle Mississippian) marine metasedimentary rocks (Sarthev schists) that were deposited in an anoxic platform setting (Beauchamp and Izart 1987), and affected by a very low- to low-grade metamorphism contemporaneous with post-Visean shortening (Huvelin 1977). Deformation and metamorphic gradients are observed towards the major shear zones and the numerous intrusions present in the unit (Essaifi et al. 2001).

The central Jebilet unit is also characterized by the presence of numerous mafic, felsic, or composite intrusions, and of minor volcanic/ volcaniclastic rocks, which together constitute a bimodal magmatic province, and peraluminous granodiorites intruded by younger (300 Ma) leucogranites (Essaifi et al. 2014). The bimodal plutonism principally occurs in three linear zones parallel to shear zones (Essaifi and Hibbi 2008). The massive sulphide deposits are generally located within the shear zones and are aligned in linear trends parallel with the magmatic lineaments.
3 Relationships between pyrrhotite and deformation/metamorphism

Regional ductile deformation in the central Jebilet is marked by the development of a widespread, sub-vertical axial-plane schistosity associated with upright and moderately to gently plunging folds. The massive sulphide deposits are typically focused in shear zones parallel to the regional schistosity. The majority of the deposits form steeply dipping lenses 1500 m long by 30–70 m wide and 500–1500 m deep (Belkabir et al. 2008; Jaffal et al. 2010). Wall rocks adjacent to the ore bodies are generally characterized by the presence of cm-scale quartz-chlorite and/or quartz-calcite mineralized veins (Bernard et al. 1988). These veins show gradational to sharp boundaries and have undergone different strain intensities. They cut the cleavage planes but do not entirely postdate the foliation (Fig. 2). The veins are variably folded and show a ductile deformation marked by orientation of sulphide minerals along the foliation plane. Hence, they are syn- to late-tectonic veins.

Many of the major deposits, including Draa Sfar, Hajjar, Kettara, and Koudiat Aicha, are dominated by pyrrhotite with minor pyrite, chalcopyrite, sphalerite, and galena. Pyrrhotite in these deposits generally forms elongated grains enclosing chlorite fragments oriented along the S1 cleavage (Fig. 3A) or localized along C/S planes in the mylonitized ore. Equigranular grains of pyrrhotite, 0.01mm in size, also display 120° triple junctions. Disseminated pyrrhotite in the wall rocks adjacent to the deposits typically forms elongated grains along the host-rock cleavage planes (Fig. 3B). The largest grains form spots that are commonly rimmed with chlorite. Pyrrhotite is also found in pressure shadows around large quartz grains. In the Roc Blanc deposit, which is located in the contact metamorphic aureole of the Tabouchent granodioritic pluton, disseminated pyrrhotite also occurs as an alteration product of the contact metamorphic minerals (andalusite or cordierite). This occurrence indicates that, in this case, pyrrhotite formed during replacement of the metamorphic minerals induced by emplacement of this granodioritic pluton.

Pyrrhotite associated with chalcopyrite and sphalerite is also found in syntectonic mineralized quartz-chlorite veins in wall rocks adjacent to the deposits. The sulphides are principally concentrated in the centers of the veins, whereas quartz and chlorite essentially occupy the margins. Where a layering composed of millimeter-scale pelite and sandstone is present in the host schists, the sulphide minerals in the veins develop only in zones that have continuity with the pelite layering (Fig. 2B). Thus the pelite banding persists through the veins by alternation of sandstone layers composed of fine-grained quartz (0.1 mm) and layers consisting of coarse-grained quartz associated with chlorite and sulphides. In the host schists surrounding the veins, pyrrhotite is present only in the pelite layers where it is localized along foliation planes. We interpret these veins as replacement features, formed by local alteration of the wall rocks along fractures during the ductile deformation phase.
mineralizing fluid. Because crystallization of syntectonic pyrite instead of pyrrhotite is restricted to the limestone layers, it can be related to consumption of excess Fe in the mineralizing fluid to form ankerite, by the reaction

\[ 2\text{Pyrrhotite} + \text{Calcite} + \text{Fe}^{2+} = \text{Pyrite} + \text{Ankerite}. \]

Figure 2. A. Outcrop showing a folded mineralized vein in shear zone of the Laachach deposit. B. Mineralized vein in wall rocks of the Kettara deposit; note that sulphide minerals in the vein occur only in zones that have continuity with pelite layers (dark) in host schist.

5 Discussion

The cleavage-parallel orientation of pyrrhotite and its subsequent deformation demonstrate that crystallization took place during a protracted period of deformation in which cleavage planes were reactivated as shear planes. This process could result either from remobilization of earlier formed syngentic pyrrhotite, or primary crystallization during deformation. However, its occurrence in pressure shadows and as an alteration product of contact metamorphic minerals that developed around the syntectonic Tabouchent granodioritic pluton (Le Corre and Saquaque 1987) indicates that at least a stage of the pyrrhotite mineralization took place by direct precipitation from a mineralizing fluid during regional ductile deformation and metamorphism. The presence of syntectonic pyrite exclusively within deformed zones of limestone layers in the Draa Sfar deposit indicates that fluid flow was focused within permeable zones where the mineralizing fluid deposited sulphide minerals. However, across much of the region, pyrite is typically late to post-tectonic and records a protracted period of hydrothermal fluid activity, extending towards the end of the Variscan event, and was likely genetically related to the magmatic intrusions.

Figure 3. Photomicrographs of pyrrhotite and pyrite from the central Jebilet. A. Massive pyrrhotite (PO) enclosing pyrite (PY) and fragments of host rocks (HR) aligned along schistosity plane in Laachach deposit. Note that pyrite (PY) crystals overgrow cleavage planes. B. Disseminated pyrrhotite rimmed by chlorite forming “spots” aligned along schistosity plane in host schists of Roc Blanc deposit. C. Sample from Draa Sfar North deposit showing syntectonic pyrite oriented along C/S planes and undeformed pyrite in pressure shadows around fossil debris (BC).
6 Conclusions

In the central Jebilet, remobilization of pre-tectonic, synsedimentary or diagenetic pyrrhotite cannot be ruled out. However, syngenetic pyrite has not been observed, nor is there evidence for it transforming to pyrrhotite during prograde metamorphism.

At least some of the pyrrhotite mineralization in the Jebilet massive sulphide deposits appears to have formed by direct crystallization from a mineralizing fluid during regional deformation and metamorphism. Pyrite in the deposits is represented by (i) primary grains formed by direct crystallization from syntectonic and late- to post-metamorphic mineralizing fluids, and (ii) secondary grains that formed by the dissolution of pre-existing pyrrhotite by late- to post-metamorphic fluids.

Microstructural and textural relationships indicate a protracted period of polymetallic sulphide mineralization. The massive sulphide deposits record a syntectonic metamorphic phase of mineralization, contemporaneous with widespread syntectonic Jebilet magmatism. A pre-existing, pyrrhotite-rich, VMS or SEDEX-type of mineralization, remobilized during regional deformation and metamorphism, is not excluded. Additional detailed studies are required to understand the complexity of the different mineralizing events in the Jebilet massif.

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References


 Nb-Ta Occurrences Associated to Late Pan-African Leucogranites, Mayo Salah Region, Northern Cameroon

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Abstract. The locality of Mayo Salah in the North-Cameroon domain of Central African Fold Belt consists of several Pan-African granitoids emplaced in a gneissic and metavolcano-sedimentary basement. One of them is a laccolith which presents the features of rare metals granitoids, with minerals such as Nb-Ta oxides, Li-micas, rutile, fluorite and tourmaline. The geochemistry of these Mayo Salah granitoids display a crustal collisional character, calc-alkaline, peraluminous, and of S type suite, with enrichment in some elements as Nb, Ta, REE, Zr, Y and Mn. It is syn- to late-tectonic related to a D2 event which is sinistral/transpressive. The Nb-Ta oxides occur in Li-Ms albitic facies. They consist pyrochlore belonging to the Columbite Group Minerals, with composition going from the ferrocolumbite to the manganocolubrite end-member. They express weakly zonation, from Nb-rich core to Ta-rich rim. The Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios of these pyrochlores may indicate a high differentiation process. Further mineralogical, geochemical, and geochronological studies will be conducted to complement these preliminary field observations, and will help to constrain these Nb-Ta mineralization in the regional geodynamic framework.

Keywords. Nb, Ta, Pyrochlores, Cameroon, Mayo Salah, Leucogranites, Pan-African, CAFB

1 Introduction

The northern part of the Central African Fold Belt (CAF B) in Cameroon appears largely unexplored. Early works in this domain focused mainly both on its tectonic evolution, and associated magmatic activity in order to characterize the geodynamic evolution, especially in Poli and Tcholliré area (e.g. Toteu et al. 2001, 2004, 2006a; Penaye et al. 2006; Ngako et al. 2008; Daouda et al. 2013; Bouyo et al. 2013, 2015). Otherwise, these works highlight intrusive granitoids often associated with REE and rare metals occurrences. (Zr, Nb, Ta, Li, Sn, Cs, Be, Y, Ga, F...). No previous studies have focused on the metallogenic potential of the North Cameroon granitoids. The aim of this abstract is to propose field observations, geochemistry and mineralogical studies on these Nb-Ta- bearing granitoids.

2 Geological setting

Mayo Salah is located about 60 km southeast of Poli in the northern part of CAF B in Cameroon (Fig. 1A). This belt is the result of continental collision between the West African craton, the Congo craton and Sahara metacraton during the Pan-African orogeny at 600 Ma (Toteu et al. 2004, 2006a; Van Schmus et al. 2008). In Cameroon, this belt have been divided into three domains (Fig. 1B) (Toteu et al. 2004; Penaye et al. 2006, Van Schmus et al. 2008):

(1) The Southern Cameroon, which is a huge allochthonous nappe unit thrust southward onto the Congo craton;

(2) The Central Cameroon, characterized by the presence of Archean to Neoproterozoic remobilized formations and several shear zones such as Tcholliré-Banou Fault (TBF), Sanaga Fault (SF), Central Cameroon Shear Zone (CCSZ);

(3) The Northern Cameroon, characterized by juvenile rocks, limited in its southern part by TBF; it continues in Eastern of Nigeria and southwest of Chad (Mayo-Kebbi).

This part of CAF B results from the tectonic collage of the three above mentioned geological domains (Central domain, Northern Cameroon and Mayo-Kebbi) which were then intruded by post-collisional granitoids younger than 600 Ma (Penaye et al. 2006; Pouclet et al. 2006; Isseini et al. 2012).

3 Structural and petrographic constraints

3.1 Structural constraints

The study zone underwent two tectonic episodes. The first event D1 affects the surrounding formations and generate lying folds with axial planes parallel to a S1 flat-lying foliation in metavolcanic-sedimentary rocks oriented NE-SW (average N45E) with low dip ≤ 35° (average 20°) oriented towards SE or NE. The second tectonic event D2 is ductile to brittle from shearing to transpressional. Ductile phase is marked by upright folds and S2 schistosity in the surrounding formations and borders of granites. S2 is oriented NE-SW (N50E average) toward NW-SE (N110E average) the dips are, 40-50° oriented towards NE to SE. This schistosity carries a southbound plunging mineral lineation (average 35 ESE to 60S). The brittle phase is late-tectonic and affects all petrographic kinds. It generates a sinistral shearing and faults that affect the veins of quartz and pegmatites got in place in the S2 schistosity planes.
3.2 Petrographic constraints

The granitoids are syn-to late-D2 tectonic and they mark moderate but distinct high and forms dome-shaped massif (tonalite, granodiorite, biotite granite, muscovite granite and leucogranite) setting up in a gneissic and metavolcano-sedimentary basement (biotite-muscovite-garnet micaschists, epidote-chlorite metabasalts, and amphibole-biotite-garnet amphibolites). Quartz vein hosting gold occurrences are described within this basement.

Figure 1. A. Sketch diagram showing the location of Fig. 1B (After Toteu et al. 2004) 1, Post-Pan-African cover; 2, Pan-African belt; 3, pre-Mesozoic platform series; 4, Archean to Paleoproterozoic cratons; 5, craton limits; 6, faults; 7, State boundaries. CAR, Central African Republic; CM, Cameroon. B. Pan-African structural map of Cameroon (After Njonfang et al. 2008) and location of the study area. 1: Quaternary sediments; 2: Cameroon Line volcanism; 3: Cameroon Line plutonism; 4: Mesozoic sediments (Benue Trough); 5: Late syntectonic subalkaline granitoids; 6: Lom syntectonic basin (meta-sediments, conglomerates, volcanic ashes and lavas); 7: Western Cameroon Domain (WCD; early syntectonic basic to intermediate calc-alkaline intrusions, 660–600 Ma); 8a: Poli Group (active margin Neoproterozoic supracrustal and juvenile intrusions) 8b: Yaoundé Group (intracratonic deposits); 9: Massenya-Ounianga gravity highs (10–30 mGals); 10: Adamawa-Yade and Nyong Paleoproterozoic remnants; 11: Craton and inferred craton; 12: S2 foliation and L2 lineation trends; 13: F2 upright and overturned antiforms; 14: Syn-D2 main frontal thrust zone; 15: Syn-D1 thrust zone (separates the LP to MP zone in the North from the HP zone in the South); 16: Syn-D3 sense of shear movement; 17: Syn-D2 sense of shear movement. Large grey arrow represents syn-D1–3 regional main stress direction. Thick lines = shear zones (SZ): BSZ = Balché SZ; BNMB = Buffle Noir – Mayo Baléo SZ; CCSZ = Central Cameroon SZ; GGSZ = Godé – Gormaya SZ; MNSZ = Mayo Nolti SZ; RLSZ = Rocher du Loup SZ; SSZ = Sanaga SZ; Ma = Magba; Wa = Wakaa; Ba = Bandja complex; Fo = Fomopéa complex.

The Nb-Ta bearing leucogranite is a lachlolith located NE of the study area, outcropping as blocks and slabs (Figs. 2a, b) in the micaschistes and/or in large veins associated with pegmatite. It is in contact with two-mica granites (Fig. 2f) and granodiorite in its SW boundary. Outcrops are generally oriented E-W (N75E–N110E) with three main facies (Fig. 2c, d, e), fine-grained, medium-grained, mesocratic medium-grained. They have a porphyritic texture (Figs. 2g, 2h; Figs. 3a, 3b), sometimes oriented in samples bounded the massif (Fig. 2a) in contact with the basement rock. The main minerals are quartz (Qtz), albite (Ab), microcline (M1), muscovite (Ms). Other less common minerals are represented by: biotite (Bt), orthose (Or), oligoclase (O1), garnet (spessartine), calcite, Nb-Ta oxides, fluorite (Fl); Manganese (Mn) oxide, ilmenite and magnetite. Accessory minerals are rutile, zircon, monazite, apatite and tourmaline.

A medium-grained and mesocratic medium-grained facies (Figs. 2c and 2e) display a minerals spot as miorolitic form constituted of rutile, tourmaline, Li-mica, calcite, and Mn oxide.

4 Geochemistry and mineralogy of the granitoids

Whole rocks analyses of samples of studied granites were performed. Their nomenclature is given by diagram of Le Bas (1986), which display the alkaline affinity of these rocks. The studied samples are felsic with 66% to
73%, SiO₂. It as high values of total alkali (7.13 to 11.63%) which define a high-K calc-alkaline suite, and Al₂O₃ (14.71 to 16.38%) and average values in total Fe, Fe₂O₃ (0.4 to 5.43%), and low values of MnO, MgO, CaO and TiO₂. When considering K₂O vs. SiO₂, the high-K character of these rocks is concordant with their high Al₂O₃ content (>14%) and with their noticeable abundance of K-feldspar (and hence of K₂O). Harker variation diagrams display a negative correlation between SiO₂ and all these oxides, except Na₂O (positive) and K₂O (constant). Some trace elements are relatively enriched, Nb (29.27-94.23 ppm), Ta (3.43-49.07 ppm), Sn (11.73-84.64 ppm), Rb (65.38-895.7 ppm), Th (18.75-38.85 ppm), Ba (19.38-1368 ppm), Y (7.72-221 ppm), Zr (10.01.524 ppm), Gd (21.11-24.6 ppm). LREE is enriched like HREE (La/Yb)N = 5.48-19.88 ppm; with heavy values of REE (166.09-669.85 ppm). The diagram of Maniar and Piccoli (1989), which use molecular parameters of shand (A/NK vs A/CNK mol %), demonstrates that these samples are strongly peraluminous and belong to an S-type suite, with A/(CNK) = 1.41-1.67 mol%.

Figure 2. Photographs of some typical granites of Mayo Salah. a. Outcrop of Ms-Leucogranite with veins of Qtz in the foliation. b. Block of the Ms-leucogranite with columbite group minerals (CGM). c, d, e. Samples of the Ms-leucogranite with CGM. f. sample of coarse-grained two-mica granite Qtz+Or+Ms±Bt. Photomicrograph in cross-polarized light of the leucogranite showing a common texture g. fine-grained. h. medium-grained.

Minerals chemistry shows that, plagioclase in leucogranite, are albite (An₀.₀₂,₁₅) and K-feldspar is a perithlth orthose or microcline (Or₉₇,₉₅). Biotite has a homogeneous composition and is located in the annite pole in the XFe vs Si diagram. The calc-alkaline affinity of these rocks is displayed by the hosting analysed biotite. Muscovite is primary, and presents Li phases in the field of phengite and muscovite. The garnet is spessartine; the identified oxides are ilmenite, magnetite and columbotantalite.

Figure 3. a, b, c, d. photomicrographs in cross-polarized light, showing the common textures of the leucogranite and form of Nb-Ta oxides; e, f. BSE showing the texture and zonation with Nb (gray) and Ta (various shades of bright).

5 Nb-Ta mineralization

Nb-Ta oxides of Mayo Salah leucogranite occurs mostly as tabular or prismatic crystals in the primary paragenesis Qtz+Ms+s+Ab+M+Na-Tb Ox±Gt±F; or small needle-like crystals in the secondary paragenesis Qtz+Ab+Ms±O±Nb-Ta Ox±Sm±Mn Ox, or as inclusions in muscovite, albite, rutile, monazite and zircon (Fig. 3). Their size is between 20 and 400 μm. Optical microscopy shows that they appear as opaque crystals (Figs. 3a, 3b, 3d), or reddish or brown to blackish (Fig. 3c). Backscattered electron images (BSE) show zoned minerals, with Nb-rich core and Ta-rich rim (Fig. 3e, 3f).

The Nb-Ta oxides belong to the columbite group minerals (CGM). In the pyrochlore supergroup, they belong to the group of pyrochlore (Ateencio et al. 2010), based on the atomic proportions of the B atoms (Nb, Ta, Tb, Ti, W), the Nb being the major mineral of the B site (Fig. 4a) what is verified in the classification of Hogarth (1977), on the basis of the contents in Nb, Ta and Ti, it is found that Nb>Ta, and Nb+Ta=2Ti (Ohnenstetter and Piantone 1992). The Ta/(Ta+Nb) vs Mn/(Mn+Fe) diagram shows that these are CGM, whose composition varies in the field of ferrocolumbite and that of manganocolumbite (Fig. 4b). The Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios of CGM are indicative of a higher degree of differentiation, [Mn/(Mn+Fe)=0.02–0.86, and Ta/(Ta+Nb)=0.03–0.65, apfu].

Metallogeny of North and West Africa 1609
for columbite group minerals.

Figure 4. a. Pyrochlores classification diagram (Hogarth 1977; Ohnenstetter and Piantone 1992; Atencio et al. 2010), according to the major elements in site B. b. Quadrilateral diagram Ta/(Nb+Ta) vs Mn/(Mn+Fe) compositional diagram for columbite group minerals.

6 Conclusion

The present study is the first one focusing on rare metals bearing granitoids of the northern Cameroon Domain. It emerges from this preliminary study that the leucogranite of this locality is:

(a) a lacholithic which presents the features of rare metals granites. It is calc-alkaline, strongly peraluminous and of S type suite, set up in a collisional context of active margin type; with a notorious enrichment in some elements as Nb, Ta, REE, Zr, Y and Mn.

(b) syn- to late-D2,

(c) It contains Nb-Ta oxides in the Li-Ms albitic facies. These oxides are the pyrochlore belonging to the CGM, with composition from ferrocolumbite to manganocolumbite.

This first work will be completed by additional mineralogical, geochemical and geochronological investigation for a better constraining the regional geodynamic setting and the colombo-tantalite mineralizations.

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References

Miller CF, Stoddard EF (1981) The role of manganese in the volcanic rocks is adjacent to visible gold mineralisation in quartz

Abstract.

In this study we focused our attention on the well economic styles of mineralisation formed during distinct

We develop a model whereby grain-scale microfractures and crystal-plastic microstructures facilitate a dissolution-

Keywords.

Gold.

In the form of ultra-high grade ore shoots with visible gold appears to have contributed to a significant upgrade

Remobilisation, multistage mineralisation, economic styles of mineralisation formed during distinct

Fougerouse et al. (in press). There are two co-located

quartz veins during NNW-SSE to N-S shortening (D3Ob). This sequence was defined using field obser-vations

resolution X-ray computed to mography that revealed

This complex deformation, mineralisation and alteration was controlled by later fracturing and folding of

Scanning Electron Microscopy (SEM) to analyse

Fougerouse et al. in press). We used a combination of

veins (Oberthür et al. 1994; Allibone et al. 2002; Pecerillo A, and Taylor SR (1976) Geochemistry of Eocene calc-

pyrochlore-group minerals in the Beauroir peraluminous leucogranite, Massif Central, France. Can Mineral 30:771-784
Gold Remobilisation from Arsenopyrite: Crystal-Plasticity and Dissolution-Reprecipitation Reactions

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Abstract. The significance of gold remobilisation in ore deposits is a contentious issue. The microstructural and geochemical evolutions of ars enopyrite ores from the 62 Moz Obuasi deposit, Ghana, reveal the mechanisms for how such a process may operate. The ars enopyrite ores were coeval with high strain deformation and metamorphism in the country rocks (400±50°C and 2 kbar). The majority of the ars enopyrite crystals are zoned with a gold-poor core and epitaxial rims (A-rims). The epitaxial rims are characterised by oscillatory zoning and high concentrations of gold (up to 1000 ppm) in the crystal lattice. Commonly, cores and A-rims are dissected by gold-depleted zones (B-rims) associated with microfractures, grain boundaries and subgrain boundaries formed during recrystallisation. B-rims are interpreted as alteration zones with sharp reaction fronts, which formed post-peak metamorphism and deformation. We develop a model whereby grain-scale microfractures and crystal-plastic microstructures facilitate a dissolution-reprecipitation replacement reaction and the release of gold from the ars enopyrite crystal lattice. At Obuasi, this gold appears to have contributed to a significant upgrade in the form of ultra-high grade ore shoots with visible gold.

Keywords. Remobilisation, multistage mineralisation, gold, ars enopyrite, replacement, crystal plasticity

1 Introduction

Gold-bearing sulphides are a common feature of orogenic gold deposits forming large, low grade disseminated mineralisation (Groves et al. 1998). Gold remobilisation from these sulphides during metamorphism is potentially of critical importance to resource upgrading or downgrading and then mineral exploration.

Two main processes have been proposed to explain trace element remobilisation: 1) hydrothermal fluid interacting with the sulphide (solid-fluid state; Putnis et al., 2009 and references therein) and 2) intragrain diffusion (solid-solid state; Vukmanovic et al., 2014 and references therein). Hybrid models have been documented where solid-solid diffusion is mediated by a fluid phase (Plümper et al. 2012).

In this study we focused our attention on the well documented Obuasi gold deposit (Ghana), where gold-bearing ars enopyrite mineralisation in metasedimentary rocks is adjacent to visible gold mineralisation in quartz veins (Oberthür et al. 1994; Allibone et al. 2002; Fougerouse et al. in press). We used a combination of high resolution Secondary Ion Mass Spectrometry (NanoSIMS), Electron backscattered diffraction (EBSD) and Scanning Electron Microscopy (SEM) to analyse gold-bearing ars enopyrites previously well constrained by field mapping and 3D modelling (Fougerouse et al., in press). We apply this approach to identify the mechanisms that contribute to the loss of gold from ars enopyrites.

2 Deformation history and relative gold timing

A complex deformation, mineralisation and alteration history has been defined at Obuasi (Fougerouse et al. in press; Allibone et al. 2002; Oberthür et al. 1994; Blenkinsop et al. 1994), and recently updated by Fougerouse et al. (in press). There are two co-located economic styles of mineralisation formed during distinct events (Fig. 1). Firstly, ars enopyrite-hosted ore formed during the main NW-SE shortening direction event (D2Ob). Subsequently, high grade visible gold mineralisation was controlled by later fracturing and folding of quartz veins during NWW-SSE to N-S shortening (D3Ob). This sequence was defined using field obser-vations from underground and deposit scales, and high-resolution X-ray computed tomography that revealed gold distributed in fracture networks overprinting the quartz veins (Fougerouse et al. in press).

![Figure 1. Structural evolution and timing of mineralisation of the Obuasi deposit (Fougerouse et al. in press)](image)
3 Crystal plastic deformation and trace element modification

3.1 Crystal zonation

Arsenopyrites from the ore zone of the Obuasi deposit are typically composed of two primary domains: a rim that appears homogeneous in BSEM images (A-rim) and an inclusion-rich internal core (Oberthür et al. 1994; Oberthür et al. 1997). The core is usually gold poor (Oberthür et al. 1997) with inclusions of pyrrhotite, chalcopyrite or rutile. The homogenous A-rims represent epitaxial zones with up to 1000 ppm Au (Oberthür et al. 1994; Fisher et al. 2014).

Commonly, there is a third domain (B-rim) crosscutting all others (Fig. 2). B-rims are characterised by a higher than average atomic mass (lighter colour in BSE images due to higher As concentrations) and preserve the original shape of the crystals. The contacts between the B-rims and other domains in the arsenopyrites are sharp, planar to curvilinear (bulbous) and penetrate in from microcracks and grain boundaries (Fig. 2). Visible gold particles can be observed in the microfractures that are associated with the B-rims.

![Figure 2. Backscattered images of arsenopyrite. Replacement rims (B-rims) cut across the primary zonation (A-rims). Top image: sample 215-7; bottom image: sample 318-15](image)

3.2 Crystal plastic deformation

EBSD and NanoSIMS analyses were conducted on sample 215-20, to identify the processes affecting mineralised arsenopyrites, given the good field constraints on mineralised arsenopyrite and later visible gold. The grain shown in Figures 3-4 was selected on the basis of its large size (up to 1 mm) and homogeneity. The arsenopyrite is located parallel to the main cleavage (S2ob) and at a high angle to a microfold of crenulation cleavage (S3ob).

The EBSD data show a relative change in crystallographic orientation from a central point to a maximum of 10°, for each grain (Fig. 3). Consistent with other studies (Reddy and Hough 2013), we define high angle grain boundaries to have misorientations >10°. All boundaries <10° are low angle grain boundaries and define subgrains. In most cases the intragrain variation does not reach 5°, though new grains are formed at a few localised points. These observations are consistent with dynamic recrystallisation by dislocation creep. The spread of crystallographic orientations in pole figures of the grain indicate deformation occurred at a high angle to the long axis of the arsenopyrite crystal, suggesting that the crystal plasticity occurred during D3ob.

Subgrains and rare new grains accommodate strain in a narrow localised domain on the top right-hand side of the crystal, coincident with a large microfracture (Fig. 3). This suggests the arsenopyrite underwent strain hardening during crystal-plastic deformation, eventually leading to embrittlement.

![Figure 3. Electron backscatter diffraction (EBSD) orientation map of arsenopyrite (sample 215-20), colored to show a relative change in crystallographic orientation up to 10°. The grain is deformed with strain localisation forming subgrains and dynamic recrystallisation producing new grains](image)

3.3 Trace element distribution

NanoSIMS analysis reveals that, within the A-rims, gold is distributed in alternating, micron- to submicron-scale concentric bands (Fig. 4), which are approximately parallel with the euhedral outline of the overall arsenopyrite grain. Up to 100 bands are present within the A-rims despite the rims homogenous appearance under BSEM. The fine resolution, oscillatory nature of these bands is much greater than previously detected using older, lower resolution techniques (Oberthür et al. 1994). These textures are interpreted to represent gold entrapment in the crystal lattice of arsenopyrite during epitaxial overgrowth.

The primary oscillatory zonation of the gold-rich A-rims is cut by B-rims characterised by high Ni and gold concentrations below detection level. The B-rims are discontinuously developed along grain boundaries and some microfractures. B-rims are not present along all microfractures suggesting different generations of fractures are present in the arsenopyrite grains. The Ni distribution also appears to be zoned in the B-rims, controlled by the crystallographic lattice, but in a manner that does not reflect the same lattice orientation as the oscillatory zoned gold (data not shown).
Arsenopyrites from the ore zone of the Obuasi deposit are typically composed of two primary domains: a rim (B-rims) cut across the primary zonation (A-rims). Top Figure 2.

Backscattered images of arsenopyrite. Replacement rims (B-rims) are nickel-rich; the gold distribution is finely zoned in the epitaxial growth bands. B-rims are deprived in gold; composite image, gold is yellow and nickel is blue. The grain and B-rims boundaries are highlighted in red.

Figure 4. a. Backscattered image of an arsenopyrite; b. NanoSIMS image of the Ni distribution in the area indicated in (a). The pyrite in the healed microfracture as well as part of the replacement rims (B-rims) are nickel-rich; c. the gold distribution is finely zoned in the epitaxial growth bands. B-rims are deprived in gold; d. composite image, gold is yellow and nickel is blue. The grain and B-rims boundaries are highlighted in red.

Figure 5. Interpretative diagram through time of crystallisation and deformation of the arsenopyrite.
In addition, the B-rim widths are up to three times greater in the recrystallised zones than in the undeformed arsenopyrite. In the recrystallised zone, the shape of the B-rim is irregular, interfering into the grain suggesting a relation between crystal plasticity, grain zoning and trace element distribution (Fig. 3 and 4).

4 Interpretation and discussion

In summary, in the example presented, B-rims cut across the primary gold zonation of the arsenopyrites. Although these rims have a different composition (enriched in As and Ni), they preserve the original shape of the parent arsenopyrite crystal but have lost all detectable gold. The transition from A- to B-rims is sharp and the morphological characteristics of the B-rims are planar to curvilinear. These relationships are consistent with gold remobilization being controlled by a pseudomorphic replacement zones strongly suggests that the recrystallisation of the arsenopyrite and the formation of subgrains influenced the replacement reaction.

We conclude gold was extracted from the crystal lattice of the arsenopyrite and released into a low volume, grain-scale fluid phase during dissolution-reprecipitation replacement. This process was facilitated by domains of crystal-plastic microstructure (Fig. 5), most likely due to enhanced diffusion pathways for trace elements to and from the reaction front, along high and low angle crystallographic boundaries (e.g. Vukmanovic et al. 2014; Plümper et al. 2012). Plümper et al. (2012) proposed that the reaction can be enhanced by solid-state diffusion along subgrain boundaries. Subsequent transport distances of the gold, outside the arsenopyrite, were on the scale of millimetres to metres. High concentrations of visible gold then precipitated in microfractures within quartz veins, to form Obuasi’s super-high grade ore shoots.

Acknowledgements

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References


A New Type of Large Ultramafic Intrusion-Hosted Fe-Ti-V Deposit in the West-African Archean Craton: The N’Guérédonké Complex, Guinea

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Abstract. A new type of large ultramafic intrusion-hosted Fe-Ti-V deposit has been discovered by BRGM in the West-African Archean craton. The N’Guérédonké intrusive complex (7 x 0.9 km) is composed of a dunite core surrounded by rims of wehrlites and pyroxenites. This syntectonic complex is emplaced within a crustal scale shear zone. The disseminated mineralisation made of ilmenite and magnetite is mainly hosted by pyroxenite units along the northern and southern contacts. Surface and drilling and exploration work (47 drill holes totalling 10,124 m) demonstrate polyphased injection of successive ultramafic melts from core to rims and also crosscutting of dunite core by a network of successive pyroxenite generations. A 3D modeling constrained by drilling and joined inversion of magnetic and gravity data ascribe the thickness of the intrusion up to 1000 m. A first very conservative titanium resource assessment on a small part of the intrusion (1000 x 100 x 250 m) lead to definition of 141.36 Mt ore @ 10.52% TiO$_2$. The lack of typical features of Ural-Alaskan type intrusions and strong differences with classical Gabbro-Anorthosite hosted Fe-Ti-V deposits demonstrate a new type of large low grade high tonnage Fe-Ti-V deposit occurring in Archean craton.

Keywords. Fe-Ti-V deposit; zoned ultramafic; archean craton; Guinea

1 Introduction

Despite occupying a large surface and hosting various types or ore deposits (eg BIF, gold, diamonds, ... ) the Archean craton of West-Africa remains poorly explored by comparison with Birimian terranes known worldwide at least for gold resources. Recently, mining exploration, on behalf of Mitsubishi Corporation, carried by BRGM in central Guinea lead to the discovery of a 7 km-long ultramafic intrusive complex, host of a disseminated low grade - high tonnage Fe-Ti-V mineralization and described here as the N’Guérédonké Ultramafic Complex (NGUC).

Fe-Ti-V deposits are known to be typically associated with mafic rocks (gabbro, anorthosites). This discovery of a non-conventional mineralization highlights the great mining potential of these largely under-explored Archean cratons.

2 Geological setting

2.1 Regional geology

The central and eastern part of Guinea corresponds to the Archean core of the Western African Craton. Five lithostructural domains are recognized within this Archean core (Thiéblemont et al. 2004): i) Early Archean orthogneiss in the Nimba Mounds area (~3540 Ma); ii) Leonian Guinean gneisses and greenstones belts (3240 - 3050 Ma); iii) Greenstones belts and metamorphic-plutonic Liberian rocks (2940 - 2800 Ma); iv) Neoarchean greenstone belts and BIF from Simandou range and Nimba Mounds and v) Late Eburnean plutonic belt (2090 – 2020 Ma).

The NGUC is hosted by post Leonian to Pre-Liberian rocks represented by the supracrustal volcanosedimentary succession of the Kambui group. The Liberian orogeny (~2900-2800 Ma) is marked by a strong metamorphic and magmatic event which reworked a large part of the Leonian domain (eg Koumané et al. 1997; Thiéblemont et al. 2004). Thus large volumes of rocks suffered a magmatic event with coeval emplacement of granitoids.

The post-Liberian and pre-Eburnean period is marked by deposition of thick supracrustal units represented by Simandou and Nimba volcanosedimentary successions. Finally, Eburnean orogeny (2250–1900 Ma) considerably reworked the Archean craton leading to metamorphism and granitoids intrusions and affect also Birimian (2155-2095 Ma) volcano-sedimentary successions.

2.2 South-central Guinea geology

The study area is localized on the north-western border of the Archean craton. The basement is represented by layered gneiss affected by the Liberian magmatic event (2872 – 2833 Ma). Liberian granitoids (2852-2781 Ma) are widespread within magmatic gneiss (Egal et al. 2004). Here, the Liberian magmatic basement is crosscut by a N130°E-trending crustal-scale shear zone, the N’Guérédonké shear zone. Along the northern side of this shear zone crops the verticalised volcanosedimentary Balandougou formation (Kambui group, 2940 ± 11 Ma, Feybesse et al. 2004). This formation, 900 to 3000 m thick, composed of alternating amphibolite and schists with BIF and mafic to ultramafic intercalations, is strongly deformed and metamorphosed in the amphibolite grade. The area is also strongly affected by early Eburnean metamorphism and late magmatic events. The Eburnean orogeny is marked by amphibolite-grade gneiss (2476-2300 Ma) and widespread granitoids (2078-2074 Ma, Egal et al. 2004).

Finally, large dolerite sills and dykes are emplaced at about 200 Ma due to the opening of the Atlantic Ocean and cover larges surfaces.
3 The N’Guérédonké Ultramafic Complex

3.1 Host rocks and geometry

The NGUC (Fig 1) is an elliptical body (7 x 0.9 km) emplaced within the N’Guérédonké shear zone and constitutes the upper part of the NW-SE N’Guérédonké hill (840 m above sea level). To the north the NGUC intrudes the Bandaloungou formation whereas to the south, the NGUC is intrusive into the Liberian migmatitic gneiss (Fig 1). The northern and southern contacts are tectonic, marked by ductile to brittle shear zones. Outcrops of ultramafic rocks are scarce due to the presence of a thick lateritic crust, and only the northern flank of the hill exhibits some outcrops and boulders of ultramafic rocks. The first evidence discovered by BRGM of the NGUC was an anomalous Ti-Cr-V-magnetite-rich lateritic crust outcropping on the top of the hill, subsequently confirmed by a huge heliborne magnetic anomaly. The part of NGUC covered by exploration permits have been explored by 47 drill holes totalling 10124 m of core drilling and distributed along six drilling profiles (profiles at 500 m spacing). 8359 core samples have been analysed by XRF method (10 major + 7 minor elements) at ALS Chemex laboratories.

3.2 Petrology and facies relationships

Basically, the NGUC is composed of four main types of rocks: dunite, wehrlite, olivine-clinopyroxenite and pyroxenite. Within these main types, the NGUC is characterized by an extraordinary diversity and variability of textures. One key-feature is also the lack of plagioclase and the great abundance of oxides, mainly ilmenite, magnetite, titanomagnetite. Disseminated base-metal sulphides occur in most rock samples.

Dunite is the first injection and constitutes the core of the complex (Fig 1). Dunite is very homogeneous with cumulus texture, composed of euhedral to subhedral olivine (Mg# 0.864 – 0.781), ± amphibole, small subhedral grains of magnetite and more rarely ilmenite. Primary magnetite is of two types: i) Cr-rich magnetite (av. 16.9% Cr2O3 and significant amount of Ti, V, Mg, Mn and Ni); ii) magnetite close to the ideal composition. Ilmenite is Ti-rich (av. 53.2% TiO2) and contain significant amount of Mg, V and Mn. One key point is the lack of chromite (disseminated, layers or pod-like) and the systematic occurrence of disseminated magnetite and ilmenite.

![Figure 1](image1.png) **Figure 1.** Geological map of the N’Guérédonké ultramafic complex. Supergene formations (e.g. lateritic crust) present all over the complex are not represented.

![Figure 2](image2.png) **Figure 2.** Facies examples from N’Guérédonké ultramafic complex. a) wehrlite made of euhedral olivine and clinopyroxene crystals in a matrix of magnetite and ilmenite; b) medium-grained type 2 clinopyroxenite; c) coarse-grained type 3 clinopyroxenite; d) type 1 strongly mineralized clinopyroxenite (30 % TiO2).

Wehrlites (Fig 2a) occurring mainly as a rim around dunite core, are strongly heterogeneous throughout the NGUC and are frequently associated with olivine-clinopyroxene. Two main types have been observed: Type 1 appears at macroscopic scale as a dark fine grained rock with homogeneously disseminated clinopyroxene crystals. The size and amount of clinopyroxene (10 - 40% vol.) is highly variable at a metric scale. At a microscopic scale, type 1 exhibits cumulus texture with euhedral to subhedral olivine (Mg# 0.829 - 0.754) commonly containing myrmekitic inclusions of oxides, clinopyroxene (Mg# 0.896 - 0.808) and subhedral grains of magnetite, ilmenite and sulphides. The amount of ilmenite and magnetite seems to be correlated with the amount of clinopyroxene. Ilmenite and magnetite crystals (>100-200 µm and ≤ 50-100µm respectively) are subhedral. Ilmenite is Ti-rich (av. 52.2% TiO2) with significant amounts of Mg, V and M.n. Magnetite are Cr-bearing (av. 4.1% Cr2O3) and contain V, Ti, Mg and Ni. Type 2 wehrlite appears as area of heterogeneous “melange” consisting of olivine aggregates and clinopyroxene aggregates. At a decimetric scale facies varies from olivine-clinopyroxene to dunite and exhibits irregular complex contacts. The bulk composition at a metric scale corresponds to wehrlite. Oxides remain scarce in this type of wehrlite. Mineral composition does no differ from type 1-wehrlite.

Olivine-clinopyroxenites are well represented throughout the NGUC and occur as a rim around wehrlite rim. Type 1 is poor in oxides and made of disseminated xenomorphic olivine within a pyroxene matrix. The range
of pyroxene content is from 60 to 90 vol%. At a meter scale, the rock appears homogenous and shows progressive variation in the olivine content. Type 2 shows various amounts of oxides and consists in 70 to 90% of pyroxene and 30 to 10% of euhedral to sub-euhedral olivine crystal. The spatial distribution of olivine crystals is either heterogeneous or homogeneous. When heterogeneously distributed, euhedral olivine appears as mass, or pockets of olivine crystals with xenomorph oxides concentrations between forsterite crystals.

Clinopyroxenite units occur along the southern and northern contact of the NGUC. Strongly mineralized, decimeter to meter in size, crosscutting veins and dykes of pyroxenite are also observed throughout NGUC. Three pyroxenite types are identified macroscopically, based on mineralogy and crosscutting relationships. Type 1 is heterogeneous in grain size (fine to coarse grained) and in oxides content. Some facies show scarce oxides whereas others, strongly enriched facies (Fig 2d, up to 30% TiO2), show dispersed pyroxene crystals within an oxide matrix. This pyroxenite is characterized by scarce sulphides and a proportion of magnetite greater than ilmenite. Type 2 occurs mainly along the southern part of the NGUC and appears as a relatively homogeneous rock crosscutting type 1 pyroxenite. This type of pyroxenite contains large amount of ilmenite, less magnetite and disseminated phlogopite and sulphides (pyrrhotite, chalcopyrite). Despite the relative homogeneity of this facies at a decametric scale, the grain size is variable from 5 mm up to 2 cm (Fig 2b). Type 3 is a very coarse grained pyroxenite (Fig 2c), with large abundant phlogopite crystals and large flakes of oxides with ilmenite exceeding magnetite. This pyroxenite occurs as restricted meter to decimeter dykes, crosscutting previously emplaced rocks.

Pyroxene compositions (Mg# varying between 0.846 and 0.750) is not related to the pyroxenite type, neither to its ore content.

3.3 Joint inversion from geophysical data to constrain complex 3D shape and depth

Geometry of different units at depth has been constrained using 3D Geomodeller software (www.geomodeller.com) which allows the combination of geological and geophysical data (Calcagno et al. 2008; Guillen et al. 2008).

At first a geometric model is built by incorporating geological data from surface (geological map, structures, bedding orientations) and drill-holes information. This results in an a priori 3D distribution of the different units (Fig. 3). The shapes of different units and ore lenses (pyroxenites) are well identified until the mean depth of drill-holes, about 300 m below topographic level. But due to the complex imbrication of ore lenses and their very elongated shapes, it is hazardous to extrapolate their existence at greater depths by only considering geological observations.

Magnetic and gravity data are used to validate or invalidate different extrapolation hypothesis by computing the geophysical effect of the geological model given the physical properties of the different units. This effect is then compared to the observed one.

Figure 3. Geological model designed from drill holes and field observations. (a) Pyroxenites bodies; (b) Dunite and wehrlite envelopes.

Figure 4. Comparison between observed gravity/magnetism anomaly and computed effect of 3D model.

The density parameters and subdivision of formations used for gravity modelling are supposed to discriminate the distribution of ore-bearing rock (magnetite-ilmenite ore) whereas the magnetic parameters are more difficult to constrain due to a greater uncertainty on the distribution of heterogeneities in magnetic remnant measurements. They don’t help to decipher pyroxenites from dunites and wehrlites because of very close magnetic parameters. However, the big contrast with surrounding rocks which have very low magnetic susceptibility and no remnant
magnetism gives good constrain on the volume and depth of the whole system. Different depths and shapes scenario have been tested. It is shown that the lowest misfits for magnetic (around 5%) and gravity (about 1%) responses are obtained at high depths (about 1000 m) for the UM complex and associated pyroxenites units (Fig 4).

The gravity and magnetic anomalies are well explained by a simple vertical prolongation of the highly magnetic UM complex and its high density pyroxenites identified at subsurface level.

3.4 NGUC Ore

Basically NGUC ores could be classified in two main classes: 1) Secondary ore from the lastetic profile (crust+saprolite) enriched in iron (up to 30.7m @ 51.8 % Fe), titanium (av. 20 % TiO2), vanadium (av. 0.20 - 0.25 % V2O5), chromium (av. 0.7 - 1.2 % Cr2O3) and nickel (0.7 -1 % Ni); 2) Primary ores including many subtypes related to the wide variety of rocks, mainly the southern and northern pyroxenites units, some low-grade wehrlite and pyroxenitic dykes stockworks within the dunite core. A first very conservative titanium resource assessment has been realized only on a part of the southern pyroxenites units (1000 m long x 100 m wide x 250 m deep) leading to definition of 141.38 Mt ore @ 10.52 % TiO2. This very conservative resource assessment and the comparison with world major titanium mines (eg Tio Mine, 75 Mt @ 34.2 TiO2; Tellnes Mine, 400 Mt @ 18.4 TiO2) underline the strong potential of such low grade-high tonnage new type of ultramafic-hosted Fe-Ti-V deposit.

4 Conclusions

The NGUC appears as a syntectonic polyphased deformed ultramafic intrusion (similar to Huangshan intrusion, Branquet et al. 2012), made of a dunite core surrounded by wehrlites and pyroxenites rims. Thus, from a geometrical point of view it shows some similarities to Ural-Alaskan ultramafic type complexes. Even if it also includes other typical features of such complexes (eg lack of orthopyroxenes), several keypoints lead to a distinct type of ore deposit, among them, the lack of chromite pods or layer, and associated PGE mineralisations, the lack of associated mafic rocks (plagioclase is totally absent) and the occurrence of magnetite and Cr-bearing magnetite in dunite instead of chromite. Moreover, recent numerical modelling (Guillou-Frottier et al. 2014) suggests that due to rheological crust constraints, Ural-Alaskan type complexes should not occur before Palaeozoic time. Conversely, the NGUC is expected to be emplaced between 2.94 and 2.1 Ga on the basis of structural and geological constraints. The general geometry of the intrusion, the relationship between the different units, suggest that the different facies correspond to ultramafic cumulates derived from various magma injections in an active magma chamber. Processes and rocks sources that lead to such oxides concentrations in such ultramafic rocks remain to be specified.

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References

Ag-Bi-Te Sulphosalt Minerals Related to the Amensif Cu-Pb-Zn-Ag-(Au) Carbonate-Replacement Deposit (Guedmiwa District, Western High Atlas, Morocco)

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Abstract. The Amensif Cu-Pb-Zn-Ag-(Au) deposit is located in the northern flank of the western High Atlas Mountains, Morocco. This carbonate-replacement deposit occurs predominantly in Lower Cambrian carbonates along a major detachment fault that separates the Basal unit from the Upper unit. Orebodies are mainly massive replacements of carbonate strata, although sulphides also occur in veins. Silicification, chloritization, local skarn formation and sulphidation are the most important hydrothermal alteration features observed. The mineralogy is dominated by base metal sulphides with subordinate sulphosalts of Ag, Bi, Sb, Pb, and Au. The ore consists of chalcopyrite, pyrite, galena, sphalerite, arsenopyrite, tetrahedrite, tennantite, and Bi-Ag-Sb-Cu-Pb-Te sulphosalt (malalite, schirmerite, freibergite, hedleyite, and krupkait). anglesite, covellite, malachite, and azurite. Silver commonly occurs as Ag-Bi-Sb-Pb sulphosalt intimately associated within galena. SEM analyses confirm the occurrence of invisible gold within sulphides. Although SEM analysis of auriferous sulphides indicates the presence of gold in sufficient quantities to explain the bulk gold concentrations; native gold has not been detected in our polished sections. Gangue minerals include predominantly chlorite, epidote, tremolite, calcite, Mn- dolomite, saddle dolomite, quartz, sericite, with minor andradite and vesuvianite. The presence of a bismuth association at the Amensif deposit is typical, and was effective in scavenging gold and silver. The Amensif deposit is a typical example of a distal skarn, and is compatible with a model for polymetallic carbonate replacement type mineralization.

Keywords. Carbonate-replacement, Ag-Bi-Te sulphosalts, base-metal sulphides, Amensif, western High Atlas, Morocco

1 Introduction

The association among Bi, Au, Ag, Te, Cu, and Pb has been extensively documented in numerous types of mineralization worldwide including intrusion-related Au, stringer zones of VMS deposits, orogenic gold, skarns, carbonate-replacement Pb-Zn-Cu-Ag-Au deposits, etc. (Ciobanu et al. 2004; Damian et al. 2008; Voudouris et al. 2008; Ciobanu et al. 2010; Fornadel et al. 2011; Voudouris et al. 2013; Ye et al. 2014; Bristol et al. 2015).

The Amensif deposit is located within the northern range of the western High Atlas. It is considered a polymetallic carbonate-replacement deposit (Ilmen et al. 2014a). Major characteristics of field relations, mineralization, and hydrothermal alteration, have been described by Ilmen et al. (2014a). The recently discovered Bi-Ag-Au-Te minerals give the deposit additional interest; this paper constitutes the first confirmed report of Bi-sulphosalts in the Amensif deposit. Herein, we briefly describe the characteristics of mineralization, with a focus on the Bi-Ag-Te-Pb-Cu-Au minerals. This study is based on scanning electron microscopy and optical microscopy.

2 Regional geology

The Guedmiwa district belongs to the northern range of the western High Atlas Mountains including base and precious metal mineralization as at the Azegour Mo-Cu-W skarn deposit (Permingeat 1957), the Assif El Mal Pb-Zn-(Cu-Ag) vein deposit (Bouabdellah et al. 2009), the Erdouz Ag-Zn-Pb vein deposit (Badra, 1993), the auriferous shear zone of Talat n'Imjad (Ilmen et al. 2014b), and the Cu-Pb-Zn-Ag-(Au) carbonate replacement deposit at Amensif (Ilmen et al. 2014a). The regional geology includes Lower to Middle Cambrian and Ordovician volcano-sedimentary formations consisting of carbonate strata (dolostone, limestone, and marble), schist, sandstone, greywacke, basalt, andesite, dacite, and trachyte (Pouclet et al. 2008). This Lower Paleozoic sequence is intruded by the Azegour granite of Permian age (271 ± 3 Ma; Mérin et al. 1992) and the Al Médinet quartz diorite, and cut by a swarm of Permian rhyolitic dikes.

Structurally, the western High Atlas was affected by three deformational events (D1, D2, D3) (Dias et al. 2011; Ilmen et al. 2014b). The Guedmiwa domain is delimited by large faults (several km in length) that have been active since Hercynian times (Fig. 1) (Labrik 1996; Dias et al. 2011; Ilmen et al. 2014a, b). These large faults delineate in this domain different blocks in which the remarkably triangular Erdouz bloc is delimited by an ENE-WSW dextral mega-shear zone (Erdouz Fault) and a second NW-ENE sinistral shear zone (Al Médinet Fault) (Fig.1). Both structures were responsible for producing the strong deformation and heterogeneity in this domain. The precious and base metal ore described in this contribution is located at the intersections of these faults (Badra 1993; Alansari et al. 2009; Bouabdellah et al. 2009; Ilmen et al. 2014b).
3 Local geology

Geotectonically, the Amensif deposit is in the western High Atlas. It is located about 85 km SW of Marrakesh city and about 5 km south of the famous Azegour W-Mo-Cu mine (Permingeat 1957). The deposit is positioned at the intersection of NE- and NW- trending tectonic belts, between the Erdoz and A1 M edinat fault zones. Host rocks are part of the Lower Paleozoic volcano-sedimentary terranes, overlain by Cretaceous sedimentary terranes. The Amensif area is cut by several rhyolitic dikes.

The stratigraphy of the study area consists of a thick succession (about 600 m) (Badra 1993; Labriki 1996; Bouabellah et al. 2009) of a Cambrian meta-sedimentary and volcaniclastic sequence, overthrust by Cretaceous sedimentary terranes (Fig. 1). The meta-sedimentary sequence was regionally affected by a low-grade, greenschist-facies metamorphism (Badra 1993; Ilmen et al. 2014b).

Two stratigraphic units can be distinguished: a lower volcano-sedimentary unit and an upper pelitic unit.
- The Basal unit is composed of carbonate rocks (limestone, marble, dolostone) overlain by calcareous and pelitic schists and calc-schists. This lower unit is marked by alternating limestone beds and lenses, interlayered with calcareous schists, volcaniclastic rocks, lavas, and pyroclastic rocks. The unit is clearly related to the Lower Cambrian by analogy with age relations of the same unit in the Anti-Atlas (Badra 1993; Alansari et al. 2009; Ilmen et al. 2014a).
- The Upper unit is composed predominantly of sandstone and green schists. Also, by analogy, we assign this unit to the Middle Cambrian (Ilmen et al., 2014a).

4 Mineralization

The carbonate replacement orebodies in the Amensif area are irregular in shape and have vein-like extensions that follow faults and fissures. Massive sulphide bodies occur within the marbles and hydrothermal dolomites as well as along the contact of rocks with different permeabilities (carbonates, schists, greywackes, rhyolites). Schists are not mineralized. Two main types of sulphide mineralization are exposed in surface and underground workings. The most common ore types form massive sulphide replacement bodies hosted in Lower Cambrian carbonates (marbles, hydrothermal dolomites). A second type is in lens-like (veins), disseminations, or semi-massive sulphide.

There is a close spatial relationship between felsic dikes (rhyolites) and ores, especially where limestones are cut by dikes. These dikes are enriched in base metals and oxidized in contact with the Lower Cambrian carbonates.

Table 1. Chemical compositions (wt. %) of selected minerals from the Amensif deposit. (Analyses by SEM-EDS).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>S</th>
<th>Sb</th>
<th>Fe</th>
<th>As</th>
<th>Bi</th>
<th>Ag</th>
<th>Au</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
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<td>Chalcopyrite</td>
<td>30.12</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>60.79</td>
<td>22.73</td>
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83.3 ppm Ag, and 0.41 ppm Au (Ilmen et al. 2014a).

The mineralization formed distal to the Azegour Permian magmatic event.

The hydrothermal system is probably related to the setting, mineralogy, paragenesis, and alteration features of carbonate replacement mineralization suggest that differences and similarities among the geological ages of the same unit in the Anti-Atlas (Badra 1993; Alansari et al. 2009; Ilmen et al. 2014a).

Two stratigraphic units can be distinguished: a lower volcano-sedimentary unit and an upper pelitic unit.

Figure 1. Geologic sketch map of the Guedmiwa area (western High Atlas), modified from Dias et al. (2011).
Hydrothermal alteration associated with the replacement deposit at Amensif is marked by silicification, chloritization, sericitization, and dolomitization. Skarn formation in the host marbles is locally observed.

The primary carbonate replacement ore is composed of chalcopyrite, sphalerite with chalcopyrite disease, galena, pyrite, arsenopyrite, tennantite-tennantite, and minor magnetite and pyrrhotite. Scanning electron microscopy reveals the presence of Ag-Bi-Te-Sb-Pb-Cu minerals. Silver occurs mainly as silver sulphosalts, such as tennantite, tennantite, freibergite, matildite, schirmerite, and Ag-Au amalgam (Fig. 2, Table 1). The Bi-minerals show an intimate association with galena (Fig. 2) and consist mainly of Bi sulphosalts (bismuthinite, matildite, schirmerite, bismuthinite derivatives [hedleyite, krupkaite]), and native elements (native bismuth, A.g-Au amalgam). Oxidizing conditions favored the formation of hypogene copper carbonates (malachite and azurite), lead sulphates (anglesite), and iron hydroxides (goethite and hematite). Detailed textural investigations of the ore assemblages reveal the presence of replacement textures among the sulphide minerals.

Chemical compositions of all above-mentioned ore minerals are given in Table 1. Arsenopyrite contains 2.74 wt.% Sb. The zinc ores are composed of two types: iron-rich sphalerite containing 3.1-10.53 wt.% Fe and iron-poor sphalerite (28-40 wt.% Fe and 59-69 wt.% S). Chalcopyrite, galena, and pyrite lack SEM-detectable trace elements. Tennantite and freibergite contain, respectively, 12.75 and 32.74 wt.% Ag. Silver is often carried by the matildite; that shows 25 to 31 wt.% Ag. Schirmerite contains 5-8 wt.% Ag. Minor amounts of native bismuth, bismuthinite, hedleyite, and krupkaite were identified in close association with galena and matildite. Gold is observed as an Ag-Au amalgam having 65.73-69.59 wt.% Ag and 30.41-34.27 wt.% Au (Table 1). The correlation coefficient (r) between Au with Bi (r = 0.754) indicates the prominent positive correlation.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Wt.%</th>
</tr>
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<tr>
<td>Arsenopyrite</td>
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<td>Tennantite</td>
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<tr>
<td>Freibergite</td>
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<td>Krupkaite</td>
<td>12.91</td>
</tr>
<tr>
<td>Hedleyite</td>
<td>-</td>
</tr>
<tr>
<td>Ag-Au</td>
<td>-</td>
</tr>
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</table>

Massive chalcopyrite-sphalerite-galena with lesser silver-gold are the principal ores exploited since mining operations began. Copper is the most abundant metal followed by zinc then lead. The potential for significant Cu-Pb-Zn ore in the deposit has been tested by drill programs since 2011. Ore reserves are ca. 0.5 Mt with grades of 3.21% Zn, 0.58% Pb, 0.86% Cu, 83.3 ppm Ag, and 0.41 ppm Au (Ilmen et al. 2014a).

Table 1. Chemical compositions (wt.%) of selected minerals from the Amensif deposit. (Analyses by SEM-EDS).

Figure 2. A. Replacement texture among sphalerite (Sp), chalcopyrite (Ccp) and galena (Gn); reflected light, scale: 1 cm = 100 µm. B. Replacement texture between galena and chalcopyrite, totally replacing pyrite (Py); reflected light, scale: 1 cm = 150 µm. C. Native bismuth (n-Bi) surrounded by matildite (Mat) which replaces galena; BSE image. D. Ag-Au amalgam included in galena with freibergite (fgb) developed between chalcopyrite and galena which is replaced by matildite; BSE image.

5 Conclusions

The Amensif ore deposit formed by a carbonate replacement system that developed in Lower Cambrian carbonates cut by a swarm of Permian rhyolitic dikes. The mineralization formed distal to the Azegour granite (Permian, 271 ± 3 Ma; Mrini et al. 1992). Differences and similarities among the geological setting, mineralogy, paragenesis, and alteration features of carbonate replacement mineralization suggest that the hydrothermal system is probably related to the Permian magmatic event.
The Amensif Cu-Pb-Zn-Ag-(Au) mineralization is lithologically and tectonically controlled. Structural control is particularly evident since the deposit is positioned at the intersection of the ENE-WSW-trending Erdouz fault and the WNW-ESE-trending Al M edinet fault.

Ore minerals consist mainly of sulphides (chalcopyrite, pyrite, sphalerite, galena) and sulpho-arsenides (arsenopyrite), native metals (Bi, Ag-Au), and sulphosalts and sulpho-bismuthinitides of Ag, Bi, Cu, Pb, and Te. The presence of Ag and Au minerals is not revealed in this assemblage, but these precious metals occur in considerable amounts in other ore minerals, principally tetrahedrite, tennantite, freibergite, maladite, schirmerite, and Ag-Au amalgam. Additionally, minor amounts of Te and Bi form fine-grained hedleyite. Sphalerite shows the chalcopyrite structure of Borton and Bethike (1987).

Hydrothermal alteration surrounding the orebodies consists of dolomite, saddle dolomite, Mn-dolomite, calcite, barite, ankerite, chlorite, tremolite, andradite, vesuvianite, and quartz.

Preliminary lead isotopic data show that the ore-forming components were derived from a mixture of upper crustal material and the mantle (Ilmen et al. 2014a). Thus, it can be suggested that this paragenesis formed under high to medium temperature hydrothermal conditions, from a complex Cu-Pb-Zn-Bi-Sb-S-Ag-Au-U-bearing fluid (Ilmen et al. 2014b).

The enrichment of Bi, Te, Sb, and Pb suggests a magmatic contribution to the ore-forming fluid. According to Ciobanu et al. (2006), the presence of T minerals in an ore is indicative of a magmatic signature. Bismuth minerals also have been considered pathfinders for Au in a variety of deposit types (skarn, stringer zone of VMS, intrusion-related Au; Ciobanu et al. 2009). Our study confirms the earlier suggestion that, in the Amensif deposit, the Cu-Pb-Zn mineralization is a carbonate replacement type.

Acknowledgements

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References


The West African Craton and its Geophysical Signatures

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Abstract. This study examines existing and newly compiled geophysical representations of the West African Craton (WAC) in terms of its large-scale tectonic architecture. In order to build an interpretation with a significant depth extent we draw upon a range of geophysical data, principally seismic tomographic inversions, receiver functions, gravity and magnetics. We present these results as a series of layers providing a series of depth slices through the lithosphere. The different geophysical methods suggest partitioning of the WAC into three tectonic elements at the largest scale which is observed in both seismic tomographic images, Lithosphere Asthenosphere Boundary models and long wavelength gravity signals. The different models of the Moho based on these gravity or seismic datasets show little or no correlation between the models, either for short or long-wavelength features, and show little correlation with receiver function inferred crustal thickness estimates. Manual interpretation of low wavelength gravity and magnetic data suggest a continuation of the WAC across the western margin of the modern boundary, and also highlight distinct domains interpreted to be of Birimian age.

Keywords. West African Craton; Seismic Tomography; Gravity; Magnetics; Receiver Functions; Moho; LAB

1 Introduction

The West African Craton (WAC) extends across Western Africa, and consists of two Archean nuclei in the northwestern and south-western parts of the craton juxtaposed against an array of Paleoproterozoic domains made up of greenstone belts, sedimentary basins and regions of extensive granitoid-TTG plutons, these are overlain by Neo-Proterozoic and younger sedimentary basins.

The WAC has a geological history that spans over 3.5 Ga, and it has witnessed many tectonic upheavals during this time, even after it became a single cratonic block around 2 Ga ago. The craton consists for the most part of a series of sub-parallel greenstone belts trending N-S to NE-SW, separated by either tonalite-trondhjemite-granodiorite (TTG) and granite domains or sedimentary basins affected by repeated deformation episodes. These terranes are overlain by 1 Ga to Quaternary depocentres. The borders of the WAC are largely defined by a combination of surface geology and gravity signature (Burke and Whiteman 1973; Lesquer et al. 1984). Debates around the first-order tectonic architecture of the craton have been based on petrographic and structural variations as measured at the surface, with depth interpretations restricted to geometric projections or limited magnetic-gravity inversions. The resulting architectures are effectively two-dimensional and limit a full understanding of crustal scale structure and large regions of metal potential.

This study combines existing analyses with previously unpublished inversions, new P-wave receiver function estimates and manual interpretations of the gravity and magnetic anomaly maps in order to examine the existing geophysical database for the WAC in terms of its large-scale tectonic architecture. In order to build an interpretation with significant depth extent we draw upon a range of geophysical data, principally seismic tomographic inversions, gravity and magnetics. We present these results as a series of horizontal slices through the crust and upper mantle leading to an integrated 3D model though the lithosphere.

2 The geophysical signatures of the West African Craton

2.1 The internal structure of the West African sub-continental lithosphere and the Lithosphere-Asthenosphere Boundary

The lithosphere-asthenosphere boundary (LAB) denotes the limit between the Earth’s "rigid" outer shell that forms the plates which translate in continental drift and sea-floor spreading and the “weak”, convecting layer, the asthenosphere (Jordan 1975; Eaton et al. 2009). The availability of large catalogues of seismic data over the last two decades has allowed researchers to undertake seismic tomography studies predicting global and local variations in P-waves (Vp), S-waves (Vs). Five studies, based on similar input data sets, but using different inversion schemes, have presented seismic tomographic images of Vs for Africa (Lebedev and van der Hilst 2008; Begg et al. 2009; Simmons et al. 2010; Fishwick 2010). These studies all produce models that are dominated by positive Vs anomalies over the West African Craton (WAC), the Congo Craton and over southern Africa to depths of at least 400 km.

At the scale of the WAC, the higher resolution models (Begg et al. 2009; Fishwick 2010; Simmons et al. 2010) resolve a NE trending lower Vs zone (within the overall high velocity difference of the WAC) trending from eastern Sierra Leone to the junction of Niger, Mali and Algeria. A global Vs model supplied by Steve Grand of the University of Texas (an 2011 update of the model...
published in Grand 2002, and reprocessed following the interpolation methodology described in Begg et al. (2009), shows a distinct partitioning into three domains of Vs values within the WAC in the 175400 km depth range (Fig. 1), with relatively fast Vs roughly over the northern and south-eastern craton, and a slow Vs zone between the two. The overall relative positive Vs perturbations in the cratons can either be interpreted in terms of lower temperature, or as a petrological contrast, and the linear lower velocity trend can equivalently therefore be interpreted either as a thermal or non-thermal anomaly.

**Figure 1.** Tomographic image S-wave velocity (Vs) of West Africa, at the 175-250 km depth interval using an updated model generated by Steve Grand (methodology outlined in Grand, 2002), and reprocessed as described in Begg et al. (2009). Reference velocity is 4.6 km/sec. Red to white colours denote Vs much faster than the starting model; blue-green colours show Vs much slower than the starting model. The 175-250 km image shows two distinct high velocity zones, one centred just south of the Reguibat Inlier in northern Mauritania and Mali, and the other centred under Ghana and Côte d’Ivoire.

**2.2 The Base of the SCLM: the Lithosphere Asthenosphere Boundary (LAB)**

The exact topography of the lithosphere-asthenosphere boundary (LAB) varies according to the measurement technique (Eaton et al. 2009). Tomographic images, especially at the scale of Africa or the West African Craton, inherently produce smoothed or broad (100-200 km ranging) depth estimates due to the nature of the inversions. We first focus on four recent tomography studies, based on similar surface-wave seismic data types but using different inversion schemes that have presented seismic tomographic inversions of Vs for Africa, and which have enabled the authors to make predictions of the topography of the LAB.

The inferred topography of the LAB as interpreted by Priestley and Tilmann (2009) resolves an elongate keel oriented NNE-SSW for the western domain of the WAC, whereas the Fishwick and Bastow (2011) and Pasyanos (2010) models both resolve a 10-15 km shallower N E S W feature traversing the overall approximately 220 km depth LAB. Finally the Li tho1.0 model of Pasyanos et al. (2014) also shows a NE-SW linear shallower lithosphere starting from Liberia, but differs from the other models by showing a shallow zone under Senegal.

**Figure 2.** Comparison of different Moho and LAB models for the WAC and western Mauritania.

**a.** Map showing location of S&P receiver function picks from Miller and Becker (2014, plus symbols); Spieker et al. (2014, star symbols) and Cooper and Miller (2014, cross symbols), as well as location of an arbitrary NW-SE profile (filled circles).

**b.** Scatterplot comparing depth to LAB models versus S wave receiver function LAB depth estimates.

Receiver functions, in particular S receiver functions (SRFs), are better at resolving vertical changes in velocities at LAB depths rather than tomographic methods. In addition, SRFs do not contain “multiples” from shallower (crustal) structure in the ~80-250 km depth range like P receiver functions. We can also
compare the tomographic results with the recent receiver functions studies of Cooper and Miller (2014) whose work principally cover the periphery of the craton in Morocco (Miller and Becker 2014; Spiæker et al. 2014) and the south-east edge of the craton in Côte d’Ivoire, Ghana and Nigeria (Fig 2a) (Cooper and Miller 2014). Although the analysis of S receiver functions produce a range of sparsely located interpretations of the Moho and LAB topography across the WAC, they represent a useful independently derived dataset for comparison.

If we compare these only the Pasyanos (2010) and Pasyanos et al. (2014) show positive correlations, and only Pasyanos (2010) is at all significant (linear regression R²=0.78). The receiver function data suggests a much larger range in LAB depths than the regional models, which may reflect the inherent lateral smoothing present in the regional models or the limited number of clean teleseismic events recorded at the sparsely located seismometers.

2.3 WAC Crustal Thickness

As with the structure of the LAB, the crust-mantle boundary (also referred to as crustal thickness or the Moho) has been imaged by different techniques, namely seismic tomography and gravity. If we compare eight of these models for our arbitrary NW-SE profile across the craton, we can see significant variations between the different models both in mean crustal thickness and the short wavelength variations (Fig. 3).

2.4 Intermediate-wavelength gravity and magnetic anomalies

Seismic tomographic models of the WAC, which only have a resolution of at best 1° (110 km), are insufficient to help us resolve structures within the crust. In order to highlight the major crustal structures we studied the regional and satellite gravity and magnetic datasets.

In order to minimise the effects of near-surface structures we tried a number of low-pass filtering techniques but finally settled on a 30 km upward continuation to both the gravity and magnetic datasets, to which we then applied a range of geophysical filters (Tilt Derivative, First Vertical Derivative, Automatic Gain Control, Analytic Signal) to enhance subtle features.

This analysis produced a map of interpreted structures characterised by multiple domains consisting of one or more sets or sub-parallel linear features with a characteristic spacing between structures of between 30 and 75 km (30 km being the effective cut-off wavelength introduced by the upward continuation). In any one subregion, up to three different sets of features with distinct orientations could be mapped. The overlapping structures could represent features at different depths, or alternatively they could result from the superposition of different structures at different times, or of course both. The majority of the WAC contained identifiable sets of sub-parallel structures, which we have attempted to identify in terms of their age of formation (Fig. 4), but not their nature, as at these wavelengths we cannot be sure that they relate to single features.

Figure 4. Interpreted structure map for West Africa based on manual interpretation of medium-wavelength gravity and magnetic data, separated into notional age groups. Combined attributed structure map for West Africa, with attributions based on correlations with other geological and geophysical datasets.

3 Discussion

A suite of recent seismic tomography studies all suggest a high velocity zone in the SCLM coupled with a thickened lithosphere under the major Africa cratons, including the WAC (Grand 2002; Lebedev and van der Hilst 2008; Fishwick 2010; Simmons et al. 2010). Beneath the WAC, there is a secondary structure trending NE-SW visible in the seismic velocity models, which reduces the depth of the estimated LAB and which correlates with a long wavelength gravity high. The depth to the LAB from MT and seismic data varies between 180 and 240 km across the craton. The division of the mantle into two distinct elements possibly supports the interpretation of Lesquer et al. (1984) for a “Ghanian Nucleus” and or could be interpreted to coincide with the boundary between the Tauodeni subcraton and the Leo-Man-Ghana sub-craton of Begg et al. (2009).
The eight models of the Moho models that we compare show very little consistency between models, and little to no correlation with the receiver function picks. At the present day this precludes us using any of the models as constraints on the tectonic evolution of the West African Craton. This is not to say that one of the models is not correct, simply that we don’t have any basis for selection. Additional receiver function studies that provide a better coverage of the inner part of the WAC could provide the constraints currently lacking for the more regional studies.

The intermediate-wavelength Archaean structures interpreted from gravity and magnetics in both the Reguibat and Kenema-Man shields exhibits a concentric pattern of structures around a western “core”. Some of these features are very likely of Palaeoproterozoic age. There is no evidence that the two Archaean domains are connected at depth beneath the Taoudeni Basin, although they may represent the parallel Pan-African structures. The only area where there appear to be oblique trends are found in the southeast part of the craton including SE Burkina Faso and Ghana. The boundary between these two domains seems to represent a first order structure within the WAC.

Acknowledgements

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References


Geochemistry, Mineralogy and Isotope Composition of Pb, Zn and Cu in Gossan from the Perkoa Lead and Zinc Deposit, Burkina Faso

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Abstract. The Paleoproterozoic Perkoa massive sulfide deposit (Burkina Faso) is capped with well-developed gossan. To assess changes that occur within primary ore bodies under tropical weathering conditions, the geochemical and isotopic signature of gossan was compared with that of primary ores. To aid the identification of gossan in exploration, geochemical properties of gossan were also compared with the same properties barren laterite duricrusts which are abundant in West Africa. Compared to primary ores, the gossan is enriched with As, Ba, Pb and Sb. On the other hand, the contents of Ag, Co, Cu, Hg, Mo, Ni and particularly Zn are significantly lower. The gossan when compared with barren laterite duricrust in the same area, is enriched with Ag, As, Ba, Hg, Mn, Mo, Pb, Sr, Sb and Zn. Isotopic composition of lead bound in gossan (206Pb/207Pb = 0.98±0.002, 208Pb/206Pb = 2.34±0.005) is practically identical with the isotopic composition of lead in the primary ore. The differences in the isotopic composition of lead in gossan and lead in the barren laterite duricrust, and in lateritic soils result from mixing of ore and lithogenic lead. Compared to primary ore (δ65Cu = +0.2 to +1.7 ‰ and δ66Zn = -0.6 to +0.88 ‰, respectively), the gossan is depleted in heavy isotopes of copper and zinc (δ65Cu = -0.02 to -0.62 and δ66Zn = -0.1 to -0.93). The chemical weathering of sulfide-rich rocks thus gives rise to considerable variations in Cu isotopes (average: -1.1‰, δ65Cu gossan–ore), but minor changes in Zn isotopes were found (average: -0.3‰, δ66Zn gossan–ore). Isotopic composition of copper from the barren laterite duricrust is different from copper contained in gossan. No such difference was found in the isotopic composition of zinc. The results suggest that isotope geochemistry can be an advisable tool for discrimination between mineralized and barren products of weathering.

Keywords. Gossan, mineralogy, isotopes Pb, Cu, Zn, Perkoa, Burkina Faso

1 Introduction

The Perkoa massive sulfide (VHM S) deposit in Burkina Faso is unique among the Paleoproterozoic Birimian Supergroup of West Africa. The estimated ore reserves are 5.7 Mt with 18.2 percent Zn. The deposit consists of a main orebody, which contains more than 90% of the reserves, and various secondary orebodies. The secondary ores are hosted by tuffite, dorrite to granite bodies which are structurally overlain by andesite, rich basic rocks and carbonaceous schist (Schwartz and Melcher 2003).

The deposit is exposed to the surface, forming a 2 to 4 m thick gossan. The aim of the present study was to (1) assess changes that occur within primary ore bodies under tropical weathering conditions using isotope geochemistry and (2) compare geochemical and isotopic signatures of primary ore bodies to those of gossan, ambient lateritic soils and laterite duricrust.

2 Methods

Samples were completely digested for xx h along soil references (SRM 2711 and SRM 2709) sealed Teflon beakers containing a mixture of HF and HClO4 at 80°C. Trace element concentrations of digested samples were analyzed using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS, X Series 2, Thermoscientific). The accuracy of the analysis was better than 5% RSD. The isotopic composition of Pb in the samples was determined using inductively coupled plasma mass spectrometry (ICP MS, X Series 2, Thermoscientific) under the conditions given elsewhere (Mihaljević et al. 2011). Correction for the mass bias was performed using NIST 981 (Common lead) between measurements of the individual samples. The standard errors for measurement of the 206Pb/207Pb and 208Pb/206Pb ratios were <0.3 ‰ RSD and <0.4 ‰ RSD, respectively. The accuracy of the measurements was tested on reference materials BCR 2 and AGV 2 certified by the US Geological Survey (1998).

Copper and Zn isotope analysis was carried out under Ultra-Clean laboratory conditions (Class 100, IS05). Copper and zinc fractions for isotope analysis were separated from acid-digested samples by ion exchange chromatography using the procedure described in Voldrichova et al. (2014). Copper and zinc isotope analyses were carried out on a MC ICP MS Neptune (Thermo Fisher Scientific) at the Czech Geological Survey. The 65Cu/63Cu ratios are reported in the δ65Cu (‰) notation relative to the SRM NIST 976 standard. Mass bias of Cu measurements was corrected by standard-sample-standard bracketing using the SRM NIST 976. The 66Zn/64Zn ratios are reported in the δ66Zn (‰) notation relative to the SRM NIST 683 standard. A 67Zn-70Zn double spike was used to correct for the mass bias (Voldrichova et al. 2014).

Metallogeny of North and West Africa 1627
3 Results and discussion

3.1 Mineralogy of primary ore and gossan

Massive sulfide ore is mainly composed of Fe-rich sphalerite, pyrite, barite, hexagonal pyrrhotite, magnetite and minor galenite. Chalcopryite, arsenopyrite, Ag-rich tetrahedrite, and molybdenite occur as trace minerals in the massive sulfide ore. A significant deposition of hydrothermal quartz is only found in the structural footwall of the deposit, where the main orebody is close to quartz diorite. A blite, (Ba, K)-feldspar, Ba-rich biotite, chlorite, tourmaline, andradite-rich garnet, ilmenite, rutile, titanite, and galena occur in minor amount. Extremely altered quartz microdiorite with disseminated zincian spinel + magnetite ± Fe-poor sphalerite are found adjacent to the massive ores in one of the satellite orebodies.

Figure 1. Photomicrographs of mineral phases from the gossan of Pb-Zn ores at the Perkoa deposit (BSE images). A: Abbreviations: goethite (G), hematite (H), quartz (Qtz), cokrite (Co), Mn-hydroxides (Mn), cinnabar (Hg). A: Botryoidal aggregates of goethite (darker) enclosing thin zones formed by hematite. Goethite formation was followed by botryoidal aggregates of Mn hydroxides with highly variable Pb contents. B: A lining of Mn hydroxide with Pb admixture, passing to a crystalline aggregate of cokrite towards the vug. C: A close-up view of solitary cokrite crystals from the preceding photo. Notable are the growth zoning of the crystals defined by the alternation of Pb-rich and Pb-poor portions and the free vugs in the center of the crystals. D: An inclusion of cinnabar in a quartz grain.

The gossan includes three lithofacies: massive, banded, and brecciated. Massive gossans show different textures ranging from cellular to colloform with many local transitions to boxwork, stalactitic, or earthy forms. Banded gossans are relatively common and reproduce metamorphic texture of the massive sulfides. Breccia gossan is the most common lithofacies. It consists of a consolidated aggregate of angular fragments of collapsed gossan that is poorly cemented by colloform goethite. Crust precipitates of Fe oxyhydroxides line the vugs and pores. Besides the high abundance of hematite and goethite, X-ray diffraction analyses identified quartz, kaolinite, illite, cokrite [PbFe₂(S₂O₄)(OH)₄], alunite [K₂[Al₆(SO₄)₂(OH)₂]], and natroalunite [NaAl₆(SO₄)₂(OH)₂]. In addition to the above minerals, microchemical analyses revealed the presence of hinsdalite [Pb₃(S₂O₄)(SO₄)(OH)₆], hidalgoite [PbAl₄(AsO₄)(SO₄)(OH)₆], and brucite-group mineral, probably pyrochlore [M₆(OH)₄].

Minerals such as hematite, goelite and brucite groups generally form colloform texture, produced by multiple alternations. (Fig. 1A) whereas sulfates are either finely dispersed in the mass of dominant minerals or form separate accumulations, especially in the pores of the rock (Fig. 1B, C). In residual quartz grains, locked inclusions of cinnabar (Fig. 1D), sphalerite, chalcocyprite and barite less than 50 microns in size are preserved.

Figure 2. Classification of Pb-bearing phases of the alunite supergroup from gossan and relative occupancy of D and G positions (Diagram after Scott, 1987).

3.2 Geochemistry of primary ores, gossan and laterite duricrust

Primary ores contain on average 26 % Zn, 0.4 % Pb, 42 ppm Ag, 226 ppm Cu and 21 ppb Au. The ores also contain 170 ppm As, 25 ppm Ba, 18 ppm Co, 39 ppm Hg, 391 ppm Mo, 952 ppm Mn, 168 ppm Ni and 7.5 ppm Sb.

In contrast to the primary ores, the gossan is strongly enriched in As (aver. 8507 ppm), Ba (618 ppm), Pb (5007 ppm) and Sb (128 ppm). However, the contents of Ag, Co, Cu, Hg, Mo and Ni are markedly lower. The prominent depletion of Zn corresponds to its high mobility during the weathering process (Fig. 2).

The gossan and mineralized gravel in its immediate vicinity show, if compared with the barren laterite duricrust, significantly higher contents of Ag, As, Ba, Hg, Mn, Mo, Pb, Sr, Sb and Zn (Table 1).

On the other hand, the laterite crust is enriched in Cr, Sc, V and Th relative to the gossan. These elements are bound to rock-forming silicates (micas, amphibole, biotite and epidote) or to heavy minerals (monazite,
rutile, tourmaline, xenotime, apatite) and their mobility within the weathering process is low.

Table 1. Average contents (means) of chemical elements in (1) the gossan of the Perkoa stratabound lead and zinc deposit, (2) in mineralized gravel (“lag”, grain size >2 mm) collected in an outcrop adjacent to the gossan, and (3) in barren lateritic duricrust in the Perkoa area, Burkina Faso. Contents of most elements in ppm, contents of Fe, Ca, P and Ti in wt%. n = number of analyzed samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>Gossan (n=5)</th>
<th>Mineralized gravel (lag) (n=2)</th>
<th>Barren lateritic duricrust (n=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>23.4</td>
<td>25.2</td>
<td>5.5</td>
</tr>
<tr>
<td>Cu</td>
<td>46.2</td>
<td>60.7</td>
<td>46.7</td>
</tr>
<tr>
<td>Pb</td>
<td>8507</td>
<td>5164</td>
<td>120.1</td>
</tr>
<tr>
<td>Zn</td>
<td>789</td>
<td>719</td>
<td>22.1</td>
</tr>
<tr>
<td>Ag</td>
<td>5.6</td>
<td>6.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Co</td>
<td>3.3</td>
<td>14</td>
<td>3.2</td>
</tr>
<tr>
<td>Mn</td>
<td>1328</td>
<td>1724</td>
<td>198</td>
</tr>
<tr>
<td>Fe</td>
<td>34</td>
<td>26.2</td>
<td>24.6</td>
</tr>
<tr>
<td>As</td>
<td>1580</td>
<td>141</td>
<td>28.7</td>
</tr>
<tr>
<td>Au</td>
<td>0.006</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>Th</td>
<td>1.1</td>
<td>2.3</td>
<td>8.9</td>
</tr>
<tr>
<td>Sr</td>
<td>122</td>
<td>79</td>
<td>9</td>
</tr>
<tr>
<td>Sb</td>
<td>128.9</td>
<td>151</td>
<td>0.3</td>
</tr>
<tr>
<td>V</td>
<td>366</td>
<td>340</td>
<td>852</td>
</tr>
<tr>
<td>Ca</td>
<td>0.2</td>
<td>0.1</td>
<td>0.04</td>
</tr>
<tr>
<td>P</td>
<td>0.18</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>La</td>
<td>7</td>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>Cr</td>
<td>72</td>
<td>278</td>
<td>500</td>
</tr>
<tr>
<td>Ba</td>
<td>618</td>
<td>898</td>
<td>27.5</td>
</tr>
<tr>
<td>Ti</td>
<td>0.04</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>Hg</td>
<td>10.1</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Sc</td>
<td>3.3</td>
<td>2</td>
<td>28.8</td>
</tr>
<tr>
<td>Ga</td>
<td>14</td>
<td>11</td>
<td>29</td>
</tr>
</tbody>
</table>

3.3 Lead isotopes

Isotopic composition of lead in fresh ore (206Pb/207Pb = 0.98±0.04, 208Pb/206Pb = 2.34±0.005) is very homogeneous and practically identical with that in the gossan (206Pb/207Pb = 0.98±0.002, 208Pb/206Pb =2.34±0.005). This indicates means that the isotopic composition of lead is practically invariable during the weathering of primary ores. This corresponds with the limited mobility of lead during the weathering process. The isotopic composition of lateritic soils in the vicinity of the gossan (206Pb/207Pb = 1.12 ± 0.004) differs from that of primary ores and displays a relatively wide range of values. This is probably due to mixing of ore lead and lithogenic lead (206Pb/207Pb ~ 1.20; Fig. 3). Such conclusion is also supported by the isotopic composition of gravel sampled in the vicinity of gossan outcrops: its values lie intermediate between those for the gossan, lateritic soils and barren laterite duricrusts from the same area.

3.4 Copper and zinc isotopes

Compared with primary ore (δ65Cu = +0.2 to +1.7 % and δ66Zn = -0.6 to +0.88 %, respectively), isotopic composition of Cu and Zn in the gossan is depleted in heavy isotopes (δ65Cu = -0.02 to -0.62 % and δ66Zn = -0.1 to -0.9 %, respectively; Figs 4 and 5). Oxidative weathering of sulfide-rich rocks that produces substantial variations in Cu isotopes (average: -1.1 %δ65Cu gossan–ore) and small variations in Zn isotopes (average: -0.3 %δ66Zn gossan–ore). For the Cu abiogenic system, the isotopic fractionation is caused by electron-exchange-driven [Cu(I)/Cu(II)] redox reaction at the surfaces of sulfide minerals that occur during subaerial chemical reactions. Under acidic conditions, these reactions tend to be enriched in fluid phase and be depleted in weathering residuum in the heavier Cu isotope (Fernandez and Borrok 2009). The fractionation of Zn isotopes during sulfide weathering is smaller probably because Zn, unlike Cu, is not a redox-sensitive element (Mathies et al. 2014).

![Figure 4](image-url)
modified within the pedogenic process, either by adsorption of heavier isotopes on secondary Fe and Mn and clay minerals, or by biologically-induced processes, i.e. extraction of isotopically lighter metals by plants (Albarède 2004). The isotopic composition of copper in the gossan and the ambient lateritic soils markedly differs from that in the barren laterite duricrust (δ⁶⁵Cu = -1.7 to -2.8 %). In zinc, no differences were proved between the δ⁶⁶Zn values in the gossan and those in the laterite crust.

Figure 5. Copper concentrations versus δ⁶⁵Cu (relative to SRM NIST 976) in sulfidic ore, gossan, lateritic soil and lateritic duricrust in the Perkoa area (Burkina Faso).

Figure 6. Zinc concentrations versus δ⁶⁶Zn (relative to SRM NIST 683) in sulfidic ore, gossan, lateritic soil and lateritic duricrust in the Perkoa area (Burkina Faso).

3 Conclusions

Results of the present study revealed that gossan rocks from the Paleoproterozoic deposit of Perkoa in Burkina Faso differ from lateritic soils and especially from barren laterite duricrust in: (1) the preservation of hematite and goethite pseudomorphs after sulfides, (2) the presence of barite, sphalerite and cinnabar enclosed in residual quartz grains, (3) elevated contents of many trace elements, particularly Mo, Pb, Zn, Ag, Mn, As, Sr, Sb, Ba and Hg (4) different values of isotopic composition of lead and copper. Contrasting isotope values of Pb and Cu in the gossan and laterite duricrust suggest the potential use of isotope studies for discriminating between mineralized and barren weathering products in a geochemical survey.

Acknowledgements

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References

Geochronology and Lithostratigraphy of the Siguiri District: Implications for Gold Mineralisation in the Siguiri Basin (Guinea, West Africa)

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Abstract. New ages and lithostratigraphic observations from the Siguiri district within the Birimian terrane in Guinea (West Africa), has resulted in a revision of the Siguiri Basin stratigraphy. This gives new insights into the tectonic evolution of the Basin and highlights the controls on the world-class orogenic gold Siguiri district location. Three distinct metasedimentary formations are recognized in the district. The Balato and Fatoya formation form a basal regressive sequence, overlain by the Kintinian formation. This last formation is dominated by shale with a stack of polymict conglomeratic interbeds at its base. These conglomerates can be mapped throughout the entire Siguiri Basin and are interpreted to represent allolistostromes. The maximum age of sedimentation of these three formations were dated at 2113±10, 2113±5 and 2120±5 Ma respectively. The minimum age of deposition of all these sediments is constrained by cross-cutting volcanic rocks dated at 2092±5 Ma. Put into the South West African Craton context, the sedimentary facies and geochronology of the Kintinian sediments suggest these are “late basin” sediments deposited during the early phases of the Eburnean orogeny, and highlight the fundamental structures controlling the early architecture of the Siguiri Basin and the location of major gold deposits.

Keywords. West Africa, Siguiri, geochronology, lithostratigraphy, early architecture, gold

1 Introduction and regional context

The Siguiri Basin is located in the north-western part of the Paleoproterozoic Baoulé-Mossi domain of the South West African Craton (SWAC; Figure 1A). The Baoulé-Mossi domain was accreted against the Archean Kénema-M domain (in the south-west of the SWAC) during the Eburnean orogeny between ca. 2200 and 2040 Ma (Aouchami et al. 1990; Egal et al. 2002; Thiéblemont et al. 2004; Davis et al. in review 2015). The Siguiri Basin is one of the biggest metasedimentary basins of the SWAC (~40,000 km²) and hosts the world-class orogenic gold district of Siguiri (Lebrun et al. in review 2015a).

Figure 1. A. Geological map of the South West African Craton. Orogenic gold deposits are displayed as small red discs. B. Geological map of the Siguiri Basin. Location of the Siguiri district map in red. Location of the Saraya geochronological sample, Si326, in white. Modified from Milesi et al. (1989).

The lithostratigraphy of the Siguiri Basin was mapped by the French geological survey (BRGM) as a dominantly homogeneous package of undifferentiated
and poorly sorted, with an average size of 2–3 grained matrix. The clasts are angular to sub-rounded metres in thickness. These conglomerates are mainly observed around the base of the fining-upward disconformable. The Kintinian formation clearly put the later stratigraphically on top of the former. This contact is sharp and observed in core and in the field. Ripple marks were also observed in core and in the field. The Balato formation is dominated by massive shale, grading to cm-thick shale-siltstone with minor fine greywacke interbeds. This formation is relatively incompetent and intensely deformed. The full thickness of the Balato formation is difficult to evaluate. The contact between the Balato and overlying Fatoya formation was not observed in the drill-core or in the field. The Fatoya formation is dominated by 10’s metre-thick to metre-thick beds of medium to coarse-grained greywacke grading up to siltstone and mudstone. Individual beds are highlighted by sharp to erosional basal surfaces. Rip-up clasts of finer material are observed around the base of the fining-upward greywacke beds. Cross-lamination and asymmetric ripple marks were also observed in core and in the field. The minimum thickness of the Fatoya formation is evaluated at ~400 m from logged drill cores. Field observations of the contact between the Fatoya and Kintinian formation clearly put the later stratigraphically on top of the former. This contact is sharp and disconformable.

The Kintinian formation is a >400 m thick formation dominated by massive shale with cm-thick, boudinaged limestone interbeds and rare thin beds of siltstone or fine graded greywacke. The formation also displays around its base two stacked conglomeratic layers of up to 100 of metres in thickness. These conglomerates are mainly clast-supported deposits with 5 to 30 vol% of fine-grained matrix. The clasts are angular to sub-rounded and poorly sorted, with an average size of 2-3 centimetres. Clast lithologies in the Siguiri district range from: shale (85 vol%), limestone (10 vol%), felsic volcanics (<1 vol%), felsic intrusive (~1 vol%), banded iron formation (BIF; <1 vol%), and possible mafic volcanics (up to 4 vol%). The conglomerates occur as thick (~10-15 m) sedimentary deposits overlain by thin (<50 cm) caps of shale to mudstone intervals. Their true thickness varies across the map and in drill cores.

Figure 2. A. Geological map of the Siguiri district tenement as interpreted from the Spectrem AEM Tau products. Deposits are structurally controlled and mostly hosted in the Fatoya formation (Lebrun et al. in review 2015a). The location of each geochronological sample is reported on the map in black. Sample Si327 was sampled further west (Figure 1B). The blue outline represents the Siguiri tenement boundaries. B. SPECTREM Late-Time Tau of the Z-component (maximum Tau for Z-channel 5-8) with overlain sedimentary formation boundaries, faults and Siguiri tenement boundaries.

In addition to these three formations, the lithostratigraphy of the Saraya area, located ~50 km west of the Siguiri district, was also characterised. It was found similar to that of the district and is crosscut by volcaniclastic rocks displaying cm to m-sized subangular felsic clasts (Cayn unpublished; Figure 1A).

Field and drill core observations were integrated over the Siguiri district and regionally using geophysical datasets such as airborne electromagnetics (AEM) and magnetics. The AEM datasets were mostly used at a district scale to help map out the different sedimentary formations and their varying amounts of conductive materials. The magnetics were used at the Siguiri Basin scale to map out the conglomeratic units which can be followed throughout the entire basin (Figure 1A).

2.2 Geochronology

A total of six samples were dated during the course of this study: five detrital samples of sediments and one sample of volcanic rocks from the Saraya area (Figure 1B and 2). Following appropriate preparation (zircon separation and mounting), each sample was analysed by Sensitivity High Resolution Ion Microprobe (SHRIMP II) at the John de Laeter Centre for Isotope Research of Curtin University, in Perth (Australia).

The maximum age of deposition for: the Balato formation (SKRCDD040 236.5 on Figure 2) is 2113±10 Ma (2σ; MSWD = 0.83); the Fatoya formation...
from: shale (85 vol%), limestone (10 vol%), felsic and poorly sorted, with an average size of 2-3 grained matrix. The clasts are angular to sub-rounded meters in thickness. These conglomerates are mainly its base two stacked conglomeratic layers of up to 100 of graded greywacke. The formation also displays around observations of the contact between the Fatoya and evaluated at ~400 m from logged drill cores. Field ripple marks were also observed in core and in the field. basal surfaces. Rip-up clasts of finer material are dominated by massive shale with cm-thick, boudinaged Siguiri district at the Siguiri Basin scale (Lebrun et al. in fundamental structures that control the location of the architecture of the Basin and into the location of the formations and their varying amounts of conductive relief, channelized depositional environment such as lobe distributaries (e.g. Bourget et al. 2010). In contrast, the stacked conglomerates sitting near the base of the Kintinian formation are interpreted as the products of subaqueous, cohesive debris flows (Mulder and Alexander 2001) which incorporated relatively local clasts. The rest of the Kintinian is interpreted as a return to a low energy marine or lake depositional setting. Overall, the Siguiri district sediments are interpreted as marine or lake sedimentary deposits that initially formed a regressive (coarsening-upward) sequence showing a transition from low-energy marine (or lake) organic-rich shales (Balato formation), to an onset of gravity-flow deposits and distal turbidite deposition (Fatoya formation), and finally to an onset of high-energy debris flow deposition (Kintinian conglomerates). The sequence then fines up and is associated with a return to lower energy marine (or lake) deposits (Kintinian shales) interpreted as a shutdown of the siliciclastic input and/or a relative increase in water depth (e.g. transgression).

The stacked Kintinian conglomerates are interpreted as allolistostrome deposits, typically described as products of submarine debris flow triggered by slope failure (Dalrymple and James 2010) and possibly associated with earthquake-induced faulting events (Cieszkowski et al. 2009). The Kintinian allolistostrome can be followed throughout the entire Siguiri Basin and contrasts strongly with the rest of the Siguiri Basin “fine sediments” described by Egal et al. (1999) and Feybesse et al. (1999). It marks an abrupt change in depositional energy and this major change in lithofacies is interpreted to represent piedmont-type deposits (short transport in an environment of active continental erosion; Bossière et al. 1996).

Based on the sedimentary facies associations, the geochronology of the Siguiri district rocks, the Kintinian conglomerates and the presence of banded iron formation clasts in them (interpreted to come from the Archean Simandou area), the Kintinian formation does not match the characteristics of most of the sedimentary formations found in the SWAC (e.g. Sefwi in Ghana, dominated by pyroclastics and volcanoclastics, or the Bambela Basin formations, dominated by flysch-like metasediments deposited at ca. 2120 Ma and showing no Archean signature; Penouy et al. 2012, Baratoux et al. 2011). Instead, we interpret the Kintinian formation as made of Lower Tarkwa Group equivalent sediments (Figure 3). We propose that the Kintinian formation formed late during the Eburnean orogeny and that the allolistostromes it displays are typical of an early stage of “late basin” sedimentation. The Siguiri district sediments are interpreted to be associated with the first stage of convergence and their morphology controlled by the fundamental structures controlling the early architecture of the Siguiri Basin.

### 3 Discussion and conclusions

#### 3.1 Depositional environment

The sedimentary facies of the Balato formation deposits suggests deposition in a low energy, marine or lake setting. The Fatoya formation is interpreted as a marine or deep lake sequence formed by turbidity current deposits in a rather distal depositional setting, such as the outer part of a channel-levee system (Piper and Deptuck 1997) and/or a distal turbidite lobe setting, or in a low-relief, channelized depositional environment such as lobe distributaries (e.g. Bourget et al. 2010).

In contrast, the stacked conglomerates sitting near the base of the Kintinian formation are interpreted as the products of subaqueous, cohesive debris flows (Mulder and Alexander 2001) which incorporated relatively local clasts. The rest of the Kintinian is interpreted as a return to a low energy marine or lake depositional setting. Overall, the Siguiri district sediments are interpreted as marine or lake sedimentary deposits that initially formed a regressive (coarsening-upward) sequence showing a transition from low-energy marine (or lake) organic-rich shales (Balato formation), to an onset of gravity-flow deposits and distal turbidite deposition (Fatoya formation), and finally to an onset of high-energy debris flow deposition (Kintinian conglomerates). The sequence then fines up and is associated with a return to lower energy marine (or lake) deposits (Kintinian shales) interpreted as a shutdown of the siliciclastic input and/or a relative increase in water depth (e.g. transgression).

The stacked Kintinian conglomerates are interpreted as allolistostrome deposits, typically described as products of submarine debris flow triggered by slope failure (Dalrymple and James 2010) and possibly associated with earthquake-induced faulting events (Cieszkowski et al. 2009). The Kintinian allolistostrome can be followed throughout the entire Siguiri Basin and contrasts strongly with the rest of the Siguiri Basin “fine sediments” described by Egal et al. (1999) and Feybesse et al. (1999). It marks an abrupt change in depositional energy and this major change in lithofacies is interpreted as a marker of the onset of increased tectonic activity during the early phases of the Eburnean orogeny.

#### 3.2 The central Siguiri Basin: a Tarkwa Group sequence?

The Tarkwa Group (defined by Davis et al. in prep), are “late orogenic basin”-type sedimentary rocks. These sediments are typically associated with the early phases of orogenic contraction (Robert et al. 2005), and display similar facies than the Tarkwaian itself. The Tarwaian (Sestini 1973) consists of intercalations of conglomerates, sandstones and phyllites, interpreted to represent piedmont-type deposits (short transport in an environment of active continental erosion; Bossière et al. 1996).

Based on the sedimentary facies associations, the geochronology of the Siguiri district rocks, the Kintinian conglomerates and the presence of banded iron formation clasts in them (interpreted to come from the Archean Simandou area), the Kintinian formation does not match the characteristics of most of the sedimentary formations found in the SWAC (e.g. Sefwi in Ghana, dominated by pyroclastics and volcanoclastics, or the Bambela Basin formations, dominated by flysch-like metasediments deposited at ca. 2120 Ma and showing no Archean signature; Penouy et al. 2012, Baratoux et al. 2011). Instead, we interpret the Kintinian formation as made of Lower Tarkwa Group equivalent sediments (Figure 3). We propose that the Kintinian formation formed late during the Eburnean orogeny and that the allolistostromes it displays are typical of an early stage of “late basin” sedimentation. The Siguiri district sediments are interpreted to be associated with the first stage of convergence and their morphology controlled by the fundamental structures controlling the early architecture of the Siguiri Basin.

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**Figure 3.** Simplified lithostratigraphic and geochronological chart of some key areas of the West African Craton. Ages from the Siguiri district and Saraya are reported in the left column. Modified from: Baratoux et al. (2011), Lahondère et al. (2002), Lebrun et al. (in review 2015a), Perrouy et al. (2012).

### 3.3 Early architecture of the Siguiri Basin and control on orogenic gold systems

Regardless of the timing of mineralisation, the structural framework associated with mineralization is intimately controlled by the early architecture (e.g. Love et al. 2004; Miller et al. 2010). Early architecture is critical for...
exploration targeting and major stratigraphic boundaries are commonly used in orogenic gold exploration (Robert et al. 2005). These boundaries typically highlight the fundamental structures that were active at the time of a basin formation and controlled its morphology. Fundamental structures are commonly reactivated multiple times and will act as important pathways for fluids produced from deep-seated sources. These structures can be visible in regional-scale geophysical datasets, and highlighted in the field by lithological variations. This study has mapped a major lithological variation in the Siguiri Basin which is interpreted to be on a fundamental architectural boundary in the Basin. We infer this acted as important conduit for mineralizing fluids and it is a key control on the location of the world-class orogenic gold district at Siguiri. This type of approach can be used as a major exploration targeting tool for orogenic gold systems.

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Developing the Lithotectonic Framework and Model for Sulphide Mineralization in the Jebilet Massif, Morocco: Implications for Regional Exploration

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Abstract. The central Jebilet massif, part of the North African Variscan Belt, hosts significant polymetallic sulphide mineralization. It is generally considered syngenetic and has many features of volcanogenic massive sulphide (VMS) mineralization. However, some characteristics are not compatible with a classic VMS model and two alternative scenarios for formation have been proposed. Our preliminary research favours a complex, multi-stage development of the sulphide deposits. Uncertainty as to the critical processes controlling the mineralization and lack of agreement on a genetic model inhibit regional exploration. We identify the key knowledge gaps regarding sulphide mineralization in the central Jebilet and outline a research program to address these, with the ultimate aim of improving regional mineral exploration targeting and unlocking the economic potential of this relatively underdeveloped district.

Keywords. Morocco, Variscan, Jebilet, VMS, exploration.

1 Introduction

The central Jebilet massif, in the Marrakech region of western Morocco, comprises a block of Carboniferous sedimentary rocks that were extensively deformed and metamorphosed during the Variscan orogeny (Moreno et al. 2008) (Fig. 1). This block, and its extension to the south of Marrakech (Guemassa massif), are characterized by bimodal intrusive magmatism and significant massive sulphide mineralization (Essaifi and Hibti 2008), e.g., the Draa Sfar deposit: 10 Mt grading 5.3% Zn, 2% Pb, 0.3% Cu (Belkabir et al. 2008). Mining is taking place at the Draa Sfar and Hajjar mines. Previously worked deposits at Kettara, Roc Blanc, and Koudiat Aicha have extensive reserves, and prospects such as Lachach and Ben Slimane are being explored (Essaifi and Hibti 2008).

The massive, polymetallic sulphide mineralization has generally been classified as volcanogenic (Bernard et al. 1988; Belkabir et al. 2008; Marcoux et al. 2008). However, whilst displaying some features characteristic of syngenetic volcanogenic massive sulphide (VMS) mineralization (e.g., sulphide mineralogy dominated by pyrrhotite; generally stratabound; hosted by a marine volcano-sedimentary succession; chlorite-sericite alteration; Bernard et al. 1988; Marcoux et al. 2008; Moreno et al. 2008), some features of the deposits and controls on their distribution remain enigmatic.

It has also been suggested that some of the deposits may be epigenetic, associated with Variscan tectonics and magmatism (Essaifi and Hibti, 2008). Interpretation of the mineralization is complicated by the Variscan deformation and metamorphism resulting in a lack of sedimentary or diagenetic textures (Moreno et al. 2008). Whilst some deposits are well characterized at the mine-scale, with good understanding of local structural controls, geometry, host rock geochemistry, ore mineralogy and hydrothermal alteration (e.g. Belkabir et al. 2008; Moreno et al. 2008), the overall structure and stratigraphy of the central Jebilet are poorly known and thus, regional controls on the distribution of mineralization are not well established.

Below we outline a collaborative research pro-
2 Geological setting

The Jebilet massif, 7 km north of Marrakech in north central Morocco, forms a component of the Western Meseta, part of the North African Variscan Belt (Fig. 1A). The massif, 170 km long and 40 km wide, is dominated by a succession of sedimentary rocks, deposited in the shallow marine environment of a Devonian-Carboniferous, continental margin, transitional rift basin (Huvelin 1977; Aarab and Beauchamp 1987; Beauchamp and Izart 1987; M. oro et al. 2008). Extension was rapidly followed by compression and basin closure during the Variscan Orogeny, resulting in low-grade metamorphism and deformation of the region (Essaifi et al. 2014). Three tectono-stratigraphic domains, separated by major shear zones, have been defined (Huvelin 1977): i) the western Jebilet, comprising unmetamorphosed Cambro-Ordovician sedimentary rocks (Huvelin 1977); ii) the central Jebilet, a block of low-grade metamorphosed, schistose, marine Visean shales (Sarhlef schists) deposited in an anoxic environment (Beauchamp 1984; Essaifi and Hibti 2008); and iii) the eastern Jebilet, composed of unmetamorphosed Visean rocks (Huvelin 1977) (Fig. 1B).

The central Jebilet hosts the polymetallic sulphide mineralization and is also characterized by the presence of minor rhyolitic and rhyodacitic extrusives, reported by Belkabir et al. (2008) at Draa Sfar to have FIIIb (see Hart et al. 2004) tholeiitic compositions. The rocks of the central Jebilet have been folded and sheared and low-grade deformation of the region (Essaifi et al. 2014). Three tectono-stratigraphic domains, separated by major shear zones, have been defined (Huvelin 1977): i) the western Jebilet, comprising unmetamorphosed Cambro-Ordovician sedimentary rocks (Huvelin 1977); ii) the central Jebilet, a block of low-grade metamorphosed, schistose, marine Visean shales (Sarhlef schists) deposited in an anoxic environment (Beauchamp 1984; Essaifi and Hibti 2008); and iii) the eastern Jebilet, composed of unmetamorphosed Visean rocks (Huvelin 1977) (Fig. 1B).

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3 Mineralization

The characteristics of the central Jebilet sulphide mineralization are described in detail by Essaifi and Hibti (2008) and references herein, and those features relevant to the subsequent discussion are summarised below and in Table 1. The host sequence, dominated by siliciclastic rocks deposited in a continental margin basin, is consistent with the "siliciclastic" class of VMS deposits defined by Franklin et al. (2005). The massive sulphide deposits occur at different stratigraphic levels of the Sarhlef metasedimentary rocks and do not appear to be confined to a specific lithological package. The mineralization is typically focused in shear zones, which have a consistent spatial relationship with the bimodal intrusions. Regional deformation means the sulphide deposits are sub-vertical, and comprise long and narrow ellipsoidal lenses in three dimensions (Essaifi and Hibti 2008). Small sulphide veins are locally present below the massive sulphide ore and interpreted to represent stockwork or stringer zones. However, their occurrence is sporadic and in some instances they have very limited vertical extent (M. oro et al. 2008).

The mineralization has variable base metal concentrations, with some deposits being distinctly Pb-Zn-rich, e.g., Draa Sfar. Pyrrhotite forms up to 90% of the sulphides, with variable quantities of sphalerite, galena, chalcopyrite, pyrite, and arsenopyrite (Essaifi and Hibti, 2008) (Fig. 2B, C). The abundance of pyrrhotite contrasts with deposits of the Iberian Pyrite Belt, which has the same lithotectonic setting (Franklin et al. 2005). The regional metamorphism results in a range of recrystallization and deformation textures in the ores with primary depositional textures largely absent (M. oro et al. 2008) (Fig. 2B).

Well-developed suergene mineralized zones, indicated by surface gossans (10–100 m in width), are a characteristic feature of the deposits (Belkabir et al. 2008; Essaifi and Hibti 2008; Marcoux et al. 2008) (Fig. 2A). Two models for the formation of the central Jebilet sulphide deposits have been proposed: (i) syngentic, representing either classic VMS or SEDEX mineralization (Marcoux et al. 2008; M. oro et al. 2008); or (ii) epigenetic, formed during the waning stages of Variscan orogenesis and associated with the abundant bimodal intrusive magmatism (Essaifi and Hibti 2008; Lotfi et al. 2010).
younger (300 Ma) leucogranites (Fig. 1B). The bimodal association (>65% mafic, felsic) is widespread, associated with peraluminous rocks and extrusives (Essaifi and Hibti, 2008). Syn-tectonic magmatism related to the subsequent discussion are summarised in the Sarhlef metasedimentary rocks and do not appear to define by Franklin et al. (2005). The massive siliciclastic rocks deposited in a continental margin grade metamorphism has resulted in a schistose fabric within the Jebilet have been folded and sheared and low-grade metamorphism has resulted in a schistose fabric within the Jebilet, central Morocco, forms a component of the Western Sahara Province. The massif, 170 km long and 40 km wide, is dominated by a succession of sedimentary rocks, Ordovician sedimentary rocks (Huvelin 1977); ii) the central Jebilet, iii) There is significant uncertainty about the source of metals and sulphur in VMS systems (Franklin et al. 2005; Gibson et al. 2007). Whilst the composition of intrusions proximal to the Jebilet deposits may explain their variable base metal composition, isotope evidence for the origin of the ore-forming fluids is inconclusive (Lotfiet al. 2010), and the importance of the sedimentary sequence as a source of metals remains unclear (Essaifi and Hibti 2008). VMS ores frequently contain a diverse suite of trace metals (e.g. Co, Sn, Cd, Bi, Te, Se, Ga) (Galley et al. 2007). Trace element data for sulphides from the Jebilet mineralization is limited (e.g. Marcoux et al. 2008), variation between deposits has not been documented, and the processes controlling the preferential enrichment of some metals (e.g. Se at Draa Sfar) are not understood.

iv) Understanding the detailed parageneses of the mineralization is essential for determining the chronology of mineralizing events and associated ore-forming processes.

v) Whilst the sheet-like sulphide ore bodies are interpreted as upturned lenses (Belkabir et al. 2008), and zones thought to represent stockwork vein mineralization are described from some deposits, the origin of the veins and their pre-deformational relationships to the paragenesis is widely debated.

4 Knowledge gaps and future research

Despite possessing some features typical of syngenetic VMS mineralization (Table 1) many aspects of the central Jebilet hydrothermal system and the geology of the district remain enigmatic, leading us to question continued application of a simple VMS mineral deposit model. The uncertain geological relationships, principally resulting from deformation and metamorphism, the unclear genetic controls on mineralization, the absence of a robust baseline regional stratigraphy, coupled with our preliminary field observations and sulphur isotope work identify the following research areas and questions to address:

i) At a district scale VMS deposits are typically concentrated at one or two stratigraphic intervals (Gibson et al. 2007). This is not apparent in the central Jebilet, due to the lack of detailed mapping and stratigraphy across the block. Does any stratigraphic control exist at the district-scale, and if so can favourable stratigraphic positions (ore-bearing horizons) be identified in the regional stratigraphy, distal from known deposits? A good quality regional stratigraphy based upon detailed (~1:50 000 scale) mapping is fundamental to assessing this.

ii) VMS deposits have a ‘spatial, temporal, and genetic association’ with bimodal volcanism (Allen and Weihed 2002; Franklin et al. 2005). Whilst the Jebilet mineralization is generally classified as volcanogenic, volcanic rocks are uncommon across much of the region, and a genetic relationship between mineralization and volcanism is unconfirmed (Essaifi and Hibti 2008; Moreno et al. 2008).

iii) There is significant uncertainty about the source of metals and sulphur in VMS systems (Franklin et al. 2005; Gibson et al. 2007). Whilst the composition of intrusions proximal to the Jebilet deposits may explain their variable base metal composition, isotope evidence for the origin of the ore-forming fluids is inconclusive (Lotfiet al. 2010), and the importance of the sedimentary sequence as a source of metals remains unclear (Essaifi and Hibti 2008). VMS ores frequently contain a diverse suite of trace metals (e.g. Co, Sn, Cd, Bi, Te, Se, Ga) (Galley et al. 2007). Trace element data for sulphides from the Jebilet mineralization is limited (e.g. Marcoux et al. 2008), variation between deposits has not been documented, and the processes controlling the preferential enrichment of some metals (e.g. Se at Draa Sfar) are not understood.

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stratiform ore are dubious. Although stockwork zones are not always well developed in VMS deposits (Franklin et al. 2005), reconstructing their pre-deformation architecture in the Jebilet would be valuable for guiding exploration at the mine-scale.

vi) Whilst many sulphide deposits in the Jebilet are associated with gossans (Marcoux et al. 2008) detailed studies of these zones and their relationships to the sulphide ores are lacking. From an exploration perspective it is vital to be able to discriminate between gossans overlying sulphide mineralization and those produced by other processes such as the pedological concentration of iron. Detailed mapping and textual and geochemical characterization studies are required to determine if the gossans can be used as a reliable indicator of buried sulphide mineralization.

vii) Refining the genetic model for the Jebilet mineralization represents the first stage in developing an effective exploration targeting system for the region. Preliminary observations indicating multi-phase evolution of the deposits suggests elements of both existing models may be valid. However, given the uncertainty about the ‘critical processes’ controlling the formation and location of these deposits and timing relationships we propose a ‘mineral systems’ approach as described by McCuaig and Hronsky (2014).

5 Conclusion

The sulphide deposits are evidence for a significant hydrothermal system existing in the central Jebilet, which has many hallmarks of an important, albeit relatively undeveloped, VMS district. However, fundamental questions remain unanswered regarding the broad-scale controls on mineralization, deposit size, morphology and composition, and, from a genetic perspective, on heat sources, deposit growth mechanisms and fluid, sulphur and metal sources. Integrated mapping and research studies (including a comprehensive stable and radiogenic isotope programme), focused on stratigraphy and structure, as advocated by Allen and Weihed (2002), are a prerequisite for making meaningful interpretations of the sulphide deposits and their local environments of formation. The research is vital for understanding the essential elements of the mineral system of the central Jebilet, which can be translated into an exploration model and strategy aimed at identifying mineralization distal from known deposits.

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References


The Geology and Mineralogy of the Sadiola-Yatela Gold Camp, Mali, West Africa: Contrasted Mineralisation Styles Derived from a Dynamic Hydrothermal System in the Late-Eburnean and Post-Birimian Karstification-Weathering Processes

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Abstract. The local geology of the Sadiola-Yatela gold camp differs from other Birimian granite-greenstone belts and sedimentary basins by the abundance of carbonate rocks. All deposits of the camp align along the Senegal-Mali lineament and lower order structures. Orogenic gold mineralisation occurred during a period of transcurrent tectonics coeval with prolonged calc-alkaline magmatism between ca. 2090-2070 Ma, soon after the cessation of region-wide contractional deformation. Three distinct types of gold mineralisation are identified on the basis of differing ore paragenesis, and are typified by the Sadiola Hill-style Au-As-Sb mineralisation, the Alamoutala-style AuZn-Pb mineralisation and the Yatela-style karst-hosted gold residuum. The diversity in ore paragenesis is controlled by a dynamic hydrothermal system in the late stages of the Eburnean tectono-magmatic activity, and reworking by later karstification-weathering processes. The Sadiola Hill deposit shares characteristics of Birimian orogenic gold mineralisation in the Ashanti belt of Ghana. In contrast, the Alamoutala deposit shows atypical mineralogical features that indicate a possible link between orogenic gold mineralisation and iron skarn development in the region (e.g. Falémé iron district). Not only distinct in style, the Yatela deposit formed distinct in time by protracted karstification and weathering, which resulted in the formation of a gold residuum of economic interest.

Keywords. Sadiola, Eburnean orogeny, carbonate-hosted gold, Birimian

1 Geology of the Sadiola gold district

Deposits of the ca. 15 Moz Sadiola gold mining camp are located in the Kédougou-Kénèbie inlier, a window of Birimian terranes (ca. 2200-2050 Ma) that crops out in western Mali and eastern Senegal. The local geology of the Sadiola-Yatela gold camp is divided into two distinct lithological domains with respect to the Senegal-Mali Shear Zone. A sedimentary domain, located east of the structural boundary, is marked by repetitions of N-S to NNW-trending stratigraphic units. From west to east within that sedimentary domain, rocks consist of shelf carbonates and sandstones (e.g. arenite, wacke) progressing to siltstone-dominated sequences including carbonaceous argillites. A second domain, west of the regional-scale lineament, is dominated by igneous rocks. It consists of andesitic-dacitic flows, detrital sedimentary rocks and numerous plutons varying in size and composition. Late- to post-Birimian dolerite swarms are common occurrences in the region and consistently present as ENE-WSW and NE-SW oriented sets. To the far east of the district, deformed Birimian terranes are unconformably overlain by flat-lying Neoproterozoic cover sequences. The structural record in rocks of the region suggests a polyphase deformation history marked by early fold-and-thrust tectonics and followed by transcurrent tectonics. Regional greenschist facies metamorphism is associated with both deformation phases. Geochemistry indicates the sedimentary sequences to have deposited between ca. 2140 and 2110 Ma. Prolonged Birimian calc-alkaline magmatism is divided into three distinct pulses (ME) that are presented hereafter in chronological order. ME1 (ca. 2120-2100 Ma) consists of belt-type andesitic volcanics and plutons of variable composition (e.g. diorite, granodiorite). ME2 (ca. 2090-2070 Ma) consists of syn-tectonic, I-type, metaluminous plutons, largely represented by biotite-granodiorite. Some of these ME2 belt-type plutons are locally associated with hornblende-hornfels to pyroxene-hornfels contact metamorphic aureoles. ME3 (ca. 2070-2060 Ma) consists of late-tectonic monzogranites.

2 Structural framework and controls on mineralisation

2.1 Ductile deformation (D1s and D2s)

The earliest structural feature consists of NNW-trending inclined folds (F1). Folding is associated with a weak to strong cleavage (S1), that sub-parallel the general orientation of the stratigraphic units in the area, and a gently NNW-plunging lineation (L1). This episode of early deformation remains poorly constrained but is associated with structural features that are consistent with WSW-ENE-directed shortening (D1s).

A second fabric is associated with refolding (F2) of early folds (F1), resulting in a fold interference pattern. F2 folds are disharmonic with upright to inclined fold
hinges. Fold axes plunge gently (15–30°) to the SSW and are associated with a 020°/75E axial-planar cleavage (S2) indicative of WNW fold-vergent. A number of NNE-trending thrusts and high-angle reverse faults are closely associated with these F2 folds. The orientation of F2 folds, fault geometries and kinematic indicators are consistent with NW-SE-directed shortening (D2).

A strong brittle overprint was recorded in outcrop and drill core and is associated with sininal reactivation of the early accretionary structures (e.g. S2, NWW-trending litho-stratigraphic contacts) and the formation of NNE-trending sub-vertical shear zones. Fault geometries and sininal kinematic indicators are consistent with NWW-SE-directed shortening (D3). Combined field relationships and micro-textural study indicate that structures which controlled the different ore-bodies were undergoing sininal shearing at the time of mineralization. The sininal reactivation of early accretionary structures and linking with belt-discordant NNE-trending shears appears a critical factor to ore deposit location and geometry.

Following D3, a conjugated set of shear-extensional veins is recorded in some of the pits but could not be correlated at regional scale. Late ENE-trending dextral faults were also identified in some of the open pits. These faults are interpreted to represent the latest Eburnean deformation imprint in the region.

A number of E-W normal cross-faults is recorded in the open pits and in outcrop over the camp. These faults cut across all ore-hosting structures and Neoproterozoic sandstone cover sequences.

3 Distinct mineralisation styles

Timing of primary mineralisation and structural controls on ore geometry are equivalent for all deposits of the district. In contrast, the diversity in ore paragenesis, nature and chemistry of wall-rock alteration recognised over the camp points toward three distinct styles of mineralisation typified by the Sadiola Hill, the Alamoutala and the Yatela gold deposits (Table 1).

3.1 Sadiola Hill-style Au-As-Sb mineralisation

The bulk of the ore is hosted by impure carbonate host rocks. Mineralisation is shear-hosted and geometric and kinematic analyses indicate that the ore-hosting structures were displaced sinistrally at the time of mineralisation (i.e. D3, NW-SE shortening). The bulk of the ore occurs as disseminated sulphides and is associated with a range of ductile to brittle textures in host rocks. Hydrothermal alteration is polyphase and includes an early calc-silicate phase (porphyroblastic growth of actinolite-tremolite) followed by a potassic alteration stage (biotite + calcite ± quartz-K-feldspar-tourmaline-actinolite-tremolite) synchronous with ore minerals deposition. Paragenetic studies reveal that ore development included an early As-rich sulphide stage followed by an Au-Sb stage and a late Sb stage. The ore is associated with the metal enrichment association Au-As-Sb ± Cu-Fe-W-Mo-Ag-Bi-Zn-Pb-Te. The Sadiola Hill deposit shares a similar timing and structural setting to that of other world-class orogenic gold systems in the West African Craton (e.g. Ashanti, Loulo). However, the temperature gradient associated with the ore-forming process and the presence of calc-silicate hydrothermal alteration raise the question of the fluid(s) and metal source(s) for the Sadiola Hill gold system.

3.2 Alamoutala-style Au ± Cu-Fe mineralisation

The Alamoutala open pit occurs in a similar lithostratigraphic position to that of the Sadiola Hill deposit. Meta-sedimentary rocks have been intruded by synkinematic, calc-alkaline, I-type, metaluminous porphyritic granodiorite stocks and dikes dated at 2083 ± 7 Ma. Contact metamorphism of impure carbonate host rocks resulted in the formation of zoned skarn aureoles. Economic gold mineralization is shear-hosted and occurred synchronous with the retrograde portion of the contact metamorphic P-T time path on the basis of combined field and micro-textural data. Ore minerals deposition is synchronous with a potassic hydrothermal alteration phase (e.g. biotite + calcite ± K-feldspar-actinolite-tremolite-quartz-tourmaline), which overprints prograde garnet-pyroxene assemblages.
Metallogeny of North and West Africa

1. Brittle deformations (D1)

2. Brittle deformation (D2 and later)

2.2 Brittle deformation (D3 and later)

A strong brittle overprint was recorded in outcrop and drill core and is associated with sinistral reactivation of the early accretionary structures (e.g. S2, NNW-trending litho-stratigraphic contacts) and the formation of NNE-trending sub-vertical shears. Fault geometries and sinistral kinematic indicators are consistent with NNW-SSE-directed shortening (D3s).

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Table 1. Deposit classification for the Sadiola-Yatela gold camp

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Sadiola Hill-style</th>
<th>Alamoutala-style</th>
<th>Yatela-style</th>
</tr>
</thead>
<tbody>
<tr>
<td>Examples</td>
<td>Sadiola Hill, Tambali</td>
<td>Alamoutala, Drugale</td>
<td>Yatela, FE1, FE4, KW18</td>
</tr>
<tr>
<td>Heat rocks</td>
<td>Limestone + diorite + marro-arenite + quartz-feldspar porphyry</td>
<td>Calc-silicate marble (after impure limestone) + porphyritic granodiorite</td>
<td>Marble (after limestone) + diorite = marro-arenite-silstone-shale</td>
</tr>
<tr>
<td>Structural controls on ore geometry</td>
<td>Sinistral displacement along N-S oriented Sadiola Fracture Zone and NNE-trending shear array</td>
<td>Sinistral-reverse displacement along NNW-trending Alamoutala Fracture Zone and NE-trending shear</td>
<td>Sinistral displacement along diorite-marble interface and NNW-trending shear array</td>
</tr>
<tr>
<td>Relative timing of gold mineralization</td>
<td>D3s NNW-SSE shortening</td>
<td>Late D3s NW-SE shortening + D3s NNW-SSE shortening</td>
<td>D3s NNW-SSE shortening</td>
</tr>
<tr>
<td>Ore mineralogy</td>
<td>Shear-hosted</td>
<td>Shear-hosted, breccia-hosted, and disseminated</td>
<td>(I) Shear-hosted, breccia-hosted, and disseminated (II) Gold residual in variscite host</td>
</tr>
<tr>
<td>Mineralisation styles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major sulphides</td>
<td>Arsenopyrite, Pyrite</td>
<td>Pyrite</td>
<td>Pyrite</td>
</tr>
<tr>
<td>Minor sulphides</td>
<td>Pyrite, chalcopyrite</td>
<td>Chalcopyrite, pyrite</td>
<td>Chalcopyrite</td>
</tr>
<tr>
<td>Minor / trace ore minerals</td>
<td>Pyrite + calcite + epidote + siderite + sprokrite + galena + jasonite + gendortite = gudmannite + uhlmannite + tellurobismuthite</td>
<td>Arsenopyrite + marro-arenite(Cu) + schelite + molybdenite ± sphalerite ± galena ± tetrahedrite-tremolite ± berthierite ± gudmannite ± uhlmannite ± gerdorrite ± sidnietite ± arninite ± synchise ± hornblendite ± mellite ± biotite ± tellurobismuthite ± coloradoite ± gerdorrite + cinnabar</td>
<td>Arsenopyrite + marro-arenite + gerdorrite ± cobaltite ± petulinite</td>
</tr>
<tr>
<td>Oxide</td>
<td>Traces magnetite</td>
<td>Abundant magnetite</td>
<td>Traces magnetite</td>
</tr>
<tr>
<td>Metal association</td>
<td>Au-As-Sb = Cu-W-Mo-Ag-Bi-Zn-Te-Fe</td>
<td>Fe-Au-Cu ± Pb-As-Ni-Cd-Ag-Zn-Ph-W-Te-Sb-K-feldspar-bi</td>
<td>Au-As-Cu = As-Zn-Fe-Pb-Sb-Ag-Ni-Cd native gold, electrum</td>
</tr>
<tr>
<td>Gold phases</td>
<td>Ag-As gold, aerobiferous, traces maldonite</td>
<td>enclosed in pyrite = tetrahedrite-tremolite crystals, locally remobilized along micro-cracks in pyrite</td>
<td>(I) disseminated free gold, gold enclosed in pyrite crystals, and gold blebs locally remobilized along micro-cracks in pyrite</td>
</tr>
<tr>
<td>Gold sites</td>
<td>Reflective gold (lattice-bound) in arsenopyrite?, disseminated free gold, lattice-bound in aerobiferous and maldonite, enclosed in arsenopyrite crystals, locally remobilized along micro-cracks</td>
<td></td>
<td></td>
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<tr>
<td>Hydrothermal alteration</td>
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<td>Alteration types</td>
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<td>Calc-silicate (1), potassic (2) and propylite (3)</td>
<td>Carbonate (1) and Potassic (2)</td>
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<td>(1) Porphyrabolic actinolite-tremolite</td>
<td>(1) Sericite + Pyroxene + actinolite-borneblende ± albite = titanite</td>
<td>(1) Fe-dolomite</td>
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<td>(2) Biotite + calcite + tremolite = K-feldspar ± quartz + apatite</td>
<td>(2) Biotite + calcite-tremolite = muscovite ± tremolite = K-feldspar + quartz ± apatite</td>
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<td>Alteration assemblage</td>
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Petrographic studies reveal that the ore is Fe-rich (pyrite ± pyrrhotite, magnetite, chalcopyrite), characterized by noticeable levels ofREE-B-P-bearing phases (monazite-Ce, tourmaline, and apatite), and contains accessory Ag-Sb-Au-Hg-Bi-Te-M-O-W-Zn-Pb-Ni-Co mineral species. The Alamoutala deposit shows mineralogical features atypical for Birimian orogenic gold mineralization, which indicate possible links among oreogenic gold mineralization and iron skarn development in the region (e.g., magnetite skarns of the Falémé iron district, Schwartz and Melcher 2004).

3.2 Yatela-style gold residuum

A sub-economic primary ore is shear-hosted at Yatela. Shearing focused along the interface between diorite and impure limestone. Mineralisation is also hosted in impure limestone wall-rocks of an array of steep NW-trending faults. Textural relationships indicate that primary ore minerals are synchronous with a potassic alteration phase defined as Fe-dolomite ± biotite ± quartz. The ore is pyrite-rich, contains abundant chalcopyrite, and accessory As-Zn-Pb-Sb-Ag-Co-Ni-Fe-bearing mineral species.

The surficial dissolution of hydrothermally altered and mineralized impure limestone host rocks resulted in the creation of karstic features (e.g., sinkhole) draped and/or filled in with an oxidized sandy-ferruginous and mineralized impure limestone host rocks resulted in the creation of a deep weathering residuum which is likely to have been a lengthy process, and/or filled in with an oxidized sandy-ferruginous and mineralized impure limestone host rocks resulted in the creation of a deep weathering residuum which is likely to have been a lengthy process, and/or filled in with an oxidized sandy-ferruginous and mineralized impure limestone host rocks resulted in the creation of a deep weathering residuum which is likely to have been a lengthy process.

The Yatela gold residuum provides a new appreciation for the diversity in Birimian geochemical and geochronological data for the Sadiola-Yatela gold camp.

4 Towards a genetic model for the world-class Sadiola-Yatela gold camp

Recent studies that integrated the structural, metamorphic, and hydrothermal evolution of Birimian gold deposits in the Kédougou-Kénieba inlier and southern Mali have shown a clear interdependence and interplay between ongoing deformation, magmatism, hydrothermal alteration, and gold mineralisation (McFarlane et al. 2011; Lawrence et al. 2013a, b; Trelor et al. 2014). The collected mineralogical, structural, geochemical and geochronological data for the Sadiola-Yatela gold camp suggest that M2 calc-alkaline intrusions emplaced in the upper Kédougou-Kénieba crust around ca. 2090-2070 Ma, coeval with a period of transient tectonics that outlasted their emplacement (D3), and have played a major role on the dynamics of the mineralising fluids along the Senegal-Mali Shear Zone and lower order structures. The composition and origin of hydrothermal fluids responsible for world-class gold systems in Mali remains debated. However, recent in-depth studies highlight the genetic role of multi-fluid sources (i.e., metamorphic and magmatic) (e.g., Morila, Hammon et al. 2011; Loulo, Lawrence et al. 2013b). Further work is needed to investigate the source of fluid(s) and metals for the Sadiola-Yatela orogenic gold hydrothermal system. Nevertheless, the current study provides an insight into the potential economic interest of Yatela-style residual ore bodies.

Acknowledgements

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Multiple Mineralisation Events, Ashanti Belt, Ghana

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Abstract. World class Birimian Paleoproterozoic gold systems in the NE-trending Ashanti Belt of West Africa occur across a broad geographic extent within volcanosedimentary belts associated with extensive granitoids. Deposit types range from shear zone hosted quartz vein systems, fault-vein systems compatible with fault-valve behaviour, paleoplacer deposits, and cryptic polydeformed deposits that formed early in the geological history. Multiple phases of gold mineralisation with different kinematics and alteration occurred. Host rock types for the gold deposits range from sediment-hosted (Obuasi), sediment and granitoid hosted (Anyankeryim), mafic intrusive hosted (Pampine), granitoid hosted (Adokrom), and placer deposits in quartz-pebble conglomerates (Tarkwa). The gold deposits also have a broad range in structural styles, ranging from ductile shear zones (Wassa) to fault-vein arrays (Damang). Regionally there is a dominant late-stage gold event associated with NW-SE shortening. The world class Paleoplacers in the Ashanti belt predate this event, which requires an older gold event to have acted as a source. The Wassa deposit is a possible analogue for an early gold system linked to the Paleoplacers.At the belt scale architectural controls appear to be a key control on the deposit locations, with a link to cryptic ENE- and Ntrending lineaments and the location of world class ore bodies. In contrast to other gold systems globally, the world class deposits are located on the largest fault in the area (the Ashanti Trend), and do not occur on the bends or jogs along this structure. Like other gold systems globally fault intersections appear to be a critical control on the location of the largest deposits.

Keywords. Orogenic gold Gold, Birimian, Ashanti Belt, Structure, Architecture

1 Introduction

The Birimian Terrane of the West Africa Craton hosts a large number of world class gold deposits, the largest of which occur in the NE-trending Ashanti Belt of Ghana (Fig. 1). The Birimian is comprised of Paleoproterozoic sedimentary basins and linear volcanic greenstone belts, both of which are intruded by a range of magmatic sequences (Leube et al. 1990). These belts were formed during the Eburnean orogeny between 2200 and 2088 Ma (Aouchami et al. 1990; Allibone et al. 2002a).

The Ashanti Belt has been relatively well studied e.g., Obuasi (60 M oz, Blenkinsop et al. 1994; Allibone et al. 2002a); Bogoso (Allibone et al. 2002b); and Damang (8 M oz, Tunks et al. 2004). Gold mineralisation in the Ashanti Belt (Fig. 1) has been previously interpreted to be an orogenic style that occurred at a late-stage, post the metamorphic peak of the Eburnean orogeny, at ca. 2100 Ma (Milesi et al. 1989; Allibone et al. 2002a; Tunks et al. 2004). Paleoplacer deposits also occur and host over 40 million ounces of gold (Pigois et al. 2003) within sedimentary sequences affected by the same deformation events linked to gold mineralisation.

2 Geology

The Birimian in the Ashanti Belt region of Ghana can be sub-divided into three major units (Loh et al. 1999):

(1) The Upper Birimian, dominated by detrital and volcaniclastic rocks of mafic to felsic affinity that include turbidites, shales, and carbonates interbedded with calc-alkaline volcanics. In the Ashanti Belt these have been termed the Kumasi Group (Kumasi and Akyem Basins) and were deposited after 2154 ± 2 Ma (Oberthur et al. 1998).

(2) The Lower Birimian, or Sefwi Group, which consists of a series of volcanics represented by dolerites, gabbros, and tholeiitic basalts; locally interlayered with sediments and carbonates (termed — volcanic rocks in Fig. 1). The Sefwi Group has been dated as being older than 2162 ± 6 Ma (Loh et al. 1999).

(3) Narrow late sedimentary basins known as the Tarkwaian (or Tarkwa Group) that were deposited between 2107 Ma and 2097 Ma (Perrouty et al. 2012; Pigois et al. 2003; Oberthur et al. 1998).

The formations have been intruded by a range of granitoids and tonalite-trondhjemite-granodiorite suites which have a large range in ages (Fig. 1). In areas localised mafic intrusive complexes have developed (Mphor Mafic complex at Hwinu-Butre; Fig. 1).

The regional deformation framework for the Ashanti Belt is complex and multiple event histories have been proposed (Milesi et al. 1989; Blenkinsop et al. 1994; Allibone et al. 2002a; 2002b, Tunks et al. 2004; Feybesse et al. 2006).

2 Deposit styles

The deposits types range from (Fig. 1, 2); Sediment hosted shear zones with disseminated sulphides that are dominantly acicular arsenopyrite (Obuasi, Bogoso, Bueschem, Salaman Trend); Fault-fill quartz veins along...
Brittle faults (Obuasi, Prestea; Fig. 2a); Quartz vein arrays (Anyankyerim, Pampe, part of Damang; Fig. 2b, 2c, 2d); Paleoplacers (Tarkwa, part of Damang; Fig. 2e); Mafic intrusive hosted brecciated shear zones with only minor quartz (Hwini Butre-Benso; Fig. 2f) and; refolded pre-Tarkwa deposits (Wassa; Fig. 2g, 2h, 2i).

**Figure 1.** Geological map of the Ashanti Belt. Modified from the Geological Survey of Ghana 1:1 000 000 map sheet. Key basins and trends are marked.

Multiple phases of gold mineralization with different kinematics and alteration have occurred within the Ashanti Belt. Regionally a dominant late-stage gold event occurred at ca. 2100 - 2080 Ma (Feybesse et al. 2006), which was associated with NW-SE shortening, and sinistral-slip on regional shear zones e.g., Obuasi and Bogoso; Allibone et al. 2002a; 2002b) and also Pampe (Fig. 2c). However, there are also differences in kinematics between some deposits. M infrared conjugate veins within the Damang deposit imply NESW shortening (Fig. 2d). The vein arrays and boudinage at Anyankyerim suggest at NE-SW directed stretching event was linked to mineralisation (Fig. 2b). There is also a variation in mineralogy; the deposits on the eastern side of the belt have a common arsenopyrite- pyrite +/- pyrrhotite assemblage, whereas the deposits on the eastern side dominantly have pyrite and lack pyrrhotite.

The Tarkwa Group, host to paleplacer deposits (Fig. 2e), is folded into regional fold closures (Fig. 1) that are related to the inversion of the Kumasi basin (Allibone et al., 2002a). This group is affected by the same deformation history as the units hosting the other gold systems.

The Wassa deposit is atypical regionally because the gold occurs in an early foliation associated with isoclinal folds (Fig. 2g) that has folded into a depositscale fold (Fig. 2h, 2i). This folding has been correlated with the large scale regional folding of the younger Tarkwa group to the west (Fig. 1). The Wassa deposit has a lot of visible gold associated with quartz.

There appears to be an architectural control on the location of the deposits. The giant Obuasi deposit is located at the intersection of the Akropong and Ashanti Trends (Fig. 1). There also appears to be a correlation with ENE-trending cross-lineaments and major deposits such as Bogoso and Obuasi (these cross lineaments are marked on Fig. 1, some of the late dykes also intrude along these trends). Perrouy et al., (2012) related these features to pre-Tarkwa Group deformation. Deposits also correlate with N-S trending lineaments. In contrast to other terranes, there is no correlation with world class ore bodies and regional strike changes, which implies that regional dilational or contractional jogs related to strike-slip movement are not a regional control on deposit location e.g. to the SE of Prestea (Fig. 1).

### 4 Discussion and conclusions

Within the Ashanti Belt there is a regional late stage event linked to NW-SE shortening, the development of crosscutting cleavages and localised sinistral-slip associated with gold mineralisation (as highlighted by Allibone et al. 2002a, 2002b). In detail there are examples of deposits with distinctly different kinematics incompatible with NW-SE shortening (Damang) which implies the structural history linked to gold mineralisation is more complex than just a late-stage sinistral wrenching event.

The deposits on the western side of the Ashanti Belt commonly contain pyrite and arsenopyrite, while the deposits on the eastern side commonly only have pyrite. This may reflect the presence of the Kumasi Group as a host rock on the western side of the belt (which may have been the source of arsenic in these deposits).

The gold at the Wassa mine occurs in an early foliation associated with isoclinal folds has been refolded into a deposit-scale fold. The Wassa deposit has a lot of visible gold with quartz and could be an analogue for the style of deposit that was the source of the paleoplacer gold within the Ashanti Belt.

Globally many orogenic gold deposits have formed on localised strike changes on regional faults (Weinberg et al. 2004). They also occur predominantly on low displacement faults and shear zones adjacent to much larger fault zones, and not generally on the major, crustal-scale shear zones (Cox and Ruming 2004).
Brittle faults (Obuasi, Prestea; Fig. 2a); Quartz vein arrays (Anyankyerim, Pampe, part of Damang; Fig. 2b, 2c, 2d); Paleoplacers (Tarkwa, part of Damang; Fig. 2e); Mafic intrusive hosted brecciated shear zones with only minor quartz (Hwini Butre-Benso; Fig. 2f) and; refolded pre-Tarkwa deposits (Wassa; Fig. 2g, 2h, 2i).

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southwest of Prestea (Fig. 1) doesn’t host any major correlation with strike changes on faults with the location other gold districts, there is not a strong regional by the Akropong Fault/Trend (Fig. 1, 2). However, unlike the first order Ashanti Fault (Trend) where it is intersected (Perrouty et al. 2012). Like other gold systems globally, regional faults are very prominent in the gravity data (e.g. Damang, Obuasi, Bogoso, Prestea, Pampé, Amanfuri and Wassa; Fig. 1, 2). These regional faults are very prominent in the gravity data (Perrouty et al. 2012). Like other gold systems globally, fault intersections within the Ashanti Belt correlate with large deposits e.g. the giant Obuasi deposit is located on the first order A shanti Fault (Trend) where it is intersected by the A kropong Fault/Trend (Fig. 1, 2). However, unlike other gold districts, there is not a strong regional correlation with strike changes on faults with the location of world class deposits e.g. the major strike change southwest of Prestea (Fig. 1) doesn’t host any major known deposits. There is also a correlation with ENE- and N-trending cross-lineaments and the location of major gold deposits (Fig. 2). These cryptic cross lineaments can be observed in regional geology maps and also geophysical data (Fig. 1, 2). There is some evidence for these structures at deposit scale - Allibone et al. (2002a) mapped E-W trending structures within the Obuasi mine region that they defined as early transfer faults. In other terranes these types of architectural features have been linked to the formation of world class gold deposits e.g. at the St Ives field in the Y ilgarn (Miller et al. 2010). We infer that these cross structures in the Ashanti Belt represent key architectural features linked to focussed crustal scale fluid flow linked to gold mineralisation. The followingsights are relevant to gold explorers; 1) giant deposits can be located on the largest fault in the area; 2) giant orebodies can occur on the regional trend of a fault system and not on the bends or jogs; 3) fault intersections are critical and; 4) cryptic early formed architectural appears to play a role in the location of world class ore bodies.

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References

Lithostructural Study of Mineralization in the Southern Part of the North Orebody of the Polymetallic Hajjar Deposit (Morocco)

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Abstract. In the southern part of the northeast of the Hajjar orebody, we report orientations of the various mineralized lenses intercepted by core drilling carried out in the area. Based on lithostructural studies of samples, the mineralization is hosted in metapelites of Visean age, with hydrothermal alteration at the base marked by abundant chlorite. The orebody is located at the northeast part of a sinistral system of Hercynian structures. These structures are locally cut by older faults. The mineralization is parallel with stratification and has a very low dip to the northeast. This alignment shows that the depositional paleo-environment was very stable and consequently was a favorable zone for mineralization. It is recommended to conduct exploration northeast of the E-W orientation in order to evaluate the extent of mineralization and further mining operations.

Keywords. Hajjar mine, massive sulphide, eastern Meseta, Morocco.

1 Introduction

Hajjar is an underground mine with mineral resources of 20 Mt at 8% Zn, 2-3% Pb, 0.4 to 0.6% Cu, and 60 g/t Ag (Eddebi et al. 1998). The sulphide mineralization is dominated by pyrrhotite, with minor sphalerite, galena, chalcopyrite, pyrite, and arsenopyrite (Halmeur 1988; Leblanc 1993; Hibbi 1993, 2001). Three main orebodies are recognized. The southern part of the northeast body is the subject of this study (Fig 1: Original documents from the GUEMASSA company mine). Although the structural geology of the whole orebodies has been studied in detail (Hibbi et al. 2001), information about the existing mineralization on the 510 and 520 levels is less well known.

The Hajjar mine is located 30 km SSW of Marrakech (Fig. 2).

2 Structural Studies

In order to characterize the evolution of the mineralization to the south of the orebody, a structural survey was conducted on the 510 and 520 levels. This work was done to highlight the different phases of deformation that affected the deposit and their effect on the geometry of the orebody.

On the 510 level, the stratification is represented by a strike direction of N70°E with an average 50° dip to the northwest. The S0 stratification is consistent with that of the mineralization. Stratification is disrupted downstream of the mineralization, probably due to the stress induced by faulting. The faults are characterized by two trends (Fig. 5). The first is a major fault striking N75°E, whereas the second has an orientation of N10°E; locally, this second fault cuts the mineralization.
variations: N30°E, N70°E, and N6°E.

arsenopyrite, this indicate a relationship with rhyolitic
associated to sphalerite, galena, chalcopyrite, pyrite, and
hosted rock, and pyrrhotite dominant (50-75%)

The Hajjar deposit is characterized by sedimentary

3 Petrographic study

Based on macroscopic observations, mineralization is
hosted in metapelite of Viséan age with hydrothermal
alteration at the base marked by chlorite, sericite,
calcite, quartz, and sulphides. Our observations do not
reveal other hydrothermal alteration in the studied drill
cores. In contrast, Hibti et al. (2001) have been
distinguished two hydrothermal alteration types from
the bottom to the upper of the ore bodies. From the
bottom, they have been observed intensively
chloritization and at the upper of the ore bodies, the
presence of intensively sericitization.

Quartz veinlets with remobilized sulphides occur in
the upper part of the orebody.

4 Ore mineralogy and textures

The Hajjar deposit is characterized by sedimentary
hosted rock, and pyrrhotite dominant (50-75%) associated to sphalerite, galena, chalcopyrite, pyrite, and
arsenopyrite, this indicate a relationship with rhyolitic

and rhyodacitic volcanism (Haimeur 1988; Hibti 1993;
Zouhry 1998; Hibti, 2001). Three mineralized aspect are
distinguished: (i) brecciated or stokwork texture
dominated by chalcopyrite, pyrrhotite, sphalerite, pyrite
and arsenopyrite association; (ii) layered texture with
sedimentary rock; it is marked by pyrrhotite, sphalerite ±
galena, chalcopyrite, arsenopyrite association; this
mineralization can be as fly is the hosted rock. (iii)
Stratiform clusters, who can be subdivided to two types
depending on its structure: (a) banded ore as occurs in all
VMS deposit in Central Jbilet; (b) a layered ores located
in the clusters bottom.

On the 520 level, structural data plotted on a rose
diagram show that the cleavage is represented by two
principal trends: N75°E and about N60°E.

From the results found on this level, three
orientations of faults are identified (Fig. 6). The first has
a strike of N75°E, the second N45°E, and the third (a
minor fault set) N45°E with an Alpine direction of
N10°E. The faults that trend N75°E include major
structures that dip between 50° and 65° to the
northwest. Stratifcation is represented by three spatial
variations: N30°E, N70°E, and N6°E.

Figure 3. Lithostratigraphic column of Hajjar deposit (Hibti
2001).

Figure 4. Map and rose diagram showing stratification planes
on 510 level of the Hajjar mine.

Figure 5. Plan map and rose diagram of faults on the 510 level
of the Hajjar mine.
The sulphide mineralization is hosted between basal volcanic series and volcano-sedimentary rocks, and an overlying clay and carbonate series (Hibti 1993, 1999; Leblanc 1993; Eddebi et al. 1998; Ferrari 1998; Zouhry 1998). The deposit has undergone three deformational phases (Gros et al. 1983, 1986; Campi 1984; Cleavers 1986; Boummane 1987; Soulaimani 1991; Hibti 1993; Raqiq 1997), including: (i) a first phase extensional phase associated with the formation of Devonian-Carboniferous basins; (ii) a second phase of post-Visan compression, characterized by a N10°E cleavage with development of folds having a N50°E axial planar schistosity. This phase took place in an epizonal metamorphic setting, and locally is more intense near fault structures (Sagon 1984; Boummane 1987; Soulaimani 1991; Hibti 1993; Raqiq 1997). In the area of N’Fis, indices of thermal metamorphism are periplutonic (Gros et al. 1986; Hibti 1993; Ouadjou 1997); and (iii) A third, post-shale brittle deformation completed the structural evolution of the deposit.

5 Conclusions

The southern part of the North East orebody in the Hajjar mine has a very complex morphology that is in the form of mineralized lenses. Lithostratigraphic study shows that the deposit is hosted in Visean metapelites.

Two aspects of mineralization are described in the Hajjar orebody: the first one localized in the NE Hercynian fault; and the second one as stratiform mineralization in visean metapelite. Both of them occurs as millimetreth to centimetreth microstructures. Being a favorable zone deposit, it is recommended to investigate the area northeast of the orebody, in a NE to EW orientation, in order to evaluate the full extent of the mineralization and find new reserves.

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Lithostratigraphy of the Bonikro Gold Deposit: Contribution to the Birimian Units in the Southern Fettékro Greenstone Belt, Côte d’Ivoire
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Abstract.
Located in the southern part of the Fettékro greenstone belt in Côte d’Ivoire, the Bonikro gold deposit offers the opportunity to set the lithostratigraphic column and to put in light its Birimian units. The geology of the deposit is made of three rock groups; mafic, felsic and sediments. The felsic group contains the ore through the granodiorite and pegmatite lithlogies and occupies the central part of the deposit. Two major lithological units are noted: the basaltic complex occupying the east of the deposit when the second unit i.e the sediments rocks associated with pyroclastics are in the western side. These two units present an interface which is occupied in the south by the north-east trending Bonikro shear zone (BSZ) whereas in the centre and the NE, the interface is occupied by the BSZ shear zone and the granodiorite. In consequence, the lithostratigraphic column realized in the south reveals that the basaltic unit and the pyroclastic unit were in contact before the setting of the BSZ. The Bonikro western side is where the different rocks groups are expressed. This side is likely where the petrographic correlation is consistent and suggests a contemporaneity between both basaltic and pyroclastics units.
Keywords.
Côte d’Ivoire, gold, Birimian, lithostratigraphy

1 Overview of the Birimian lithostratigraphy
The Fettékro greenstone belt is one of the Birimian volcano-sedimentary belts or Birimian volcanic and sedimentary units. These belts are commonly associated with granitoids and are belonging to the Baoulé-Mossi domain of the West African Craton (WAC) formed between 2.2 and 1.9 Ga (Feybesse et al. 2006). The relation between the Birimian volcanic and sedimentary units has been discussed for decade. For some authors, the volcanic formations are younger than the sedimentary sequences (Junner 1935, 1940; Milesi et al. 1989, 1991). Historically, this stratigraphy is admitted by the geologists in Ghana where in the birim valley these volcanics were firstly described. An inverse stratigraphy is proposed by Arnould (1961) and Tagini (1971). From others, there is a contemporaneity between these two units (Leube et al. 1990; Hirdes et al. 1996).

2 Lithostratigraphy of the Bonikro gold deposit
2.1 Methodology
Our investigations started by the petrographic description in the Bonikro open pit and in the different coresheds. Firstly, 25 thin sections were realized in Abidjan and observed at the University Félix Houphouët-Boigny. The second 30 thin sections have been prepared and observed at GeoRessources, Université de Lorraine, Nancy, France.

2.1 Lithostratigraphy
The Bonikro gold deposit is made of three rocks groups; felsic in the centre and striking NE, mafic in the east and sediment in the west (Fig. 1).

Figure 1. Map showing the different geological units of the Bonikro gold deposit.
Lithostratigraphy of the Bonikro Gold Deposit: Contribution to the Birimian Units in the Southern Fettékro Greenstone Belt, Côte d’Ivoire

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1 Overview of the Birimian lithostratigraphy

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2.1 Lithostratigraphy

The Bonikro gold deposit is made of three rocks groups; felsic in the centre and striking NE, mafic in the east and sediment in the west (Fig. 1).

Figure 1. Map showing the different geological units of the Bonikro gold deposit.
The felsic group is dominated by the K-feldspar porphyritic granodiorite (Fig. 2) but locally we also have the pegmatite, the dacite, rhyodacite and the aplitic dykes. The acid dykes namely dacite and rhyolite cut the Birimian formations. The mafic rocks are made of porphyritic basalt and the Basalt sensus stricto with sometimes the amygdular textures. The Bonikro sediments are represented by the siltstone, black shales and pyroclastites. All of these lithologies are structured around the Bonikro shear zone (BSZ) and are affected by the greenschist facies metamorphism. In the south, the basaltic unit and sediment unit are separated by the BSZ. The area is not appropriate to identify the primary rocks in the BSZ. The granodiorite appears from 100 to 300 m under the basalt units.

In the centre, the interface between the sediments and the basalts is occupied by the granodiorite and the BSZ. A part of the sheared basalt is in the west due to the the brittle component of the BSZ.

In the north, the granodiorite has intruded both the basaltic and sediment units (Fig. 2). The shape of the granodiorite shows that the lithology comes from the East (beneath the basaltic unit) then has been re-oriented probably the shear zone contact between both basaltic and sediments unit (Fig. 3).

The west Bonikro is where the pegmatite, the acid dykes and sometimes the granodiorite appear in relation with the sediments and basalts units. The stratigraphy presents three horizons (Fig. 4). From the surface to 250 m, both basalt and sediments are mixed with some granodioritic intrusions. The second horizon from 250 to 550 m is made of granodiorite. The third horizon starts around 550 m and continues deeply. The basalt is likely the Birimian basement in Bonikro but in the first horizon, the sediments are contemporaneous with the later volcanic activity.

**Figure 2.** Macroscopic views of the Bonikro porphyritic granodiorite. A. in the pit; B. from a core

**Figure 3.** Lithostratigraphic column of the northern Bonikro. A. a view in the pit; B. a transversal section

3 Discussion

The Bonikro gold deposit is made of volcanic mafic rocks in the East and volcanoclastics and sediments in the West. These rocks groups are separated by the Bonikro shear zone (BSZ) and the felsic rocks dominated by the granodiorite. These rocks have been metamorphosed to greenschist facies. This geologic distribution has been evoked elsewhere in this birimian greenstone belt. The Agbahou deposit in the South-east of Bonikro shows a similar distribution (Houssou, 2013). Even if at Agbahou, the pluton is not a granodiorite. The observation of pyroclastic in the Western side suggests that the volcanism is the area has an explosive character. In Toumodi, Yacé (1982) also concluded in the Fettêkro the influence of this explosive volcanism. In the West of Bonikro, the volcanoclastics associated with sediments are alternated with the basaltic rocks. These alternations are common to greenstone belts and helped Leube et al. (1990) to evoke a contemporaneousness between these groups. The interface between the mafic volcanic and volcano-sedimentary rocks in the Birimian is known to contain gold mineralisation (Olson 1989; Assié 2008; Kadio et al. 2010). Mostly this interface shows a relation with a non-mineralised pluton, except to Bonikro where the pluton is mineralised. In Ghana, the plutons have been mentioned around the gold deposit (Oberthur et al. 1997; Wille et Klemd 2004). This observation gives the opportunity to distinguish Cape Coast plutons to the...
4 Conclusion

The primary rocks of the Bonikro gold deposit are likely the mafic sequences and the sediments. The mafic rocks include the basalt and the mafic volcanoclastics. Then, these have been eroded and formed the sedimentary rocks. Some of the volcano-sedimentary and sediments show some contemporaneity with the mafic volcanic rocks. The presence of the volcanoclastic in the area is consistent with the fact that the eruptive volcanism occurred in the Fettèkro greenstone belt. These aforementioned rocks have been affected by the shearing and intruded by the granodiorite, and as a result, we have an exceptional deposit where gold is primarily associated with the pluton. The Bonikro gold deposit is likely an example an intrusive gold mineralisation in the Birimian.

Acknowledgements

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Figure 4. Lithostratigraphic column of western Bonikro.
Proterozoic Gold Mineralizing Events at the Scale of the West African Craton

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AMIRA-WAXI program (2006-2013). Access to open pits and underground mines, as well as trenches and drill holes, has also reinvigorated metallogenic studies of the West African craton, comprising the Archean Kenema-Man domain in the west and the Paleoproterozoic Birimian Baoulé-Mossi domain in the southwestern part of the West African craton. The West African craton (WAC) has played a major role in world gold production since antiquity, owing mainly to the significant gold production of Ghana, formerly named the Gold Coast. Motivated by an increased interest in mining, reassessment of the geology in the WAC within the geodynamic framework of the geodynamic/tectonic and the gold occurrence relationships in this craton, makes it difficult to establish relationships between the main geodynamic/tectonic and the gold mineralization events. This study describes six gold deposits of the WAC, but also the presence of other mineral deposits in the region such as porphyry (Gaoua, Kérima, Nassara, Kiaka, Wassa, Damang, and Obuasi). These gold deposits in Ghana and Burkina Faso (Gaoua, Kérima, Nassara, Kiaka, Wassa, Damang, and Obuasi) are dated from isotopic and chronological constraints on the formation of several structures having protracted tectonic histories. However, the gold mineralizing events are still hypothetical and highly debated.

The West African craton (WAC) hosts numerous gold deposits in Birimian terranes that formed during the ~2.25-2.15 Ga Eburnean orogeny. Absolute geochronological evidence for multiple Paleo-Eburnean gold mineralizing events in the WAC, but also the presence of other ore deposits, has been obtained directly from mineralized zones. The geodynamic context of the West African craton is characterized by low gold contents, whereas late-orogenic deposits, which formed during the D1-D2 stages of the Eburnean orogeny, are marked by structurally controlled deposits that are localized in veins, breccias, characterized by brittle structures, which formed during the Eburnean tectonic accretion (D3, D4, and D5 stages).

Keywords: Gold deposits; West African craton; Re-Os geochronology
Re-Os Geochronological Evidence for Multiple Paleo-Proterozoic Gold Mineralizing Events at the Scale of the West African Craton

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Abstract. The West African craton (WAC) hosts numerous gold deposits in Birimian terranes that formed during the ~2.25-2.15 Ga Eburnean orogeny. Absolute dating and timing of mineralization is poorly constrained in this craton, making it difficult to establish relationships between the main geodynamic/tectonic and the gold events. This study describes six gold deposits of the Baoulé-Mossi domain in the southwestern part of the WAC. For each deposit, mineralization is structurally characterized and dated by the Re-Os geochronometer on sulphides linked to gold mineralization, in order to place the auriferous events within the revised geodynamic scenario recently proposed for the Eburnean orogeny by the West African Exploration Initiative (WAXI) project. Results illustrate the predominance of orogenic gold deposits in the WAC, but also the presence of other deposit types in the region such as porphyry (Gaoua deposit, Burkina Faso) and paleoplacer (Damang deposit, Ghana). Re-Os dating provides ages that allow two groups of deposits to be distinguished: (1) early-orogenic deposits, which formed during the D1-D2 stages of the Eburnean orogeny; and (2) late-orogenic deposits, characterized by brittle structures, which formed during Eburnean tectonic accretion (D3, D4, and D5 stages). Our observations highlight the polyphase nature of gold in nearly all of the studied deposits. In these cases, early-orogenic mineralization is disseminated and characterized by low gold contents, whereas late-orogenic mineralization is marked by structurally controlled deposits that are localized in veins, breccias, or shear zones, resulting in higher gold contents within these structures.

Keywords. Gold deposits; West African craton; Re-Os geochronology

1 Introduction

The West African craton (WAC) has played a major role in world gold production since antiquity, owing mainly to the significant gold production of Ghana, formerly named the Gold Coast. Motivated by an increased interest in mining, reassessment of the geology in the WAC during the last two decades has provided new comprehensive geologic and geodynamic models from cratonic to regional scales, notably as a result of the AMIRA-WAXI program (2006-2013). Access to open pits and underground mines, as well as trenches and drill cores, has also reinvigorated metallogenic studies of various gold deposits within the WAC.

Most gold mineralization in the WAC is hosted in Birimian rocks of early Paleoproterozoic age, although exploration is ongoing also in some Archean regions of Liberia, Sierra Leone, and Guinea (Fig. 1). All deposits and occurrences are proximal to major first-order structures having protracted tectonic histories. However, because the ages of these gold deposits are poorly constrained by absolute dating, correlations with specific geodynamic settings and Paleoproterozoic events are still hypothetical and highly debated.

Geochronological constraints currently available for gold deposits in the WAC are deduced from isotopic dating of host rocks that include volcanic or plutonic rocks, and sedimentary rocks hosting the mineralization and hydrothermal alteration zones. However, few ages have been obtained directly from mineralized zones (McFarlane et al. 2011). This paper presents new Re-Os chronological constraints on the formation of several gold deposits in Ghana and Burkina Faso (Gaoua, Nassara, Kiala, Wassa, Damang, and Obuasi). These ages allow us to propose a broad temporal scenario for gold mineralizing events in the southern part of the WAC within the geodynamic framework of the Eburnean orogeny.

2 Geodynamic context of the West African Craton

2.1 Geological setting

The southern part of the WAC, known as the Leo-Man craton, comprises the Archean Kenema-M domain in the west and the Paleoproterozoic Birimian Baoul-Mossi domain in the east. Birimian terranes are composed of a succession of volcanic belts and volcano-sedimentary basins that formed between 2250 and 1980 Ma, and were intruded by several generations of granitoids. Birimian volcanic rocks are products of bimodal
tholeitic to calc-alkaline volcanism that occurred in an immature volcanic arc setting. These Birimian formations were accreted during the Eburnean orogeny, which began ca. 2150-2100 Ma and lasted about 130 m.y.. This orogeny was responsible for the major deformational episodes that affected the WAC and for a regional greenschist-facies metamorphism well represented at the craton scale. Locally, amphibolite-facies conditions were reached, mainly in contact aureoles of granitoid intrusions or along some shear zones.

Figure 1. Simplified geological map of West African craton showing settings of main gold deposits (yellow dots).

2.2 Tectonic scenarios within the WAC

Over the past ~20 years, several regional or local tectonic scenarios have been proposed for the WAC as synthesized in Table 2 (Milesi et al. 1992; Aillilone et al. 2002; Tunks et al. 2004; Feybesse et al. 2006; Vidal et al. 2009; Hein 2010; Baratoux et al. 2011; Perroux et al. 2012). The first deformational event (D1) recognized in the Eburnean orogeny occurred between 2180 and 2160 Ma, and produced a NE-SW to N-S shortening, resulting in major folding of Birimian terranes. This deformation evolved into a NW-SE compression (D2) that lasted until 2120 Ma, accompanied by a local extensional event in the Ashanti belt ( Ghana) associated with deposition of the Tarkwaian detrital sediments. During the following D3, D4, and D5 deformational phases, thought to be very close in age, regional tectonic events are represented by transpressive movements with orientations ranging from NW-SE to SW-NE.

Six gold deposits from Burkina Faso and Ghana were selected for dating based on their use for illustrating the different types of events that led to gold concentration in the WAC (Table 3).

2.3 Deposit-scale geology

Figures 1 and 2 illustrate, respectively, the position of the six studied gold occurrences/deposits within the craton, their spatial relationships with major shear zones, and links between geodynamic events of the WAC and local deformational events. The Gaoua mining district is situated at the southern extremity of the Boromo-Goren greenstone belt, in Burkina Faso. It comprises three copper-gold occurrences (Dienemera, Gongondy, and Mont Birii) in which gold mineralization is minor compared to that of copper; the gold occurrence of Nassara essentially lacks copper. Copper and gold mineralizations are hosted in dioritic-andesitic rocks that are strongly affected by greenschist-facies metamorphism.

The Kiaka gold deposit is situated at the intersection between the volcano-sedimentary Tenkodogo greenstone belt and the Markoye shear zone, in southeastern Burkina Faso. The Markoye shear zone is a NNE-SSW structure that underwent at least two reactivation phases (dextral-reverse and sinistral-reverse) during the Eburnean orogeny. This major structure hosts several orogenic gold deposits including Essakane, the largest gold deposit in Burkina Faso in terms of production.

The Wassa, Damang, and Obuasi gold deposits are all hosted within the Ashanti greenstone belt in southwest Ghana. The Wassa gold deposit, a few kilometers to the north of Tarkwa and Waasa, is situated in the southeastern part of the Ashanti belt, and is hosted by a wide variety of rocks, including mafic volcanic rocks, Tarkwaian volcaniclastic rocks and greywacke, thin magnetite-rich sedimentary units, and rare layers of...
pyrite-rich black shale. These rocks are intruded by diorites and a plagioclase-rich felsic pluton that has a U/Pb zircon age of 2192.7 ± 4.6 Ma (U/Pb SHRIMP on zircon, Parra et al. 2015). All of these lithologies are highly deformed and hydrothermally altered. The Wassa deposit was affected by four main episodes of deformation, referred to as D1Wa, D2Wa, D3Wa, and D4Wa events. Although it seems evident that D2Wa to D4Wa events correspond to the regional D3 to D5 events, respectively (Table 3), uncertainty remains on timing of the first deformation observed at Wassa.

Situated a few kilometers to the north of Tarkwa and Wassa, and hosted by Tarkwaian sedimentary rocks intruded by microdiorite (Fig. 2), the Damang deposit displays two distinct types of gold mineralization. Indeed, Damang consists of a Tarkwaian-type gold paleoplacer overprinted by an epigenetic orogenic lode-gold system (Pigois et al. 2003; Tunks et al. 2004; White et al. 2014).

### 3 Re-Os geochronological constraints on West African craton orogenic gold mineralization

An isochron age of 2161 ± 23 Ma has been obtained for the Gaoua deposit by Re-Os dating of pyrite linked to the porphyry copper stage (L Mignot et al. in revision). This age is younger than those obtained by Brownscombe (2008) on gabbroic intrusions and the hosting diorite in the Gaoua district (2171.6 ± 9.3 Ma and 2185.3 ± 12.0 Ma, respectively) and with the age of 2171 ± 7 Ma for a rhyolite in the Boromo greenstone belt (U-Pb on zircon; Castaing et al. 2003). This latter age is also in agreement with studies conducted on a pre-Eburnean magmatic accretion event predating the Eburnean orogyny that is dated, according to different authors, between 2250 and 2150 Ma (Feybesse et al. 2006; Baratoux et al. 2011).

The Re-Os ages of the late-orogenic pyrite from the Nassara deposit are imprecise, with uncertainties on individual ages up to 8%. However, the calculated weighted average age of 2094 ± 58 Ma seems to correlate with the other constraints, suggesting that this orogenic gold event postdates the porphyry copper episode, even if the large uncertainty on the age prevents an estimate of the time interval between the two stages of mineralization.

Re-Os dating of pyrrhotite from the Kiaka occurrences (Fig. 3) in early-orogenic Po-Bt assemblages within metagreywacke yields an isochron age of 2149 ± 36 Ma (Fontaine et al. submitted), which suggests mineralization took place during the long-lived D2 deformation. Moreover, these geochronological data also provide a minimum age for an early mineralizing event that formed disseminated invisible gold mineralization.

At Wassa, early-orogenic pyrite yields a Re-Os isochron age of 2164 ± 22 Ma, which can be considered the age of major gold mineralization. This age suggests that the first deformation affecting the Wassa deposit occurred during the D1 phase. Visible gold is also contained within a second generation of quartz veins that cut the predominant foliation, and is accompanied by recrystallization of pyrite. This type of pyrite is dated at 2054 ± 11 Ma, providing a timing constraint on the minor late gold event occurring at Wassa during the D4 regional event, which is a major period of gold mineralization elsewhere in the A shanti belt (also observed in Pampa, Obuasi, and Bogoso). These age data permit an estimate of the interval between the two mineralizing events of ~100 m.y.

For the Damang deposit, Re-Os analyses on pyrite yield a poorly constrained age of 2039 ± 120 Ma obtained from the dating of four replicates. The large uncertainty is due to the very low content in the pyrites of Re (~0.35 ppb) and of 187Os (~8 ppt), and to the resulting only moderately radiogenic osmium composition.
At Obuasi, an arsenopyrite sample was dated by the Re-Os method, providing an isochron age of 2040 ± 87 Ma. This age seems too young to correspond to the early-orogenic gold mineralization, which is supposed to have formed prior to or during the regional D3 event, although the large uncertainty on this age makes this interpretation problematic. Nonetheless, assuming that a ~2040 Ma age corresponds to late deformational stages in the Obuasi deposit and that multiple generations of arsenopyrite are possible, we suggest that the Re-Os age was obtained on a second generation of arsenopyrite that crystallized during the last stage of deformation. Indeed, this age is very close to those obtained for orogenic gold mineralization in the same area, as at Damang (~2040 Ma) and Wassa (2054 Ma) (Fig. 3).

4 Conclusions

This paper presents a study of mineralization and Re-Os ages of six gold deposits within the Baoulé-Mossi Birimian domain, in Burkina Faso and Ghana. Results highlight the polyphase character of gold mineralization throughout the WAC, which is typically characterized by a first early-orogenic stage of disseminated gold and a second late-orogenic stage of structurally controlled mineralization marked by visible gold and higher grades. For the first time in the WAC, the existence of early-orogenic gold mineralization is demonstrated by direct Re-Os dating. Also important is the fact that gold deposits older than 2130 Ma provide clues for the identification of the source of gold in the Tarkwaian-type palaeoplacers. Moreover, four late-orogenic gold events were also dated. Although the late stages of the Eburnean orogeny seem to have been a prolific period for high-grade gold mineralization, this study shows that previously unknown, early-orogenic gold deposits can also contain large quantities of gold.

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References


Multistage Mineralization of the Inata Gold Deposit, Burkina Faso: Insights from Sulphide and Fluid Inclusion Geochemistry

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Abstract. The Inata gold deposit formed during the Eburnean orogenesis and is hosted in meta-volcano-sedimentary rocks. Gold mineralization is directly linked to disseminated arsenopyrite and pyrite assemblages which are associated to a quartz-ankinite-albite-tourmaline vein system that formed inside a N-NNE-striking, steeply dipping, D2 deformation zone. LA-ICP-MS analyses reveal that early sulphides, which formed parallel to the metamorphic D1 foliations, have low Au/Ag ratios of <0.03. The ore-bearing sulphides, which crystallized during early D2, show visible gold inclusions and are marked by high Au/Ag ratios (>40) in contrast to late D2 sulphide overgrowths which show more or less equal Au/Ag ratios. These assemblages are locally crosscut by narrow D3 fault corridors, where visible gold is observed within fractured sulphides and is interpreted being the result of late stage remobilization during D3. Extraction of fluids indicates that veins associated to D1 and D3 are characterized by high CO₂ content whereas especially early D2 veins are dominated by H₂O-rich fluids. δD values of fluid inclusions versus δ¹⁸O isotopic compositions of hosting quartz veins indicate two distinct sources, one of metamorphic/magmatic origin, rich in H₂O, and the other one being the result of extensive fluid-rock interactions with C-rich volcano-sediments.

Keywords. Burkina Faso, Inata deposit, gold, sulphide and fluid inclusion geochemistry

1 Introduction

Burkina Faso has become Africa’s 4th biggest producer of gold since 2012 and there are nowadays at least 6 major operative gold mines, one of them held by AVOCEM Mining, namely the Inata gold deposit in NE Burkina Faso (Fig. 1) part of the gold bearing Belahouaro district (Béziat et al. 2008). The Inata deposit is a classical orogenic gold deposit (Groves et al. 1998) and can be classified as type-2 of Mîlesi et al. (1989) “shearzone hosted” disseminated Au-sulphide mineralization associated to a stockwork of quartz veins. More specifically, Béziat et al. (2008) pointed out that mineralized sulphides are associated to a strong albitionization and carbonatization of the host rocks.

This study focuses on the geochemical and structural distinction of different generations of sulphides as well as associated fluids trapped within quartz veins linked to the different deformation stages in order to identify specific characteristics of mineralized zones compared to barren ones.

Defining fluid sources, fluxes and pathways related to the different deformation stages falls within the scope of this work. The Inata gold deposit is one of the key localities where the fluid characteristics of multistage gold mineralization can be investigated. Moreover, textural and geochronological features of different sulphide generations have been identified in order to distinguish different stages of sulphide crystallization and associated gold mineralization and/or remobilization.

2 Geological setting

The Inata deposit is located in the Belahouaro region of the Birimian Bouroum Greenstone Belt in northern Burkina Faso (Fig. 1). The stratigraphic sequence is formed of interlayered volcanic (andesites) and volcano-sedimentary rocks (black shales and volcanoclastics) crosscut by a series of felsic dykes. All rock types are deformed and metamorphosed to greenschist facies.

Figure 1. Simplified geological map of the north-eastern part of the Leo-Mian Craton (modified after Baraboux et al. 2011), with the Inata gold deposit indicated (star).
A consistent sequence of events (D1 to D4) is recorded across the Inata deposit (Fig. 2). All stratigraphy is affected by a regional NNE-SSW compression event (D1), producing a layer parallel fabric. Gold mineralization is hosted along a 4 km long N-NNE striking, steeply W-dipping D2 deformation zone that obliquely cuts across the host shales, volcanoclastic rocks and felsic dykes. Subsequent to this D2 event, the region was subjected to NE-SW compression (D3) and the formation of NE-trending narrow shear-fractures that are particularly rich in graphite within the Inata North pit. They transect and offset the D2 fabrics. The final deformation event (D4) is a brittle E-W trending fracture cleavage associated with small scale thrust faults and folds that are only locally well developed.

2 Sulphide characterization and association with gold

2.1 Primary sulphides related to D1

Primary pyrite (Py1) and minor arsenopyrite (Apy1) have been identified throughout the volcano-sedimentary sequence. They are anhedral, rich in inclusions of host rock minerals and distributed along the D1 foliation planes (Fig. 3A). They are mostly observed in small clusters associated with chalcopyrite, galena, sphalerite, cobaltite and gersdorffite. Quartz veins (V1) that are overgrown by euhedral, inclusion-free, millimetre-scale pyrite (Fig. 3B). In-situ LA-ICP-MS analyses of these sulphides show high Au concentrations ranging from 1 to 10 ppm and Au/Ag ratios higher than 40. Moreover, these sulphides are generally highly concentrated in Te, Sb, B1, Pb and Cu which systematically accompany Au (Velásquez et al. 2014).

At later stages of D2 deformation, Py2 and Apy2 are overgrown by euhedral, inclusion-free, millimetre-scale pyrite (Fig. 3B). These pyrites show lower Au concentrations (0.1 to 1 ppm) as well as lower Au/Ag ratios (−1) than early stage D2 sulphides (Fig. 3B).

2.2 Disseminated sulphides related to D2

Secondary pyrite (Py2) and arsenopyrite (Apy2) are found in high amounts at the vicinity of quartz-albite-ankerite-tourmaline stockwork veins (V2) (Fig. 3B) which are associated to the main D2 fluid circulation and deformation event. These are the only sulphides that commonly contain micrometric “visible” gold inclusions often associated to chalcopyrite, sphalerite and galena (Fig. 3B). In-situ LA-ICP-MS analyses of these sulphides reveal high Au concentrations ranging from 1 to 10 ppm and Au/Ag ratios higher than 40.

The late to post-orogenic deformational episode (D3), affected all preceding sulphide generations and caused extensive fracturing of these grains. These microfractures commonly contain visible gold (Fig. 3C). LA-ICP-MS spectra for this episode are not shown in the diagram, because this event does not precipitate sulphides. Free gold can also be found in the host rock associated to Fe-rich minerals such as chlorite and ankerite (Fig. 3C). However, associated V3 quartz-calcite veins are barren and the extension of these higher concentrated gold occurrences is localized at intersections between D2 mineralized zones and D3 shearfractures.

3 Fluid geochemistry

Quartz vein samples related to D1, D2 and D3 respectively were collected from within the Inata North Pit as well as outside the mineralized zone in order to collect representative samples of barren zones. The δ18O isotopic compositions of quartz were measured using a VG SIRA 10 triple-collector mass spectrometer at the University of Rennes 1. NBS 19 and internal lab standard reference materials (Prolobo Rennes) were continuously measured during the course of this work.

Fluids were extracted by heating of pure quartz, inducing decrpetiation of fluid inclusions. The δD isotopic compositions were measured using Finnigan Mat-Delta S mass spectrometer equipped with a dual inlet system. In-house, MOW and LIF standards were used for corrections. These analyses were done in the Stable Isotope Lab at the University of Lausanne.
Compex 102 nanosecond laser from LambdaPhysik, Excimer ArF automated platform housing a 193 nm

Analyses were performed using a Geolas (Microlas) (France), to determine trace element concentrations.

performed at the Géosciences Montpellier laboratory could be established (Fig. 3A). Both, veins and sulphides
completely transposed into the D1 foliation are barren cobaltite and gersdorffite. Quartz veins (V1) that are
planes (Fig. 3A). They are mostly observed in small rock minerals and distributed along the D1 foliation
sequence. They are anhedral, rich in inclusions of host minerals.

Primary pyrite (Py1) and minor arsenopyrite (Apy1) 2.1 Primary sulphides related to D1

2 Sulphide characterization and association

Figure 2. Inata North pit. They transect and offset the D2 fabrics. The final deformation event (D4) is a brittle E-W
deformation event. These are the only sulphides that affected all preceding sulphide generations and caused
remobilization during D3.

H2O and CO2 were separated in a closed cryogenic system allowing measuring respective volumes of both components independently for each vein sample. A particular quartz pocket associated to early D2 deformation stages sampled at the vicinity of a felsic dyke (Fig. 2, black arrow), shows highest water content and lowest CO2 concentrations (Fig. 4A). D1 related quartz-ankerite veins (V1) as well as D3 related quartz-calcite veins (V3) show highest concentrations of CO2. Quartz-albite-ankerite-tourmaline veins (V2) related to the main D2 mineralization event show also high H2O concentrations (Fig. 4A).

The δD isotopic compositions of extracted H2O plotted versus δ18O of the hosting quartz minerals indicate a distinct signature for early D2 quartz veins compared to all other vein samples (Fig. 4B). D1, late D2 and D3 veins show a wider range of compositions, especially for δD.

4 Discussion

This study highlights several stages and types of mineralization at the Inata gold deposit that are linked to different deformation and fluid circulation events.

Even though no visible gold as well as economic grades could be identified within the host rocks away from the D2 shear zone, early sulphides (Py1) related to D1 regional metamorphism contain up to 0.1 ppm of “invisible” gold trapped within the lattice of pyrite. These very low grade concentrations contained in the metavolcano-sediments could form the stock of low amounts of gold distributed within a large volume for later remobilization during D2.

At early stages of fluid flow during D2, particular H2O rich fluids could be identified which indicate potentially less fluid-rock interaction with host rocks given their most positive values in δ18O of quartz and low amounts of CO2.
to D1, much richer in CO₂ and capable to remobilize sulphides. During D3, the fluid composition is similarly element signatures are completely different from Py1 Py2 contain visible gold inclusions as well as up to 10 ppm “invisible” gold and their geochemical trace element signatures are completely different from Py1 sulphides. During D3, the fluid composition is similarly to D1, much richer in CO₂ and capable to remobilize gold as attested by visible and free gold within fractured sulphides and host rock minerals respectively. However, this effect is only local since D3 shearbands are barren outside intersections with the D2 deformation corridor. Stable isotope signatures of fluids linked to D1 and D3 point to a host rock buffered fluid reservoir which attained its characteristics from extensive fluid-rock interactions with carbon-rich volcano-sediments. H₂O rich fluids linked to the mineralization stage indicate an external inflow of hydrothermal fluids throughout the shearzone. During later stages of D2, fluids get enriched in CO₂, potentially related to H₂O reactions with the C-rich black shales, concomitantly with a drop in Au concentrations within Py3. Dewatering reactions during progressive metamorphism at depth or hydrothermal fluids from nearby magmatic intrusions may be the source of H₂O-rich fluids. Similar findings were reported at the Ashanti gold district in Ghana (Oberthür et al 1994, 1996). However the Inata deposit is one of the rare cases in the West-African craton where gold mineralization could eventually be related to H₂O dominant fluids, since most studies carried out so far on other deposits in Burkina Faso show mostly CO₂ dominated mineralizing fluid systems (Béziat et al. 2008 and references therein).

Research is ongoing to investigate the geochemical characteristics of the H₂O fluids by in situ LA-ICP-MS analysis on single fluid inclusions. Coupled with microthermometry and Raman spectroscopy analyses the results should help to better constrain the source and potential role in gold transport of these specific fluids.

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References


Figure 4. A. CO₂ versus H₂O concentrations of extracted fluids from the different quartz vein generations. Black arrows indicate mixing trend of two endmember fluid compositions, one rich in H₂O (early D2 veins) and the other one rich in CO₂ (D1 and D3 related veins). B. δ²⁰⁰H of hosting quartz veins versus δD of extracted fluid isotopic compositions. Black arrow indicating mixing trend of H₂O rich endmember (early D2) with host rock buffered fluid compositions (left side of the dashed line).
Gold Mineralisation during Progressive Deformation along the Ashanti Belt: Wassa Mine, Ghana

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Abstract. Ghana’s 250 km long Ashanti Greenstone Belt is home to numerous highly productive gold deposits, including Golden Star Resources’ structurally complex Wassa Mine. Hosted in the Paleoproterozoic Birimian Sefwi Group (2195-2170 Ma) mafic to intermediate metavolcanics, Wassa is the oldest deposit in the Ashanti Belt. Six deformation events have affected the region during the Eoeburnean (2187-2158 Ma) and Eburnean Orogenies (2125-1980 Ma), at least four of which can be observed at Wassa: D₁ N-S shortening, D₂ NW-SE shortening, D₃ NNW-SSE shortening and D₄ vertical shortening. D₁ produced tight, isoclinal folds and was responsible for the initial gold mineralisation at Wassa. This study demonstrates that during D₃ gold mineralisation emplaced during D₁ was either remobilised into F₂ fold hinges, or possibly represents a further addition of gold during D₄. The subsequent folding by D₄ produced the large synform at Wassa, and caused the refolding of D₂ folds. Initial modelling of gold grade suggests that the gold is focused within the hinges of F₂ folds and decreases in grade out of the attenuated limbs. In addition there is an apparent lithological control on mineralisation with the highest gold grade located within the hinges of F₂ folds in metasediment and Banded Magnetic Unit (BMU) host rocks at Wassa.

Keywords. Orogenic gold, Deformation, Ashanti Belt, 3D Modelling, gold remobilisation

1 Introduction

Ghana’s 250 km long Ashanti Belt is the renowned host to a number of Paleoproterozoic hydrothermal gold deposits, including Golden Star Resources’ Wassa Mine. The Ashanti Belt is one of four NE-SW trending greenstone belts in the western region of Ghana: Bui-Banda, Sefwi-Bibiani and Kibi-Winneba (Perroud 2012). The highly productive deposits hosted by the Ashanti Belt vary greatly in mineralisation style from the paleoplacer of Tarkwa, to shear zone related fractures and fault fill mineralisation of the world class deposit, Obuasi (Bourassa 2014). Wassa, however, is unique in the Ashanti belt as it is the only deposit to be located in the Birimian volcanic, on the eastern limb of the regional Tarkwa Syncline (Bourassa 2003). Wassa is affected by at least four of the six major deformation events in the region, and is consequently extremely structurally complex. This study aims to constrain the timing on the initial gold mineralisation and subsequent remobilisation or additional mineralisation events relative to the major deformation events affecting Wassa. These new data and interpretations are intended to help constrain 3D models of mineralisation that form the basis for exploration, future estimation of Mineral Resources and underground mine planning.

2 Geology

2.1 Regional Geology

The main lithological units of the Ashanti region are the Birimian and Tarkwaian meta-sediments and volcanics, which are variably intruded by syn-tectonic granitoids (Perroud et al. 2012). Most important in terms of the current study are the Paleoproterozoic Lower Birimian aged rocks (2195-2170 Ma) which are part of the Sefwi Group (Perroud et al. 2012). This Group comprises a thick sequence of mafic to intermediate metavolcanics and hypabyssal rocks, micaschists (Bourassa 2003) and hosts most of the large orogenic gold deposits in the Ashanti Belt: Obuasi, Bogoso, Prestea, Wassa and Hwini Butre, as well as hosting the Wassa deposit. Overlying the Sefwi Group is the Kumasi Group (2150 Ma), composed of metamorphosed turbiditic and phyllitic sequences (Papo et al. 2012), and the Tarkwaian Series (2130-2116 Ma), a succession of conglomerates interbedded with sandstones and phyllite (Pigois et al. 2003). The Tarkwaian rocks host hydrothermal gold mineralisation at Damang and as a series of paleoplacer deposit in the Banket Conglomerate near the town of Tarkwa.

2.2 Geology of the Wassa Deposit

The Wassa deposits are hosted by highly folded and altered lithologies belonging to the Sefwi Group. The main lithologies represented within the Wassa Mine and exploration drillholes are arenaceous turbiditic metasediments, mafic and intermediate metavolcanic flows, dioritic and felsic porphyritic intrusions (Papo et al. 2012). Distributed throughout the metasediments are discontinuous layers of a unit defined as the Banded Magnetite Unit (BMU) which are located within the meta-volcanosedimentary sequence of the Sefwi Group with very high magnetic susceptibility values, up to 10 times higher than its surrounding host rocks (Papo et al. 2012), and could potentially be interpreted as a proto-BIF unit.
As the Wassa gold deposits are contained within the Sefwi Group, they have been affected by multiple ductile deformation events associated with various phases of the Eoeburnean and Eburnean orogenies. The deformation events have resulted in a highly folded rockmass with gold mineralisation distributed throughout selected units as thin, discontinuous quartz veins, strongly affected by subsequent deformations. The deformation framework is summarised below.

3 Deformation framework

At least six deformation events have occurred in the Ashanti belt between 2187-1980 Ma during the Eoeburnean and Eburnean Orogenies (Perrouty et al. 2012). These are as follows:

- **D1** - a NN-S shortening event that produced very tight to isoclinal, layer-parallel regional and local scale folds. This occurred towards the end of the Eoeburnean Orogeny (2187-2158 Ma) and is thought to be responsible for the initial gold mineralisation at Wassa (Perrouty et al. 2012).
- **D2** - a regional-scale extensional phase dated at 2154-2125 Ma (Perrouty et al. 2012), but not identified at Wassa.
- **D3** - NE-SW shortening of the Birimian and Tarkwaian Groups occurring at the beginning of the Eburnean Orogeny. Folds associated with this event are the most common fold-type at Wassa, and are refolded by subsequent deformation events. D3 coincided with a peak in amphibolite grade metamorphism at 2092 Ma and the Ashanti thrust fault (Perrouty et al. 2012 and Bourassa 2014).
- **D4** - a NNW-SSE shortening event associated with greenschist retrograde metamorphism (Perrouty et al. 2012). At Wassa, D4 is mainly represented by a large synformal fold, which is the main mine contours around.
- **D5** - a vertical shortening event occurring at the end of the Eburnean Orogeny, which produced horizontal to small-scale folds with sub-horizontal axial planar cleavage. These structures are clearly represented throughout the Wassa Mine.
- **D6** - a later regional NE-SW shortening event (Bourassa 2014) occurred at 600 Ma. Very little evidence for this event is observed at Wassa.

In summary, structures related to four of the principal deformation events can be observed at Wassa, with D1 and D3 representing the most intense periods of the orogenesis within the belt.

4 Controls on gold mineralisation

4.1 Structural controls

The geometry and distribution of gold within the Wassa deposits have been modelled and evaluated in three dimensions using Au assay data from exploration and grade control drilling programmes in Leapfrog Mining software (Fig. 1).

The assay data in Figure 1 illustrates the overall plan view geometry of the mineralisation, but particularly highlights that although Wassa’s large D4 synform is a first-order control on the deposit geometry, it is the tight hinges and attenuated limbs of F3 folds that host the majority of economic and higher grade gold values. Moreover, this data shows how the D1 folds have been refolded around the larger D4 synform.

Using this map view and multiple cross-sections through the same dataset, block diagrams have been produced to show detailed geometry of this refolded system in 3D (Fig. 2). In these diagrams, the interpreted distribution of the higher gold grades (>3g/t) is shown to be concentrated in the hinges of the refolded D3 folds, with the grade decreasing along the attenuated limbs.

Earlier studies of the Ashanti Belt, such as Perrouty et al. (2012), suggest that the initial gold mineralisation occurred during D3 deformation. This would therefore be indicated by the large F3 synform at Wassa controlling the mineralisation in the hinge north of the mine. When modelled in detail, the high grade assay data follows the tight to isoclinal F3 folds which have been refolded around F3. The large F3 fold is defined by the assay grade because of the attenuated limbs of F3.

We therefore argue that initial gold mineralisation is likely to have occurred during D3 (Perroux et al. 2012), and was later remobilised into the hinges of F3 folds. As the limbs are attenuated and gold grade decreases away from the hinge lines, remobilisation or additional mineralisation must have occurred syn-D3, with progressive shearing causing the extension of the limbs.
At Wassa, D 4 is mainly represented by a large greenschist retrograde metamorphism (Perrouty et al. 2014). Ashanti thrust fault (Perrouty et al. 2012 and Bourassa in amphibolite grade metamorphism at 2092 Ma and the subsequent deformations. The deformation framework is gold mineralisation distributed throughout selected units deformation events associated with various phases of the Sefwi Group, they have been affected by multiple ductile throughout the Wassa Mine. D3 representing the most intense periods of the orogenesis 4.1 Structural controls Controls on gold mineralisation At least six deformation events have occurred in the Wassa. These are as follows: Eoeburnean and Eburnean Orogenies (Perrouty et al. 2012–2014) occurred at 600 Ma. Very little evidence for this event is observed at Wassa. This occurred towards the end of the Eoeburnean Orogeny to isoclinal, layer-parallel regional and local scale folds. Section lines are shown for Figures 3a and 3b trends. Selected F3 folds refolded by F4 are highlighted in white.

Figure 2. Block diagrams with areas of high grade gold in red. Foremost faces of the diagrams correspond to section lines shown in Figure 1. The concentration of the gold occurs within the hinges of the F3 folds.

4.2 Lithological controls
Although the distribution of gold mineralisation is mainly controlled by D3 folding, mineralisation also has a particular affinity to certain lithologies at Wass. The lithological map in Figure 3 illustrates how the lithologies are affected by F3 folds and refolded by F2. As the F3 folds in the lithology concur with those of the Leapfrog assay map, Figure 1, it indicates that there is also a lithological control on the gold grade distribution.

Figure 3. Lithological map interpretation for Wass (1000 m elevation). Interpreted refolds are represented, and coincide with F3 refolds shown in the assay data (i.e. Figure 1).

What is apparent from the above observations is that there appears to be both lithological and structural controls on high grade gold.

General observations of the drillcore and in the mine itself indicate that areas of very intense folding coincide with the highest gold grades. In particular, high grades are prevalent in the phyllite and BMU units. The relationship between gold mineralisation, lithology and deformation was investigated using a semi-quantitative index of the strength of deformation, based mainly on the fold intensity for structural domains logged in drillcore. The deformation intensity scale used is as follows: 1 (massive) to 7 (isoclinal, rootless folds). The lithology and deformation intensity for these domains relative to the highest assay value within each domain are shown in Figure 4.

Gold values > 4 g/t are found mainly within metasediment and BMU, with one in altered mafic volcanics. Furthermore, in the area of highest deformation, metasediments, BMU and altered mafic volcanics have the greatest values of gold grade. However, this is not exclusive as some of these units show intense folding and low gold values. These lower values have been identified in 3D space to correspond to the limb regions of F3 folds, rather than the hinges, and also occur in areas predominantly affected by F2 folds, which are known to post-date mineralisation. It is concluded that the remobilised mineralisation seems to be concentrated in the intensely deformed hinges of F3 folds, particularly in the phyllite and BMU lithological units.

Figure 4. The relationship between highest Au grade for structural domains logged in drillcore, intensity of the folding, and dominant lithology.

5 Mineralisation Styles
Preliminary studies indicate that the paragenesis of gold mineralisation at Wassa is complex. Initial gold mineralisation appears as electrum inclusions within
pyrite in the host rock, though these can be split into four distinct stages, summarised below:

**Figure 5.** Images from the Scanning Electron Microscope (SEM). (a) Parallel fractures of chalcopyrite perpendicular to the long axis of the pyrite elongation. (b) Fractures of chalcopyrite showing Au association. (c) Au following fractures in pyrite, though associated with a Mn-Fe oxide, possibly jacobsite. (d) Late stage Mn-Fe oxide cutting pyrite and host rock.

**Stage 1.** Pyrite is present as elongate, sheared grains with a fabric consistent with the S1 cleavage and thus is interpreted to be syn-D1. Gold is present as inclusions of electrum in the pyrite. There are also inclusions of Bi- and Te-bearing minerals hosted within the pyrite.

**Stage 2.** Post-D1 chalcopyrite infills fractures within the Stage 1 pyrite, and as shown in Figure 5a-b, run parallel to each other, perpendicular to the long axis of the S1 fabric. Fractures of this orientation imply emplacement of the chalcopyrite during stretching of grains defining the existing fabric, likely to have formed during syn-D1 shearing along the limbs of major F1 hinges. Gold is associated with these chalcopyrite occurrences and is interpreted as being remobilised.

**Stage 3.** Cubic, well-formed pyrite is associated with magnetite in the highly magnetic layers of BMU, and in the wall rock surrounding late-stage quartz veins. Gold occurs as electrum inclusions within the pyrite.

**Stage 4.** The Stage 3 cubic pyrite is cross-cut by a fracture containing Mn-Fe oxide, possibly jacobsite, from the magnetite series. Figure 5c shows the Mn-Fe-oxide association with gold, indicating a clear remobilisation of gold into these fractures. The microveins cross-cut the host rock as well as the pyrite although, as seen in Figure 5d, within the wall rock, the Mn-Fe-oxide has a sheared appearance. This suggests that when the Mn-Fe-oxide was emplaced, the pyrite deformed brittlely, but the wall rock was undergoing syn-deformational shearing.

**6 Discussion and Conclusions**

Within the six major deformation events recorded throughout the Ashanti Belt, four are recorded at Wassa. N-S shortening associated with the late Eoeburnean D1 event coincided with the initial gold mineralisation, but remobilisation of the gold occurred during a subsequent deformation event.

Previous work by Perrouty et al. (2012) suggested that, on a regional scale, remobilisation of mineralisation occurred during the NNW-SSE shortening of the D4 folding event. However, results from pit mapping, drillcore analysis and 3D modelling of assay and lithology data at Wassa indicate that there is a correlation between high gold grade and F1 fold structures. Therefore, we suggest that either remobilisation of the initial D1 gold or influx of additional gold mineralisation, into the hinges of the F1 folds during D3 is principally responsible for redistributing the gold into economically significant concentrations with planar to linear geometries at Wassa.

Several phases of mineralisation have been identified using electron microscopy. These styles have then been provisionally correlated with the regional deformation framework: (1) initial gold replacement as electrum inclusions in pyrite at the beginning of D1. Subsequent syn-D1 deformation caused the flattening and elongation of the pyrite along $S_1$ cleavage planes. Intense refolding of $F_1$ folds during D2 caused tension along the fold limbs opening fractures in the pyrite and causing boudinage of the syn-D1 quartz veining. (2) gold associated with syn-D1 chalcopyrite in the fractures syn-D1 elongate pyrite. (3) gold associated with manganese iron oxide (possibly jacobsite) within well-formed, cubic pyrite. (4) gold along fractures in cubic pyrite generally associated with the manganese iron oxide. Further extension and remobilisation of the pyrite is responsible for (3) and (4), though it is unclear if this is from a subsequent deformation event or prolonged continuation of D3.

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New Insight on the Magmatic and Tectono-Metamorphic Evolution of the Paleoproterozoic Gold-Bearing Toulépleu-Ity district (SW Ivory Coast)

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Abstract. Within the Kénéma-Man Archean craton, the Toulépleu-Ity district of SW Ivory Coast is characterized by Paleoproterozoic calc-alkaline granitoids intruding Birimian volcanosedimentary rocks and marble that underwent metamorphism under greenschist facies PT conditions. Primary gold mineralization at the Ity mine is mainly located within skarns generated at the contact between granodiorite and marble. Integration of regional geophysical and drilling datasets, and new structural analyses in the open cast mine suggest that the granodioritic intrusion was emplaced in a transtensional regime during the last stages of the Eburnean orogeny. Petrological investigations, thermodynamic modelling, mass transfer studies and fluid inclusions analyses are underway to decipher the complex magmatic and tectono-metamorphic evolution that led to skarn-hosted gold mineralization.

Keywords. West African craton, Paleoproterozoic, Skarn, Gold mineralization

1 Introduction

Many gold deposits in the West African craton are hosted by metamorphic terranes and have been related to the Eburnean orogeny. These gold deposits could be classified as intrusion-related gold deposits (Olson et al. 1992; Oberthür et al. 1998; Alibone et al. 2002; Pigois et al. 2003; McFarlane et al. 2011), structurally controlled, epigenetic lode or orogenic gold deposits (Groves et al. 1998, 2003). The genesis of these diverse gold deposits has been recently shown has polyphased and controlled by a dynamic hydrothermal system wherein both magmatic- and metamorphic-derived fluids are linked to the formation of the gold deposits (Hammond et al. 2011; Lawrence et al. 2013; Le Mignot et al. accepted). The Ity gold deposit, in the southwestern Ivory Coast, shows an atypical character for West Africa gold mineralization. Indeed, the Ity gold deposit has been described as the deeply weathered part of an intrusion-related skarn deposit (Milesi et al. 1989).

In this contribution, we present new structural and petrological investigations in the Birimian meta-volcanosedimentary sequence and intrusives at Ity. The study of more than 700 drill cores helps us to better constrain geological contacts in the mine area and to propose a new structural model. Ongoing thermodynamic modelling, chemical mass transfer calculations and fluid inclusions analyses are intended to characterize the complex magmatic and tectono-metamorphic evolution of the hosting lithologies and to understand the processes of primary gold mineralization within skarn.

2 Geological setting and background

The southern part of the West African craton, known as the Leo-Man shield consists of an Archean unit (older than 2.7 Ga; Faybesse and Milesi 1994) tectonically juxtaposed against Paleoproterozoic terranes composed of Birimian meta-volcanosedimentary, Tarkwaian sedimentary and several magmatic sequences. Both Archean and Paleoproterozoic units are deformed during the Eoeburnean (2187-2158 Ma) and Eburnean orogenies (2125-1980 Ma) (Faybesse and Milesi 1994; Hein 2010; Baratoux et al. 2011; Perrouty et al. 2012, and reference therein).

Two Birimian volcanic and sedimentary sequences have been described in the Paleoproterozoic of West Africa (Faybesse et al. 1990; Milesi et al. 1992; Faybesse and Milesi 1994): a Lower Birimian (B1) unit composed of metasediments, underlying basic volcanic rocks, interbedded flyschs deposits and volcanosediments; an Upper Birimian (B2) unit characterized by calc-alkaline magmatic rocks (Faybesse et al. 1990; Milesi et al. 1992; Faybesse and Milesi 1994). The Tarkwaian sedimentary sequence, composed of conglomerate and sandstone, unconformably overlies the Birimian sequences (Hein 2010; Baratoux et al. 2011; Perrouty et al. 2012, and reference therein).

Distinct tectonic events and evolution models have been recognized for the Paleoproterozoic terranes of the West African craton, during the formation of the Eoeburnean and Eburnean orogenic belts (Perrouty et al. 2012, and reference therein, Le Mignot et al. accepted, and reference therein). Although the Eoeburnean phase proposed for the Birimian meta-volcanosedimentary sequences is different in Ghana, Burkina Faso and Ivory Coast, the Eburnean phase is characterized by a first NW-SE shortening event (dated at around 2.1 Ga, Faybesse et al. 2006) during Tarkwaian sedimentation. This event is related to a major collision phase and develops a S1 foliation subvertical and subparallel to the lithological contacts and units boundaries. It is accompanied by a zonation of metamorphism from lower greenschist to amphibolite facies. The gold mine-
eralization is associated with N-S to NNW-SSE major transcurrent event recognized in both Birimian and Tarkwaian sedimentary and magmatic units. It is characterized by the development of sinistral strike-slip faults and shearing. The last stages of the Eburnean orogeny are characterized by brittle dextral strike-slip and/or reverse faults (Perrouty et al. 2012, and reference therein, Lé Mignot et al. submitted, and reference therein).

The Toulépleu-Ity Birimian domain (Figure 1) lies as a klippe (Feybesse et al. 1990) within the Kénema-Man Archean domain and is composed of volcano-sedimentary and sedimentary sequences which are distinguished from other Birimian sequences by the presence of intercalated black schists and marbles, and the development of staurolite and kyanite bearing metamorphic rocks during the latest stage of D1 deformation when thickening occurred. This unit is crosscut by intrusive rocks (upper B2 unit) (Feybesse et al. 1990; Milesi et al. 1992; Feybesse and Milesi 1994).

3 Sampling and methodology

Due to deep weathering and absence of outcrops, geological and structural observations are based on study of both drill cores and saprolite in the opencast mine. Samples (around 40), collected at the Ity mine during the study, include meta-volcanosedimentary rocks, marble, metasediments and various intrusive facies. Four lithological profiles across diorite (ca. 55 wt% SiO2) and granodiorite (ca. 65 wt% SiO2), two of them gold mineralized and the two others barren, have been sampled perpendicular to its contact with marble. Each profile contains ca. 20 samples, one meter apart from each other, from the intrusive towards marble, through endoskarn and exoskarn.

Major- and trace-element analyses were performed on samples from the four lithologic profiles at Université de Lausanne by X-ray fluorescence (major elements) and LA-ICPMS (trace elements).

Chemical mineral analyses of rocks were determined using a SX100 electron microprobe at Ecole Nationale Supérieure de Chimie of Lille, equipped with 4 wavelength-dispersive spectrometers with an accelerating voltage of 15 kV and a beam current of 12 nA for silicated minerals and 1nA for carbonates.

4 Structural and petrological studies

4.1 Structural observations

Structural analyses of drill-cores show that foliation of the meta-volcanosedimentary unit is parallel to the lithological contacts and is oriented NE-SW and steeply dipping toward the NW. This foliation is interpreted as S01 foliation. The meta-volcanosedimentary sequence is intruded by S-shaped magmatic bodies of granitic to dioritic composition. The main granodioritic intrusion (~3 km²) is NE-SW broadly oriented with N-S tails.

Structural investigations in the opencast mine show that the granodiorite has locally developed a foliation (S2), the attitude of which varies, from core to rim of the intrusion, from N080° to N065°, i.e. getting progressively parallel to the regional S01 NE-SW strike.

The main observed structures steeply dip toward the northwest and are coherent with the evolution of a N020° sinistral strike-slip shear corridor. Such structures include N110° normal faults which are crosscut by sinistral N170° to N010° and N030° fault zones. On the field, the N030° faults are in turn cut by dextral N080° faults and develop centimetric pyrite cores in quartz veins. The late N080° orientations are often associated with pegmatite intrusions.

4.2 Petrographical observations

Based on mineralogical investigations, the paragenetical evolution in the different profiles is quite similar:

- magmatic rocks are composed of quartz, plagioclase, K-feldspar, biotite and amphibole and magmatic epidote in the most basic facies. Closer to the contact with marble, the amount of biotite decreases whereas quartz and K-feldspar proportion apparently increase. Secondary minerals are characterized by...
Toulépleu massif. The Ity granodiorite is represented within the square to the NE of Toulépleu-Ity area in the Kénéma-Man Archean domain. The development of staurolite and kyanite bearing presence of intercalated black schists and marbles, and distinguished from other Birimian sequences by the sedimentary and sedimentary sequences which are a klippe (Feybesse et al. 1990) within the Kénéma-Man orogeny are characterized by brittle dextral strike-slip ralization is associated with N-S to NNW-SSE major faults and develop centimetric pyrite cores in quartz field, the N030° faults are in turn cut by dextral N080° synthetic strike-slip faulting (N170°- N10°) and N110° normal faulting during intrusion of the granodioritic magma. Subsequently, rotation and propagation of the strike-slip faults (N030°) around the intrusion(s) (Figure 3B-C) would result in a fault-bounded S-shaped granodiorite body which would be finally disrupted by antithetic dextral strike-slip faults (N080°) (Figure 3D).

The two mineralized profiles display some differences regarding skarn development and associated of gold mineralization: within the most basic (granodiorite profile, the skarn volume is limited but richer in gold.

5 Discussion

Orientation and evolution of observed structures at Ity are consistent with the development of a transtensional deformation during the D2-D3 tectonic event. Based on published analogue modelling (Wu et al. 2009; Dooley and Schreurs 2012), this type of structural evolution is initiated by a vertical strike-slip basement fault. In our model (Figure 3), we suggest that granodiorite emplacement into the meta-volcanosediments is controlled by incipient NNE-SSW sinistral strike-slip faulting, possibly reworking an earlier structure slightly oblique to S01 foliation (Figure 3A). (Re)activation of the sinistral strike-slip corridor appears consistent with synthetic strike-slip faulting (N170°- N10°) and N110° normal faulting during intrusion of the granodioritic magma. Subsequently, rotation and propagation of the strike-slip faults (N030°) around the intrusion(s) (Figure 3B-C) would result in a fault-bounded S-shaped granodiorite body which would be finally disrupted by antithetic dextral strike-slip faults (N080°) (Figure 3D).

In this model, skarn mineralization at the contact between granodiorite and marble seems to be oriented along the NNE-SSW sinistral shear zone corridors. An estimate of the metamorphic PTDt conditions will be soon carried out, using thermodynamic modelling through the establishment of pseudosections (Perple X software), and taking into account fo2 and fc02. Mineral datation (U-Pb on zircon, monazite and titanite in skarn and hostrocks) is also planned. Finally, the characterization of metasomatic processes occurring
during the emplacement of granodiorite magma into carbonates will be addressed by chemical mass transfer calculations along the different exo/endoskarn profiles (Ague and van Haren 1996). This will be correlated with analyses of polyphase fluid inclusions in garnet, quartz and calcite, in order to decipher the evolution of fluid-rock interactions synchronous with metamorphic and deformation processes.

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Zircon LA-ICP-MS Dating and Mineralogy of Mokong Magmatic Epidote-Bearing Granites from the Northern Part of Cameroon Pan-African Fold Belt

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Abstract: The Mokong pluton at the northern part of the Cameroonian Pan-African fold belt consists of intrusions of various sizes of biotite granitoids cross-cutting or interleaving the magmatic epidote (mEp)-bearing granites intruded in the Neoproterozoic (~830-700 Ma) medium- to high-grade schists and gneisses of the Poli-Léré group. This pluton is weakly deformed, with solid-state deformation increasing toward its margins where it is sheared with narrow mylonitic bands trending NNE-SSW. The mEp pluton is classified into quartz monzodiorite granodiorite, monzogranite and syenogranite. The syenogranite which is the most abundant rock type is dated at 670 ±5.1 Ma (U-Pb on zircon, LA-ICP-MS). These rocks are porphyritic to equigranular medium-to coarse-grained granitoids composed by K-feldspar + plagioclase + biotite + amphibole + magnetite + titanite + epidote. Pistacite [atomic Fe³⁺/(Fe³⁺+Al)] in epidote in these granitoids ranges from 16 to 29%. High oxygen fugacity (log fO₂ ~−14 to ~−11) and the preservation of epidote suggest that the magma was oxidized. Al-in amphibole barometry indicates hornblende solidification between 5.3 and 7.8 kbar, at 633 to 779°C according to the hornblende-plagioclase thermometer. Zircon saturation thermometry attests to a near-liquidus temperature range from 504 °C to 916 °C.

Keywords. Central Africa Pan-African Fold Belt; North Cameroon; Magmatic Epidote bearing- granites

1 Introduction

The late Neoproterozoic (Pan-African) Central African Fold Belt, north of the Congo Craton, underlies Cameroon, Chad, and the Central African Republic, between the Congo Craton to the south and the Western Nigerian Shield to the north (Figs. 1a and 1b) and corresponds to the southern part of the Saharan macrotecton (Abdelsalam et al. 2002 2011; Liégeois et al. 2013). This belt continues into the Borborema Province in NE Brazil, where the shear zones control the emplacement of Brasiliano-Pan-African granitoids (Fig. 1a). It has long been recognized that there is strong geological correlation between NE Brazil and west-central Africa (e.g., Oliveira et al. 2006; Dewit et al. 2008; Van Schmus et al. 2008; Neves et al. 2012). In the Borborema Province late Neoproterozoic plutonism consists of several associations of which the high-K calc-alkalic rocks are the most voluminous (Guimarães et al. 2004 and Sial et al. 2008). Magmatic epidote-bearing granitoids are widespread in northeastern Brazil, having been identified in five Neoproterozoic terranes: Seridó, Cachoeirinha-Salgueiro, Riacho do Pontal, Alto Pajeú and the Macurué (Sial 1986 Ferreira et al. 1998; Galindo et al. 1995 and Long et al. 2005). In the central African fold belt, the tectonic evolution involved voluminous granitic magmatism, but no granite bearing magmatic epidote has been studied in Cameroon while experiments on epidote dissolution kinetics (Brandon et al. 1996) and on epidote stability in granitic melts (Schmidt and Thompson 1996) suggest that epidote textures offer a powerful means to estimate crystallization depth, pressure and oxygen fugacity which are fundamental to understanding of pluton emplacement and growth and crustal differentiation. In this paper, we report preliminary field observation, epidote texture, mineral chemistry and zircon LA-ICP-MS dating on the Mokong granitoids.

2 Field observations

The Mokong plutons belong to the NNE-trending elongate syntectonic granitoids (Fig. 1b) and consist of two main groups of granitoids: the magmatic epidote-bearing granitoids and biotite granitoids cross-cutting or interleaving the mEp-granites (Fig.2d).
Most of the Mokong granitoids present NE-SW to NNE-SSW trending magmatic foliation (Fig. 2a and 2b). Major rock types of mEp-granites are porphyritic to equigranular medium-to coarse-grained granite with plagioclase and K-feldspar megacrysts up 3 cm long in random orientation in a medium-grained matrix (Fig. 2c and 2a).

3. Zircon LA-ICP-MS U-Pb dating

Zircon grains from the mEp-granite (sample MS-1) were separated, imaged in cathodoluminescence and dated by LA-ICPMS method at the State Key Laboratory of Continental Dynamics, Northwest University in Xi’an (China). All of these analyses are concordant, and the 

$^{206}\text{Pb}/^{238}\text{U}$ ages scatter between 664 and 673 Ma, averaging at 670 ± 1 Ma (n=18, MSWD = 0.115; Fig. 3). This result is interpreted as the zircons crystallization age and can be considered as emplacement age of Mokong mEp-granite.

Figure 1. a) Pre-Mesoic fit between the northern Borborema Province (NE-Brazil) and Cameroon (after Caby, 1989, modified); (1) Post-Braziliano-Pan-African sediments; (2) Brazilian-Pan-African belt; (3) Cratons; (4) Suture zone; (5) Shear zones: PaSZ: Patos; PeSZ: Pernambuco; φ: Sanaga fault (after Ngako et al., 2008); φ: Rocher du Loup shear zone (after Toteu et al., 2004); φ: Central Cameroon shear zone (after Ngako et al., 2003); φ: Tcholliré-Banyo shear zone (after Toteu et al., 2004); φ: Godé Gormaya shear zone (after Ngako et al., 2008). b) Geological sketch map of northern Cameroon (modified from Penaye et al. 2006 and Dawai et al., 2013): (1) Post-Pan-African sediments; (2) Late to post-tectonic Pan-African granitoids; (3) Syntectonic granite; (4) Mayo-Kebbi batholith: tonalite, trondhjemite and granodiorite; (5) Medium- to high-grade gneisses of the NW-Cameroon domain; (6) Mafic to ultramafic rocks: gabbro, gabbro-diorite, and dolerite; (7) Ilmenite-magnetite-garnet schists and Mokong mEp-granite mEp-granite

Figure 2. Fields photographs. (a) Eastern border of the Mokong mEp-granite showing marks of the NNE-SSW magmatic foliation sheared with dextral movement. (b) Elongate quartz doric enclaves outline the magmatic foliation in Mokong mEp-granite. (c) The core of the Mokong mEp-granite showing irregular distribution of megacrystic feldspars. (d) Dyke of biotite granite biotite cross-cutting the mEp-granite mEp-granite
4 Microscopical petrography and epidote chemistry

Epidote occurs in several textural relationships in Mokong mEp-granites: (a) as euhedral to subhedral crystals which contain minor inclusions of Fe-oxide, plagioclase and allanite; some crystals are partly altered (Fig. 4a and 4b); (b) as a late-crystallized phase, observed in intergranular spaces between plagioclase, biotite, and amphibole; (c) as partly embayed subhedral grains within amphibole crystals; (d) as secondary texture crystals associated to quartz and albite.

5 Estimation of physical parameters of emplacement

5.1 Al-in-hornblende barometry

According to the considerations of Anderson (1996) and Anderson and Smith (1995), we have applied the barometry proposed by Hammarstrom and Zen (1983; 1986) to the samples characterized by the mineral assemblage includes quartz, ferromagnesian silicates, euhedral titanite, and magnetite, and Fe/(Fe+Mg) in hornblende is in the 0.40–0.65. The pressure of crystallization of the magma (5.3–7.8 kbar) was calculated according to the following equation (Schmidt, 1992): P (± 0.6 kbar) = -3.01 + 4.76A ln. 10

5.2 Hornblende-plagioclase and Zr thermometry

Solidification temperatures were calculated from the semi empirical thermometer of Blundy and Holland (1990) and Holland and Blundy (1994), applied to chemical analyses of coexisting plagioclase and amphibole. The calculated crystallization temperatures for the studied mEp - granites lie between 633 to 779°C. The Zr thermometric obtained from Watson's (1987) zircon saturation equation [T (°C) = - 273 + 12.900/17.18-ln(Zr)] are 504 °C to 916 °C. These temperatures can be interpreted as minimum liquidus temperature.

5.3 Oxygen fugacity f(O2) estimate

Wones (1989) demonstrated that the titanite+magnetite +quartz assemblage in granitic rocks allows an estimate of relative oxygen fugacity, as follows: log f (O2) = -30930+14.98x1.0142n(P−1)/T; where T is temperature (K elvin) and P is pressure (bar). We adopted average pressures calculated from Schmidt's (1992) Al-in hornblende barometer for each sample. Accordingly, the above equation yields the log oxygen fugacity range between -11 to -14 for the Mokong mEp- granites. The high values of Oxygen fugacity is supported by the presence of M g-rich amphiboles (Fe/(Fe+Mg) = 0.40 to 0.65) and early crystallizing biotite, euhedral titanite, and magnetite in felsic rocks indicate that the host magma was relatively oxidized (Anderson and Smith, 1995). Pistacite of Mokong epidote (Ps25-29) is compatible with crystallization at higher oxygen fugacity.

6 Conclusions

The Mokong mEp- granites dated at 670.0±5.1 Ma by zircon LA-ICP-MS method are porphyritic to equigranular medium-to coarse-grained granite with plagioclase and K-feldspar megacrysts. This pluton is weakly deformed in its interior, but solid-state deformation increases toward its margins where it is sheared. Mineralogical composition consists of plagioclase, K-feldspars, quartz, amphibole, biotite, epidote and accessory minerals represented by apatite, titanite, zircon and oxide minerals.

The compositional variation of epidote (25–29% Ps) is consistent with values proposed for magmatic epidote. Other grains that seem to be formed at the expenses of plagioclase have Ps16-24, compatible with values of secondary epidote. The aluminum-in-hornblende barometer and hornblende-plagioclase thermometer indicate Mokong mEp- granites emplacement within a pressure interval from 5 to 8 kbar (20–25 km) and a solidus temperature.
between 633 and 779°C. The log oxygen fugacity ranges between -11 to -14, the pistacite of primary epidote (P_{SS-25}) and Fe(Fe+Mg) in amphibole (0.40 to 0.65) indicate oxidizing conditions for the Mokong mEp-granites.

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Geological Setting and Types of Carbonate-Hosted Gold Deposits in the Birimian of West Africa

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Abstract. The Paleoproterozoic domain in the West African Craton (WAC) encompasses numerous world-class gold deposits. These deposits are located in the volcanic and volcano-sedimentary Birimian greenstone belts pre- to syn- Eburnean orogeny in age. The orogenic-type gold mineralizations are coeval with the NW-SE compressive stage (D2) of the Eburnean orogeny. Several deposits are hosted within carbonates showing various purity and deformation degrees in western Ivory-Coast, Guinea and the Senegal-Malian Kenieba-Kedougou Inlier. To date, the role of these lithologies in terms of preferential traps for hydrothermal and/or metamorphic gold-bearing fluids has likely been under estimated. Moreover, the typology of these deposits remains poorly constrained, in part because of their poor outcropping conditions and complex post-emplacement history.

Keywords. Birimian, gold, carbonates

1 Geodynamic evolution of the Birimian

The Birimian is a major gold deposits province (Milesi et al. 1989; Milesi 2001; Beziat et al. 2008) related to the geodynamic evolution of the West African Craton, during early Paleoproterozoic. The Birimian consists of supracrustal rocks (volcanic greenstone belts and sedimentary basins) and TTG gneisses, granitoids and granitic intrusions of different ages. Deposition and emplacement of Birimian rocks date from 2230 Ma to 2060 Ma (for younger magmatic rocks).

Birimian evolution was driven by a protracted geodynamic evolution characterized by convergence and subduction processes. It resulted from the convergence between a southern Guyana shield Craton (Rosa-Costa et al. 2003) and the Kenema-Man Craton of Western Africa. Detailed studies of magmatism particularly in French Guyana (Delor et al. 2001) and Burkina Faso (Thiébault, see Castaing et al. 2003), indicate oceanic subduction processes (Ganne et al. 2012) associated with oceanic magmatic arcs. This convergence caused tectono-metamorphic and magmatic events in Western Africa (Delor et al. 2001), termed Eburnean orogeny and starting circa 2220 Ma. The Eburnean orogeny is related to SE-NW convergence and closure of oceanic domains that led to tectonic accretion of older or younger crustal terranes (micro-continent blocks, volcano-plutonic arcs, etc.) around the edges of a stable Archean continent (Kenema-Man craton). The Birimian evolution was a long process taking more than 150 Ma (e.g. Andean realm (~100 Ma)) and various stages of evolution can be defined. The Eburnean D1 tectono-metamorphic stage is roughly estimated to date to around 2120 Ma using ages from French Guyana, Ghana and Guinea (Delors et al. 2001; Feybesse et al. 2003 2006). D1 is associated with reverse faulting, foliation and metamorphism locally reaching upper greenschist to amphibolite facies. In SW Ivory Coast (Itty-Toulepleu), where the San-Pedro Archean terrane is confronted to the Man-Kenema Craton, D1 tectono-metamorphic events are notably intense (Triboulet and Feybesse 1998). The Eburnean D2 deformation stage, at about 2100 Ma, was due to an oblique convergence evolution, associated with transient faulting along regional-scale shear zones. During D2, faults and associated folds were generally sub-vertical, with a main sinistral kinematics and epizonal metamorphism (retromorphnic when D1 is higher). At a very shallow level, major strike slip faults may generate, pull-apart basins infilled bclastic rocks including sandstones and conglomerates (e.g. Toulepleu conglomerate) and volcaniclastic rocks. Upper Birimian sub-marine to aerial volcanism comprising mafic pillows, andesites, tuffs and felsic bodies, is named B2. Indeed B2, which is not deformed by D1 but underwent D2, is geographically associated with these faults. Later stages of deformation (e.g. D3: Hein 2004) are limited and heterogeneous in western Africa. Late to post-orogenic magmatism is represented by muscovite-bearing granites (~2080 Ma), differentiated granites and syenites.

2 Birimian gold mineralization

2.1 Early mineralization (ante- 2120 Ma)

Base metal sulfide mineralizations with no significant gold potential, related to active margins have been identified (Schwartz M.O. 2008). Low gold grades Cu-Mo porphyry-type mineralization have been identified in Burkina Faso (Goren, Diénémara-Gogondi) (Le Mignot et al. 2013). Massive sulfides bodies (Perkoa, N Benia Tenga, Burkina Faso), emplaced around 2160 Ma in a back-arc setting (Castaing et al. 2003), are characterized by pyrite-pyrrhotite-sphalerite (Ag, Cu). However, gold is not significantly associated with these styles of mineralization, except near N Benia Tenga where gold was probably introduced to the system later (during a D2 gold event, see below).

2.2 Syn-orogenic mineralization (post-2120 Ma)

Gold mobilization may be coeval to thermal and structural events from D1 to D2 (around 2100 Ma), followed by gold mineralization coeval to D2 and D3. Various major types of gold mineralization have been identified (Milesi et al. 1989), each of them associated with late Birimian evolution (~2100 Ma). These include: “orogenic type” (e.g. Ahafo in Ghana); “Tarkwaian type”, related to conglomerates (e.g. Tarkwa district in Ghana); “hypovolcanic associated type” (e.g. Metallogeny of North and West Africa 1675
Angovia in Ivory Coast); and deposits associated with "intrusive rocks associated type". Orogenic-type mineralization is dominant (Groves et al. 1998). Nevertheless, the influence of deformation on gold deposits and occurrences associated with felsic to intermediate magmatic rocks (sub-volcanic to hypovolcanic, and plutonic bodies) located outside of major D2 shear zones (Milesi 2003; Robert et al. 2007) is debated.

Additionally, typology and critical parameters controlling emplacement of gold deposits are generally poorly understood, especially the discrimination between "orogenic" and "magmatic" gold end-members. Influence of magmatism on carbonate-hosted gold deposits is still under debate while calc-silicates minerals are diagnostic of magmatic involvement.

3 Carbonate-hosted gold mineralization

Carbonate rocks are very uncommon in the Birimian domain (also in Guyana and Reguibat Shields), even if carbonate rocks can be found close to the Birimian-Archean boundary. Indeed, there is a sub-continuous line extending from Mali (Kenieba-Kedougou Inlier) to the south-west of Ivory-Coast and along the Cestos River in Liberia (Fig. 1). Carbonate layers consist of metamorphosed limestones, impure sandy and possibly greywackeous carbonates, marbles and calc-silicate gneisses probably derived from impure carbonates. The stratigraphic position of such carbonate rocks is poorly understood. However, carbonate rocks seem to be consistently deposited in lower parts of the Birimian (i.e. ante-D1 stage). Carbonate layers underwent medium grade metamorphism and deformation (locally intense with pronounced stretching lineation) during D1 (e.g. Bohodou area in Guinea and Ity in Ivory Coast). Their restricted geographic location, along the Archean-lower Birimian boundary, suggests a paleogeographic control. Carbonates are thought to be deposited in discrete episodes, during the lower Birimian, along the shore line bordering the continental domain (Kenema-Man archean eroded craton).
3.1 Kenebia inlier

The sedimentary Birimian association includes carbonate-bearing layers: calcareous turbidites, impure limestone and marble beds that have been metamorphosed. Close to the major Senegalo-Malian shear zone (SM SZ), gold is frequently hosted by carbonates intruded by late Eburnean magmatic rocks associated to gold-bearing sulfide disseminations.

Sadiola: Gold mineralization is associated with disseminated sulfides in sheared carbonate sediments with subvolcanic intrusive rocks (dioritic sill intrusions, quartz-feldspar porphyry dykes and late dioritic dykes). Carbonate units consist of impure metapelites interbedded with thin clayey-silty beds and massive metapelites. Gold is found in association with pyrrhotite, pyrite, arsenopyrite, minor antimony sulfides (stibnite - $\text{Sb}_2\text{S}_3$ and gudmundite - FeSbS$_5$), chalcopyrite, sphalerite and traces of molybdenite and scheelite. Mineralization hosted by carbonates along the sheared contact is associated with calc-silicates (porphyroblastic tremolite-actinolite, scapolite, minor epidote and accessory magnetite), albite and carbonate alteration.

Alamatoula: In this deposit, host-rocks and structures are very similar to Sadiola, and disseminated mineralization is hosted by carbonates. However, at the local-scale (northern part of the open-pit), the massive carbonate lens is skarnified along the contact, and some endo-skarns are located in a granodioritic intrusion.

Yatela: Gold mineralization is related to supergene concentration. The deposit has been interpreted as a paleo-placer deposited in paleo-karst cavities (Hansen, unpublished 2004), over deeply altered carbonates. Primary disseminated mineralization is hosted by a breccia along the fault zone between carbonate sediments and an intrusive dioritic body, similar to neighboring Alamatoula and Sadiola deposits.

3.2 Siguiri Basin deposits:

Along the southern boundary of Siguiri basin (Guinea) most carbonate rocks are medium to high grade metamorphosed constituting banded paragneiss probably derived from impure carbonates (greywacke and arkosic sandstone) (Feybesse et al. 2004). Rocks consist in a bedded sequence of calc-silicate paragneisses composed of plagioclase, quartz, calcic clinopyroxene (ferrosalite, from diopside-hedenbergite), amphibole, titanite, ± scapolite, ± wollastonite. These rocks host small occurrences (placer and associated primary mineralization) where gold is associated with disseminated sulfides (pyrrhotite, pyrite, and chalcopyrite) in veins hosted by calc-silicates gneiss (Mamouroudougou, Bohodou) or in late granitic bodies (Balatindi in Bohodou district). Mineralization is disseminated into intrusions and along the carbonate boundaries without any significant evidences of skarn processes, probably because the calcic gneisses were poorly reactive during the Birimian D2 gold event.

In the Siguiri basin, due to tropical weathering, outcrops of carbonate are uncommon, except in the Léro-Fayalala gold district where carbonate-hosted gold deposits are known near Siguiri (Firifirini and Toulepleu deposits). Gold is associated with skarn related to monzodioritic intrusions into carbonates. Skarn lenses are composed of garnet, clinopyroxene-diopside, epidote, magnetite and sulfides (pyrrhotite and pyrite) associated with disseminated gold.

The weathered Diatiféré deposit (70 km west of Siguiri, Guinea) is presented as a residual deposit (similar to Yatela) probably derived from a primary mineralization hosted by skarn in carbonate intruded by a “dioritic body” (Feybesse et al. 2004).

3.3 Toulepleu-Ity domain

The Ity deposit is a gold-bearing skarn enriched by weathering associated with karstification processes. Primary mineralization is composed of skarn lenses, garnetite masses, magnetite and sulfides (pyrrhotite-chalcopyrite) but also of veins and veinlets of various types. The carbonate unit is composed of calcic marbles, calc-magnesian hornfels and metasomatic skarns. Limestones and impure carbonates are interleaved (tectonic D1 contacts) in a sequence of lower Birimian beds that underwent D1 mesozonal metamorphism and deformation. Mineralization occurred during D2 with an early orogenic stage cross-cut less than 10 Ma later by monzogranite to granodiorite intrusions developing high temperature alterations and associated exo-skarns (Billa et al. 2000). Skarn lenses are composed of garnet, clinopyroxene-diopside, epidote and magnetite ($\pm$ carbonate, quartz, chlorite, pyrrhotite and pyrite). Veinlet networks and disseminations are more complex and are characterized by an assemblage dominated by pyrite and pyrrhotite, with minor amounts of chalcopyrite, molybdenite, electrum, gold inclusions, and traces of sphalerite, arsenopyrite, galena rich in tellurides (altaite, volynskite) and Cu-As-Sb sulfosalts (tennantite – tetraedrite series) inclusions. The Zeitouo and Toulepleu occurrences are very similar and are characterized by a more pronounced orogenic style than the Morgan or Doui deposits.

4 Conclusions

Carbonate rocks are very uncommon in the Birimian domain, except along the western part of the Archean craton boundary, where they appear as a sub-continuous band from Mali to Ivory-Coast and possibly Liberia. Such specificity suggests a paleogeographic control on carbonates deposition, along the shore line bordering the Archean continental domain. These rocks were deposited before the D1 orogenic stage (i.e. before ~2120 Ma) and underwent metamorphism and deformation. The pure carbonaceous marbles, in particular, played a crucial role in trapping any gold-bearing fluids (metamorphic or magmatic).

More than ten deposits and occurrences are known locally in this geological setting, demonstrating a close relationship between early Birimian carbonates, 2100 Ma shear zones, and later Birimian intrusive rocks. The typology of these deposits is hotly debated due to limited information on their non-oxized part. For some highly weathered deposits, interpretations are limited to the
description of supergene enrichment of a concealed primary mineralization (e.g. Yatela deposit in a karst setting).

Three hypotheses can be proposed for primary gold mineralization hosted by carbonate rocks: (i) sensu stricto orogenic-type, (ii) skarn-type related to a magmatic intrusion and associated fluids, or (iii) a combination of orogenic and magmatic types.

The preferred interpretation concerning the so-called "skarns-type" is the interaction of an early "classical" orogenic gold mineralization related to the 2100 Ma deformation stage reworked by younger magmatic intrusions and their associated high temperature fluids. Such an interpretation has been proposed by Lawrence et al. (2013) to explain the differences observed between the Yalea and Gara deposits in Loulo camp (Kenieba-Kedougou inlier, Mali).

In Kenieba-Kedougou and Siguiri gold districts, the influence of the magmatism does not appear as a generality. This is contrary to Ity-Toulepleu district in the context of the crustal distribution and relationship to other gold deposit types. Ore Geo Rev 13:7-27


Geology and REE Geochemistry of the El Hammam REE-Rich Fluorite Deposit (Central Meseta, Morocco)

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Abstract. The El Hammam REE-rich fluorite ± barite ± sulphide vein system in central Morocco is hosted in folded and low to medium metamorphic grade sedimentary and volcanic rocks of Cambro-Ordovician to late Carboniferous age, locally intruded by minor Variscan granitic stocks, and by dike swarms of unknown age. Mineralized structures consist mostly of calcite and fluorite, and occur principally as ENE-WSW-trending, trans-tensional sub-vertical veins. The fluorite is characterized by high total REY contents ranging from 523 to 3586 ppm, and a slight fractionation of LREE relative to HREE, resulting in roughly flat REY patterns. The REY compositions, together with fluid inclusion data, point to the role of hot sedimentary brines and fluid-rock interaction at high fluid-rock ratios. The fluid system is likely related to Pangea rifting and subsequent Central Atlantic opening during Permian-Triassic time.

Keywords. El Hammam, Morocco, vein system, fluorite, REE.

1 Introduction

Variscan inliers scattered throughout the Moroccan territory host numerous base metal-fluorite-barite veins mainly of post-Carboniferous to Early Cretaceous age. Most deposits are within a Paleozoic succession of greenschist-facies sedimentary and volcaniclastic rocks locally intruded by multiple phase Variscan granitoids. Among these, the El Hammam fluorite deposit located at 33°33’N and 5°48’W (Fig. 1) is exploited by the largest and sole operating fluorite mine in North Africa. Mining dates back to the 1930s and continues today, with an overall annual production of 110,000 t of fluorite concentrate at 98% purity. In this contribution, we review the geological setting of the deposit and present new ICP-MS analyses, and based on these data reevaluate the temporal and spatial relationships between the fluorite mineralization and associated late Variscan granitoids.

2 District geology

The Central Massif of Morocco in which the El Hammam fluorite district occurs is a ~100-km-wide Variscan belt of folded, cleaved, metamorphosed, and faulted quartz-rich turbidites of Cambro-Ordovician to late Carboniferous age (Fig. 1). The generalized stratigraphic column comprises, from base to top, a succession of Silurian to Visean-Namurian (early Carboniferous) variably colored schistose pelite, and lesser continentally derived quartz- and lithic-rich sandstone, graywacke, and siltstone, with carbonate intercalations, locally intruded by minor Variscan stocks and dike swarms of unknown age (Fig. 1).

Figure 1. Geological map of the El Hammam district showing the spatial distribution of major REE-rich fluorite veins and their relationship to stratigraphy, igneous rocks, fault systems, and metamorphism (modified after Agard 1966).

No large exposure of granitoid intrusions is evident in the vicinity of El Hammam mine, but a buried granitic body, whose presence has been inferred both by geophysical data (i.e., negative Bouguer gravity anomaly; Jébrak 1982) and a 16 km x 4 km-wide surface...
thermal metamorphic aureole (Fig. 1), was intersected at 200 m depth during exploration drilling. Thermal metamorphism produced by the emplacement of the buried El Hammam pluton gave rise to a regionally developed 16 km x 4 km, ENE-trending metamorphic aureole that consists predominantly of spotted-textured schists containing porphyroblasts of cordierite, andalusite, chlorite, muscovite, and biotite (Sonnet 1982; Rahho 1996). These mineral assemblages indicate peak thermal conditions of ≤610°C and estimated pressures of ≤2.3 kb (Sonnet 1981).

3 Fluorite mineralization

Fluorite mineralization occurs along a crustal-scale strike-slip shear corridor locally known as the El Hammam shear zone (Tahiri et al. 1996) that resulted from a NW-SE compressive event. The mineralized structures consist of massive open-space fillings of an array of transtensional, mostly ENE-trending, veins (Fig. 1). Overall, three major, roughly continuous, subparallel and steeply dipping structures have been and/or are currently being mined, both from open pits and underground workings: the Moufrès-Bergamou, Tlaltezma-Achemache, and Mizourza vein systems (Fig. 1). These veins extend laterally for as much as ~10 km along strike, dip sub-vertically, and vary in thickness from several cm to 10 m. Known vertical extents of fluorite ore are greater than 700 m. All of the mineralized structures are confined to the thermal metamorphic aureole centered on the buried El Hammam intrusion (Fig. 1). The vein fill is strongly banded, indicating multiple dilatational and depositional events. Most vein margins are brecciated and cemented by drusy or comb-textured quartz, cubic fluorite, and calcite. Wall-rock alteration surrounding the veins is generally subtle and includes the presence of hydrothermal clays, quartz, and carbonates. Well-developed cubic crystals of fluorite are common as linings of vugs.

All of the veins display similar mineral assemblages dominated by fluorite and minor sulphides together with sparry calcite and quartz, and lesser barite although the proportion of fluorite relative to other minerals varies among the veins. Overall, El Hammam fluorite is massive and greenish throughout the orebodies but locally displays a wide spectrum of colors ranging from purple to colorless through emerald blue; yellow varieties also exist. Sulphides, locally abundant, consist of variable proportions of pyrrhotite, galena, sphalerite, pyrite, and chalcopyrite. Barite occurs in places (i.e., Bergamou vein; Fig. 1), either as massive aggregates or crested white to pink crystals encrusting voids.

The sequence of mineral deposition shows four successive stages of hydrothermal mineralization, (designated I to IV), two of which (II and III) are of economic importance (Fig. 2).

4 REE and trace element compositions of fluorite

Overall, the El Hammam fluorite is characterized by high total REY concentrations (ΣREE) ranging from 523 to 3586 ppm (Table 1), and roughly flat REY patterns between La and Y that are greatly inclined between Y and Lu, reflecting strong depletion in heavy REE (HREE) (Fig. 3). The analyzed fluorites also exhibit positive Eu and Y anomalies. Moreover, pre-ore hydrothermal calcite shows the highest total REY abundances with ΣREE ranging from 206 to 6954 ppm, in addition to having strong positive Eu and subtle negative Y anomalies, on a chondrite-normalized basis. Conversely, there is a slight fractionation of light REE (LREE) relative to HREE, resulting in roughly flat REY patterns. In the Tb/La vs Tb/Ca discrimination diagram of Möller et al. (1976), data for both the analyzed fluorite and pre-ore calcite samples plot within the pegmatite field (Fig. 4).

Figure 2. Summary paragenetic sequence illustrating the various hydrothermal stages of the El Hammam fluorite ± barite ± sulphide hydrothermal vein system. Width of bars is roughly proportional to intensity or volume of event. Abbreviations: Cpy = chalcopyrite; Gn = galena; Po = pyrrhotite; Py = pyrite; Sp = sphalerite.

Figure 3. Chondrite-normalized REY patterns of pre-ore hydrothermal calcite and greenish fluorite from El Hammam vein system, compared to the spatially associated Late Variscan granite. PAAS normalization values from McKee (1989).

Compared to green fluorite and pre-ore hydrothermal calcite, whole-rock compositions of the late Variscan granite show substantially lower ΣREE concentrations (Table 1). In this regard, the chondrite-normalized REE pattern of the El Hammam granite (Fig. 3) displays a weak fractionation and a large negative Eu anomaly, both of which are typical of A-type, highly fractionated, high-K, calc-alkaline granites (Taylor 1982; Pérez-Soba and Villaseca 2010).
5 Discussion

The high REE contents of the El Hammam fluorite and related pre-ore hydrothermal calcite (up to 6954 ppm; Table 1) impose specific requirements in terms of fluid source(s) and fluid-rock interactions. Classically, REE enrichment has been shown to occur during magmatic evolution in alkaline-carbonatite or A-type granite intrusive environments (Schönenberger et al. 2008; Chellet et al. 2010; Bouabdelah et al. 2010).

The discrepancy between the chondrite normalized REY patterns of El Hammam fluorite and of whole rocks from the adjacent granitic intrusion (Fig. 3), along with fluid inclusion data indicate disconnection between the fluorite-barite mineralization and this felsic magmatism. Indeed, microthermometric measurements suggest that the ore-forming fluids were evolved NaCl-CaCl$_2$-KCl-MgCl$_2$ basin-derived, hot (100 ± 20°C) saline brines (>20 wt% NaCl equiv) (Yajima and Touray 1970).

Because there is no clear genetic connection between the El Hammam fluorite mineralization and the spatially associated late Variscan granite, the hypersaline Na-Ca-Mg-Ba-bearing fluid compositions suggest a sedimentary source, thereby supporting an epigenetic hydrothermal evaporitic model. From textural evidence (i.e., hydrothermal brecciation) and pressure estimates, it is inferred that El Hammam mineralization occurred at relatively shallow depths (<2 km; Sonnet and Verkaeren 1989). Based on the constraints highlighted above, we propose that the high REE contents of the El Hammam fluorite are inconsistent with the involvement of purely magmatic fluids, pointing instead to the role of hot basin-derived brines and subsequent fluid-rock interaction at high fluid/rock ratios as being the main factors that controlled the distribution of REE. Moreover, structural constraints (Rahho 1996) together with $^{39}$Ar/$^{40}$Ar ages (Chellet et al. 2010) indicate that the El Hammam fluorite-barite mineralization occurred during the Permian-Triassic, coincident with Pangean rifting and later opening of the Central Atlantic Ocean (Muttoni et al. 2003; Martins et al. 2008). This interval of time fits within the Late Triassic-Early Jurassic period during which most of the Western Europe fluorite province formed (Sizaret et al. 2009).

![Figure 4](image4.png)

**Figure 4.** Logarithmic plot of Tb/Ca vs. Tb/La for greenish fluorite separates from the El Hammam REE-rich fluorite vein system. Pegmatitic, hydrothermal, and sedimentary fields from Möller et al. (1976). Abbreviations: CCF, primary crystallization trend; RRF, remobilization trend.

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<th>Table 1. LA-ICPMS trace-element compositions (ppm) of selected greenish fluorite separates and pre-ore hydrothermal calcite from the El Hammam REE-rich fluorite deposit. Whole-rock trace-element composition of the El Hammam Late Variscan granite is listed for comparison.</th>
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