# PACROFIXII The Edwin W. Roedder Pan-American Current Research on Fluid Inclusions Conference



### May 24-26, 2016

May 23, 2016 - Preconference Short Course | May 26-28, 2016 - Field Trip University of Missouri-Columbia



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Welcome to the University of Missouri. We are pleased to host the thirteenth biennial PACROFI conference and thank you for your participation. We hope that you find the conference stimulating and enjoyable. A total of 57 oral and poster presentations are scheduled in the following topical categories: Recent Innovations in Technique and Application, Phase Relations, Sedimentary Basins and Diagenesis, Fluid and Melt Inclusions in Igneous and Metamorphic Systems, and Hydrothermal Ore Deposits. Countries represented by conference participants include Algeria, Canada, Chile, China, India, Norway, and the United States.

We would like to thank the following sponsors for their generous support: Doe Run Mining Company, The Geochemical Society, McCrone Microscopes and Accessories, Olympus Corporation, The Society of Economic Geologists, and the University of Missouri Department of Geological Sciences. We would also like to thank Barbara Wills and Leanne Boyd of the University of Missouri Conference Office for their indispensable help.

Included with your conference program are copies of the Columbia and University of Missouri visitor's guides that show maps of campus and downtown Columbia, and lists of restaurants and attractions. Please plan to attend the conference dinner at Les Bourgeois Vineyards in nearby Rocheport on Wednesday evening. Round-trip transportation from Gannett Hall will be provided.

We have been looking forward to the conference and hope to see many of you again at PACROFI XIV in 2018.

The Organizing Committee,

Martin Appold Kevin Shelton Peter Nabelek

# ACKNOWLEDGEMENTS

### **Keynote Speakers**

Kathleen Benison West Virginia University

**Robert Burruss** U.S. Geological Survey—Reston

Alan Anderson St. Francis Xavier University Dan Marshall Simon Fraser University

> **Robert Bodnar** Virginia Tech

#### **Other Invited Speakers**

**Rosario Esposito** University of California—Los Angeles Iain Samson University of Windsor

### The Organizing Committee

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Department of Geological Sciences, University of Missouri-Columbia





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#### Monday, May 23, 2016

9:00 am – 5:00 pr	n Full Day Preconference	Geological Sciences Bldg. 108
	<b>Dr. Robert Goldstein</b> , University of The Right Tool for the Job: Fluid I	of Kansas nclusion Applications to Research on Diagnetic Systems
5:00 – 7:00 pm	Ice Breaker Reception	

#### Tuesday, May 24, 2016

	All Presentations will be held in the Fisher Auditorium (Gannett Hall)				
8:30 am	Announcements — Martin Appold, Conference Chair				
	RECENT INNOVATIONS IN TECHNIQUE AND APPLICATION				
8:40 am	Kathleen Benison, Keynote Fluid inclusions in bedded halite and gypsum as paleoenvironmental indicators				
9:20 am	<b>Lowell Moore</b> The CO <sub>2</sub> content of primitive bubble-bearing island-arc melt inclusions: a comparative study of Raman-spectroscopy and experimental homogenization				
9:40 am	<b>Vivekanandan Nandakumar</b> <i>Hydrocarbon Fluid Inclusions: Fluorescence Spectral Signatures - An indicator of API</i> <i>Gravity</i>				
10:00 am	Sabina Strmic Palinkas Chemical geothermometry applied to adularia-sericite epithermal Au-Ag deposits: A case study from the Hauraki Goldfield, New Zealand				
10:20 am	Coffee break				
F	LUID AND MELT INCLUSIONS IN IGNEOUS AND METAMORPHIC SYSTEMS				
10:35 am	<b>Rosario Esposito,</b> Invited Representative CO <sub>2</sub> , H <sub>2</sub> O, and S Concentrations of Volcanic Silicate Melt Inclusions				
11:00 am	<b>Daniel Kontak</b> Fluid inclusion study of the Brazil Lake LCT-type pegmatite, Nova Scotia, Canada provides insight into the origin of rare-metal enrichment and occurrence of wallrock-derived CO <sub>2</sub>				
11:20 am	<b>Elizabeth Gammel</b> <i>Li, B, F, and Cl controls on transition from magmatic to hydrothermal crystallization in</i> <i>low pressure pegmatite dikes</i>				
11:40 am	<b>Peter Nabelek</b> Properties of fluids attending recrystallization of quartzite in the contact aureole of the Eureka Valley-Joshua Flat-Beer Creek Pluton, California				
12:00 pm	Lunch Break				

1:30 pm	<b>Alan Anderson,</b> <i>Keynote</i> <i>Discreditation of diomignite and its petrologic implications</i>
2:10 pm	Yury Klyukin Fluid evolution at the North American Emerald Mine, Hiddenite, NC
2:30 pm	<b>Drew Barkoff</b> Formation conditions of the Casting Copper skarn, NV, based on spectroscopic analysis and elastic modeling of mineral inclusions
2:50 pm	John Ridley Variability of major-element chemistry of magmatic-hydrothermal fluids
3:30 pm	Begin poster session Palmer Room
5:30 pm	End poster session

#### Wednesday, May 25, 2016

3:30 am Announcements — Martin Appold, Conference Chair				
PHASE RELATIONS				
8:40 am	<b>Robert Bodnar,</b> Keynote It's like déjà vu all over again: Parallels in the evolution of fluid and melt inclusion research			
9:20 am	<b>Hector Lamadrid</b> Synthetic fluid inclusions as mini batch reactors to monitor serpentinization reactions in the oceanic lithosphere			
9:40 am	<b>Pilar Lecumberri-Sanchez</b> <i>Evidence from the fluid inclusion record of halite saturation in magmatic-hydrothermal</i> <i>systems</i>			
10:00 am	<b>Maocheng Luo</b> Fluid inclusions that homogenize by halite disappearance in porphyry copper deposits: Heterogeneous entrapment along the liquid-vapor-halite curve			
10:20 am	Coffee Break			
10:40 am	<b>Matt Sublett</b> <i>Partitioning of Na and K between liquid and vapor in the</i> H <sub>2</sub> O-NaCl-KCl system at 600-800°C and 500-1000 bars			
11:00 am	<b>Matthew Steele-MacInnis</b> <i>Liquidus relations in multi-component, saline aqueous fluid inclusions: Application to</i> <i>salinity estimation and LA-ICPMS analysis</i>			
11:20 am	Luke Bickerton Defining the PTX of fluids associated with greisen and vein formation at the East Kemptville Sn-Cu-Zn-Ag(-In) deposit, Nova Scotia, Canada			

11:40 am	Martin Appold How metal-rich are the fluids that form carbonate-hosted Zn-Pb ore deposits? Lunch Break			
12:00 pm				
	SEDIMENTARY BASINS AND DIAGENESIS			
1:30 pm	<b>Robert Burruss,</b> Keynote 3D multiphoton, multimodal microscopy of fluid inclusions			
2:10 pm	<b>Georgina Lukoczki</b> New fluid inclusion evidence of multi-phase hydrocarbon migration in fracture systems of Triassic—Jurassic strata of SW Hungary			
2:30 pm	Joshua Field Insights into MVT Ore Genesis from Fluid Inclusions in Trace Occurrences of MVT Mineralization			
2:50 pm	<b>Stuart Kenderes</b> Measuring fluorine concentrations of ore fluids in the Illinois-Kentucky district: An SEM- EDS analysis of fluid inclusion decrepitates			
3:10 pm	<b>Sarah Smith</b> <i>Constraints from fluid inclusions on MVT ore fluid metal concentrations predicted from</i> <i>solid solution metal concentrations in ore-stage calcite</i>			
3:45 pm	Begin poster session Palmer Room			
4:45 pm	End poster session			
5:45 pm	<b>Depart for dinner from circle drive on MU Quad</b> Dinner at Les Bourgeois Vineyards, Rocheport			
9:00 pm	Leave from dinner			

#### Thursday, May 26, 2016

8:30 am	Announcements — Martin Appold, Conference Chair		
HYDROTHERMAL ORE DEPOSITS			
8:40 am	<b>Dan Marshall,</b> <i>Keynote</i> <i>Melt inclusions of native-silver and native-bismuth at Cobalt, Ontario: An example of</i> <i>native-metal enrichments using experimental and in-situ melting</i>		
9:20 am	<b>B. Munoz</b> Characterization of mineralized fluids from Chancón mining district; applications in energy-related technologies		

9:40 am	<b>Daniel Kontak</b> Evidence for pressure cycling and flid unmixing as relevant processes in gold deposits from fluid inclusion studies of Archean and Phanerozoic orogenic and intrusion-related settings in Canada
10:00 am	<b>Richard Hagni</b> Studies of Fluid Inclusion Temperatures and Salinities for Fluorite Crystals at the Okorusu Fluorspar Mine in North-Central Namibia
10:20 am	Coffee break
10:40 am	<b>Jiuhua Xu</b> Ore Genesis of the Keyinbulake Cu-Zn Deposit, Altay, China: Ore Textures, CO <sub>2</sub> -rich Inclusions, and Isotope Geochemistry
11:00 am	<b>Kevin Shelton</b> Fluid inclusion and sulfur isotope studies of a new kind of Zn-Cu-rich MVT orebody at the Lamotte Sandstone/Bonneterre Dolomite contact, Viburnum Trend district
11:20 am	Abdelsalam Hassan Geochemistry of fluid inclusions in the Vazante hypogene non-sulfide Zn and the Morro Agudo Irish-type Zn-Pb Deposits, Minas Gerais, Brazil
11:40 am	<b>Wyatt Bain</b> The Origin of Hydrothermal Apatite at the Humboldt Iron-Oxide Apatite (IOA) Deposit, West-Central Nevada
12:00 pm	Lunch Break
1:30 pm	<b>Iain Samson,</b> Invited Fluid Inclusion constraints on the character and role of fluids in the genesis of syenite- related rare metal deposits: evidence from Thor Lake, NWT, Canada
1:55 pm	Halima Chaa An investigation into the genesis of the Zaccar iron deposit with special reference to its fluid inclusions (MILIANA, AIN DEFLA, ALGERIA)
2:15 pm	<b>Pilar Lecumberri-Sanchez</b> <i>Fluid chemistry in a tungsten-vein deposit: Panasqueira</i>
2:35 pm	<b>Ivan Borisenko</b> <i>Physicochemical conditions of ore formation at the Samolazovskoye gold deposit, Central</i> <i>Aldan</i>
2:55 pm	Coffee Break
3:10 pm	Business meeting
4:10 pm	End of business meeting
5:10 pm	Depart for field trip

# POSTERS

Poster #	1 <sup>st</sup> Author/Presenter	Title			
1	<b>Alvear, B</b> Presented by Moncada, D.	Tracking Hydrothermal Fluid Evolution in Geothermal Systems by Textural Characteristic and Fluid Inclusions Assemblage Study			
2	Bennett, Mitchell	Cathodoluminescence and fluid inclusion investigations in quartz: Preliminary results from the Yellow Pine Au-Sb deposit, Idaho			
3	Bernau, Jeremiah	Fluid inclusion evidence for acid saline lake systems in the modern, Permo-Triassic, and Neoproterozoic			
4	Childress, Tristan	Iron and oxygen isotope signatures of the Pea Ridge and Pilot Knob magnetite-apatite deposits, southeast Missouri, USA			
5	Coveney, Raymond	Are Trace and Minor MVT Occurrences Related to the Ore Deposits of the Mississippi Valley, U.S.A.? Evidence from Fluid Inclusions and Field Observations			
6	<b>Encina, Alonso</b> Presented by Moncada, D.	A new technology for exploration for precious metal deposits: application of a portable fluid inclusion crushing stage			
7	Garmon, Travis	Isotopic Identification of Multiple Contributors of Metal Ions in Mississippi Valley-Type Ore Deposits along the Cincinnati Arch			
8	Gion, Austin	Partitioning of Indium Between Biotite and Felsic Melts			
9	<b>Gomez, A</b> Presented by Moncada, D.	Mineralizing fluids from the Alhué mining district, Chile			
10	Hahn, Katherine Presented by Turner, Elizabeth and Kontak, Daniel	Diagenetic history of deep-water carbonate mounds in the Mesoproterozoic Nanisivik zinc district, Nunavut			
11	Haroldson, Erik	Cathodoluminescence imaging and fluid inclusions of the Reef deposit, a Paleoproterozoic Au-Cu occurrence in central Wisconsin, USA			
12	Lamadrid, Hector	Reassessment of the Raman $CO_2$ densimeter			
13	Lin, Xiaobao	Investigating differentiation of MORB to plagiogranite through phase equilibrium experiments in the SiO2-Al2O3-Na2O-H2O system			
14	Logan, Leslie	Chemical and isotopic comparison of Illinois Basin brines and fluid inclusions in the Illinois-Kentucky Fluorspar District: Implications for the origin, paleohydrology, and preservation of Permian ore fluids			
15	Marsh , Erin	Fluid inclusions in stibnite from the Yellow Pine deposit, Idaho			
16	Matthieu, Jordan	Integration of fluid inclusion studies with in situ micro-analysis (SIMS, LA ICP-MS) to address the nature of fluids in diagenetic settings			
17	Matthieu, Jordan	Characterization of copper mineralization at the Storm copper showing, Cornwallis District, Arctic Canada			
18	Meighan, Corey	Chemistry of ore fluids during sphalerite growth: OH Vein, Creede Mining District, San Juan Mountains, Colorado			

# POSTERS

19	Mohammadi, Sahar	Diagenetic history of Mississippian carbonate rocks in the Nemaha Ridge area, north-central Oklahoma, USA
20	Sendula, Eszter	Preliminary results of trace element abundances in Permian seawater from LA-ICP-MS analysis of fluid inclusions in halite
21	Temple, Britney	Petrology and Geochemistry of the Arbuckle Group (Upper Cambrian and Lower Ordovician), NE Oklahoma and SW Missouri

# FIELD TRIP ITINERARY

#### Thursday, May 26

Following the PACROFI meeting, we will drive to the town of Viburnum in southeast Missouri (about a 2 ½ to 3 hour drive). The vans will depart from the Geological Sciences Building at 5:10 pm, and Martin Appold will organize the departure schedule. (*You will need to have eaten an early dinner or have packed a meal to take on the vans before departure, as we will arrive in Viburnum after the motel's restaurant has closed.*)

After we check into our rooms at the Miners Inn in Viburnum, Kevin Shelton will present an overview of the field trip and the geology of the Viburnum Trend, the world's largest lead-mining district.

#### Friday, May 27

Have breakfast on your own at the Miners Inn (the restaurant opens at 6:00 AM).

We will leave the Miners Inn promptly at 7:55 AM to arrive at the Brushy Creek Pb-Zn mine by 8:30 AM to get outfitted for our underground mine and mill tour. (*It's about a 25 to 30 minute drive from the Miner's Inn to the mine.*) Lunch will be provided by the Doe Run Company.

In the afternoon we will make our way across the St. Francois Mountains toward the city of Farmington. Along the way, Kevin Shelton will lead us in examining Cambrian dolomites that represent the backreef *(lagoonal)* facies of the Bonneterre Dolomite, including well-preserved microbial laminites and extensively recrystallized "white rock".

We are staying at the Crown Pointe Lodge.

#### Saturday, May 28

Eat breakfast at the motel (included in the field trip registration fee).

During the morning and early afternoon we will visit several outcrops representing the diversity of Precambrian geology of the St. Francois Mountains.

We will depart at 8:00 AM to meet Cheryl Seeger of the Missouri Geological Survey at 8:30 AM at an outcropping of the St. Francois Mountains caldera complex.

Cheryl will lead us through several stops throughout the day to see diverse caldera lithologies, and possibly, associated hydrothermal iron oxide mineralization.

Later in the afternoon, Kevin Shelton will lead us to some of his favorite outcrops in the Old Lead Belt representing various depositional facies of the Cambrian Bonneterre Dolomite and Davis Formation.

You will have the opportunity to see one of the largest Cambrian stromatolite (*microbial*) reefs on the planet. These reef structures are a major ore-controlling feature in Pb-Zn mines in southeast Missouri. Another stop contains storm deposits and microbial thrombolites (boulder beds), above which is a horizon that has recently been shown to record one of the earliest examples of extensive predatory activity by animals (*trilobites vs. worms*).

If time permits, on our return to Columbia, we may stop at Meramec Spring Park, the site of the earliest iron foundry in Missouri. It also contains an extensive trout hatchery fed by Meramec Spring, the fifth largest spring in the state with a daily discharge of 363 million liters.

# PACROFI XIII ABSTRACTS

#### Tracking Hydrothermal Fluid Evolution in Geothermal Systems by Textural Characteristic and Fluid Inclusions Assemblage Study.

Alvear, B., Morata, D., Moncada, D., and Reich, M

### Department of Geology and Andean Geothermal Centre of Excellence (CEGA), Faculty of Physical and Mathematical Sciences, Universidad de Chile, Plaza Ercilla 803, Santiago, Chile.

Silica phases are, together carbonates, ubiquitous minerals in hydrothermal systems and, consequently, would provided a powerful tool to exploration of both active terrestrial geothermal systems and their fossil equivalents, the epithermal precious metals deposits. Some characteristics of silica minerals, like its morphology, crystal structure, chemical composition and physical chemical proprieties, might reflect differing hydrothermal conditions during vein growth (Dong et al., 1995). Quartz veins show variable textures that provide significant information on the nature of precursor fluid-filled cracks under crustal conditions (e.g. fluid chemistry, fluid flow, etc.). Vein textures reflect the various crystallization mechanisms that operate in fluid-filled cracks. The crystallization mechanisms are probably affected by different factors including P-T conditions, fluid chemistry, water rock interaction, and precipitation rate of minerals. In this study, we describe textural characteristics and fluid inclusions assemblage of gangue from the Tolhuaca geothermal field, S. Chile.

The Tolhuaca Geothermal Field is located on the NW flank of the inactive Tolhuaca Volcano in southern Chile (Melosh et al., 2010). This area presents two fault systems, Liquiñe-Ofqui fault system (LOFS) and arc-oblique long-lived fault systems (ALFS; Sanchez et al.; 2013). More than 20 samples representing different silica and calcite textures styles were collected from the 1,073 meters long Tol-1 drill core, where argillic and propylitic alteration of hosted volcanic rocks were observed. Thin sections of each sample were examined using a petrographic microscope and the mineral textures and fluid inclusion characteristics were recorded. Tolhuaca Geothermal Field shows primary Fluid Inclusion Assemblage (FIAs) consisting of coexisting liquid-rich and vapor-rich fluid inclusions (FI) hosted in bladed calcite from a deep 909 meters (Fig. 1A). Secondary FIAs consisting of coexisting liquid-rich and vapor-rich FI hosted in jigsaw quartz from a deep 992 meters (Fig. 1B).



Figure 1. Photomicrograph showing under plain transmitted light. Primary FIA consisting of coexisting liquid-rich and vapor-rich in bladed calcite. B) Secondary FIAs consisting of coexisting liquid-rich and vapor-rich FI hosted in quartz

The textural study shows that at Tolhuaca geothermal system colloform, jigsaw, flamboyant, euhedral and comb textures in silica minerals and rhombic calcite and bladed calcite are presents (Fig. 2A). The common observed is colloform, jigsaw and euhedral quartz. Additionally, cathodoluminescence imaging obtained by Scanning Electron Microscopy (SEM-CL) allow us to a better classification of the different textural families observed in this geothermal field (Fig. 2B). Textural and FIAs study show Tolhuaca geothermal field has different processes through its history, example of these is boiling on later stages, because quartz have secondary FIAs consisting of coexisting liquid-rich and vapor-rich FI.



# Figure 2. Diagram of texture and fluid inclusions from Tolhuaca drill core (A). SEM-CL image and microscope image from red area (in A) from Tolhuaca drill core show different textures in silica minerals (B). Photomicrograph showing silica (quartz) under crossed nicols (C).

In the present paper, we demonstrate the relevance of a precise textural characterization of alteration minerals present in geothermal systems as a best way to understand fluid evolution during hydrothermal alteration. Working with different analytics methods, like textures study (together with SEM-CL) and fluid inclusions, allow us to improve the conceptual model needed for a better understanding of active geothermal fields.

Ackwoledgments: The research described above was supported by FCFM-UChile granted to Moncada D. and the CEGA Fondap-Conicyt Project 15090013, FONDEQUIP EQM 140009 and Millenium Nucleus130065.

#### REFERENCES

- Dong, G., Morrison, G., Jaireth, S. (1995). Quartz Textures in Epithermal Veins, Queensland-Classification, Origin and Implication. Economic Geology. 90. 1841-1856.
- Melosh, G., Cumming, W., Benoit, D., Wilmarth, M., Colbin, A., Winick, J., Soto-Neira, E., Sussman, D., Urzúa-Monsalvez, L., Powell, T., Peretz, A. (2010). Exploration results and resource conceptual model of the Tolhuaca Geothermal Field, Chile. Proceeding World Geothermal Congress.
- Sanchez, P., Pérez-Flores, P., Arancibia, G., Cembrano, J., Reich, M. (2013).Crustal deformation effects on the chemical evolution of geothermal systems: the intra-arc Liquiñe–Ofqui fault system, Southern Andes. International Geology Review. 55. 1384-1400.

#### Discreditation of diomignite and its petrologic implications

Anderson, A.J.\*

#### \*Department of Earth Sciences, St. Francis Xavier University, Antigonish, NS, Canada B2G 2W5

Diomignite ( $Li_2B_4O_7$ ), the first mineral to be described solely as a daughter mineral in fluid inclusions, is discredited as a valid mineral species. It will be shown that the evidence given in the original description (IMA 84-58) is circumstantial, incorrect, or equivocal. Diomignite was reported to occur in virtually every crystal-rich inclusion in spodumene from the Tanco pegmatite (London et al. 1987). However, the analysis of 30 randomly selected crystal-rich inclusions in the apparent type material deposited at the Smithsonian Institution, National Museum of Natural History, 30 inclusions in the apparent type material from the American Museum of Natural History, and several hundred inclusions in self-collected samples, indicates that diomignite is absent in every inclusion examined. Because no holotype specimen exists, and a neotype specimen was not provided by the surviving authors of the original description, the existence of diomignite could not be validated. The discreditation of diomignite was approved by the International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification (CNMNC) in January 2016.

The reported boron-rich (12 mass%  $B_2O_3$ ) composition of the fluid represented by crystal-rich inclusions in spodumene and petalite from the Tanco pegmatite (London 1986) was based entirely on the assumption that diomignite occurs in most spodumene-hosted inclusions (London et al. 1987, London 2008). However, the nonexistence of diomignite and other borate daughter minerals in these inclusions, and recent LA-ICP-MS analyses (Paslawski et al. 2016), indicate that the boron concentration of the fluid was overestimated by more than an order of magnitude. These findings refute the contention that the bulk composition of crystal-rich inclusions in Tanco spodumene is similar in all respects to experimentally generated boron-rich (>10 mass%  $B_2O_3$ ) boundary-layer melts (London 2005, 2008). Mass % concentrations of boron in the form of boric acid has, however, been reported in some secondary quartz-hosted fluid inclusions in the core of the Tanco pegmatite (Thomas and Davidson 2015). The similarities in the average concentration of boron in fluid inclusions in the quartz from the intermediate and core zones of the Tanco pegmatite (Channer, D.M.DER. and Spooner, E.T.C. 1992) and primary spodumene (Paslawski et al 2016) are in accord with the interpretation that spodumene trapped an aqueous carbonic fluid which subsequently reacted to form an assemblage of step daugther minerals consisting mainly of quartz, cookeite and zabuyelite (Anderson 2013).

The name diomignite was derived from Homeric Greek *dios mignen*, meaning divine mix, in allusion to the fluxing properties of  $Li_2B_4O_7$  on silicate-water systems. The discreditation of the divine mix, however, negates its purported role in the evolution of the Tanco pegmatite and in the generation of the tantalum oxide mineralization in the aplitic units (London 1985, 1986, 2008).

#### REFERENCES

- Anderson, A.J. (2013) Are silicate-rich inclusions in spodumene crystallized aliquots of boundary layer melt? Geofluids. 13. 460-466.
- Channer, D.M.DER. and Spooner, E.T.C. (1992) Analysis of fluid inclusion leachates from quartz by ion chromatography. Geochimica et Cosmochimica Acta. 56. 249-259.
- London, D. (1985) Origin and significance of inclusions in quartz: a cautionary example from the Tanco pegmatite, Manitoba. Economic Geology. 80. 1988-1995.
- London, D. (1986) Magmatic-hydrothermal transition in the Tanco rare-element pegmatite: evidence from fluid inclusions and phase equilibrium experiments. American Mineralogist. 71. 376-395.
- London, D. (2005) Granitic pegmatites: an assessment of current concepts and directions for the future. Lithos. 80. 281-303.

London, D. (2008) Pegmatites. The Canadian Mineralogist, Special Publication. 10. p. 347.

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London, D., Zolensky, M.E., and Roedder, E. (1987) Diomignite: natural Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> from the Tanco pegmatite, Bernic Lake, Manitoba. The Canadian Mineralogist. 25. 173-80.

- Paslawski, L., Anderson, A.J., MacFarlane, C. and Boucher, B. (2016) Boron concentrations in spodumene-hosted inclusions from the Tanco pegmatite, Manitoba. The Atlantic Geoscience Society 42<sup>nd</sup> Colloquium and Meeting, Program with Abstracts, Truro, Nova Scotia. p. 39.
- Thomas, R., and Davidson, P. (2015) Comment on "A petrologic assessment of internal zonation in granitic pegmatites" by David London (2014). Lithos. 212-215. 462-468.

# How metal-rich are the fluids that form carbonate-hosted Zn-Pb ore deposits?

Appold, Martin S.

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Though occurrences of Zn and Pb are widespread in carbonate rocks in the Earth's crust, only rarely do these metals accumulate in sufficient mass and concentration to form ore deposits such as Mississippi Valley-type, Irish-type, or Hypogene Non-Sulfide. Previous research conducted over the last several decades has identified many of the geological, structural, hydrological, and chemical factors that can be important in forming ore deposits of Zn and Pb in carbonate rocks. One factor that has long been hypothesized to be important is high concentrations of Zn and Pb in the ore fluids. Evidence to support this hypothesis has been sought from several sources but remains equivocal.

Because carbonate-hosted Zn-Pb deposits appear to have formed from ancient sedimentary basinal brines. modern sedimentary basinal brines may provide insights into the Zn and Pb concentrations of the ore fluids. However, the concentrations of Zn and Pb in modern sedimentary brines vary by orders of magnitude from up to about 800 ppm Zn and 100 ppm Pb to undetectable concentrations below about 100 ppb. These variations lead to corresponding orders of magnitude ranges of uncertainty in fluid flow rate and longevity of the ore-forming system. In theory, Zn and Pb concentration could be calculated from solubility constraints. However, large uncertainties exist in the pH, redox potential, and sulfur content of the ore fluids, leaving orders of magnitude uncertainties in the concentration of Zn and Pb. Analysis of individual fluid inclusions using LA-ICP-MS offers a way to measure directly the concentration of Zn and Pb in the ore fluids. Concentrations of Zn and Pb in fluid inclusions hosted by dolomite and quartz gangue have been found to reach up to 1's of ppm, but more commonly were undetectable. Ore fluid Zn concentrations of this order are supported by partitioning calculations based on Zn concentrations in solid solution in ore stage calcite. Sphalerite and fluorite are the two transparent ore minerals that commonly contain primary fluid inclusions. Strong LA-ICP-MS signals for Pb in sphalerite-hosted fluid inclusions and for Pb, Zn, and Cu in fluorite-hosted fluid inclusions equating to aqueous concentrations of up to 1000's of ppm have commonly been observed. However, these high concentrations tend not to be consistent within fluid inclusion assemblages. In addition, the low solubility of Cu relative to Zn and Pb but the high apparent concentration of Cu relative to Zn and Pb in the fluid inclusions would lead to the formation of ore deposits that are much richer in Cu than Zn and Pb than observed in the field. Thus, the strong LA-ICP-MS signals for Pb, Zn, and Cu in sphalerite and fluorite-hosted fluid inclusions may result from sulfide mineral accidentals rather than aqueous solute. If accidentals exist in the fluid inclusions, then they are likely sub-micron in size, as this is the resolution of petrographic observations and synchrotron XRF elemental mapping, which so far have not yielded evidence of accidentals.

Thus, a great deal of uncertainty still exists regarding the concentrations of Zn and Pb in the fluids that form carbonate-hosted Zn-Pb ore deposits. Key areas of future research include extending the search for fluid inclusion accidentals using higher resolution techniques, calibrating more closely the response of the LA-ICP-MS to Zn and Pb using synthetic fluid inclusions, determining the pH, redox potential, and sulfur content of ore fluids, and calculating the concentrations of Zn and Pb from their solid solution concentrations in ore stage minerals.

# The Origin of Hydrothermal Apatite at the Humboldt Iron-Oxide Apatite (IOA) Deposit, West-Central Nevada.

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The magnetite-dominated Humboldt Fe-oxide-apatite (±Cu-Co) deposit (IOA) in west-central Nevada is a voluminous metasomatic system associated with a mafic igneous complex formed during Jurassic backarc extension. This system is characterized by early widespread scapolite-dominated sodic-calcic alteration composed of scapolite-hornblende (± clinopyroxene, titanite, magnetite, apatite). Magnetite mineralization occurs as massive to disseminated magnetite-apatite replacing scapolititzed volcanic and intrusive rocks, or as open-space filling veins in vertically oriented breccia bodies. Based on field and petrographic relationships, Johnson and Barton (2000) interpreted that the Humboldt system many have formed via circulation of surface-derived brines, driven by magmatic heat. This interpretation is broadly supported by the observation that a significant amount of primary, apatite-hosted fluid inclusions are predominately halite-saturated brines, which suggest that the apatite-forming fluids were high-salinity fluids, consistent with the inferred connate (basinal) origin of these fluids (Johnson and Barton, 2000). However, the source of hydrothermal fluids (as well as sources of metals) in Fe-oxide-copper-gold (IOCG) and IOA systems is still a point of controversy (Barton, 2014). For example, the mineralization in the Nori/RA IOCG prospect in the Northwest Territories, Canada (Ootes et al., 2010) and the IOCG deposits of the Mantoverde district, Chile (Rieger et al., 2012) are thought to have formed from magmatic hydrothermal fluids, rather than from external basin-derived brines. Given the close association between intrusive rocks and the mineralization in the Humboldt system it is possible that magmatic hydrothermal fluids might also have played a role in forming the voluminous metasomatic apatite at the Humboldt system.

In the present study, we conduct detailed petrographic, microthermometric and microanalytical investigation of apatite(±calcite, scapolite)-hosted fluid inclusions from the Humboldt complex, in order to constrain the source and evolution of metasomatic and mineralizing fluids in this system. The majority of the fluid inclusions characterized thus far are either high-salinity brines or moderate-salinity aqueous liquid inclusions. Microthermometric analysis on the moderate-salinity inclusions indicate salinities between ~12-22 wt% NaCl equivalent (~15 wt% NaCl equivalent average), whereas the brine salinities exceed 35 wt% NaCl equivalent. All inclusions homogenize between ~100-140°C, excluding three outliers homogenizing above >170°C. LA-ICP-MS analysis on moderate salinity inclusions showed that fluids trapped in these inclusions have consistently low K, Cs, and Li concentrations and high Mg concentrations. These results suggest that the apatite-forming fluids are unlike typical magmatic fluids, at least those reported from granitoid-related hydrothermal systems, according to available microanalytical data from literature (e.g., Audétat and Pettke, 2003 Yardley, 2005). The fluid compositions recorded by inclusions in Humboldt apatite are, however, broadly consistent with basinal brines (Yardley, 2005). These data do not preclude the possibility that apatite-hosted inclusions may represent atypical magmatic fluids, perhaps reflecting the mafic pluton composition. However, our preferred interpretation is that these fluid compositions support the model proposed by Johnson and Barton (2000), that hydrothermal fluids at Humboldt were predominantly amagmatic (basinal brine) in origin. Fluid-inclusion analysis is ongoing to refine and test this hypothesis. Further work using the techniques employed in the research presented with this abstract will focus on comparing the trace element concentrations in apatite-hosted fluid inclusions from Humboldt to those from other IOCG/IOA systems, in order to assess the physical and chemical controls on hydrothermal apatite precipitation, and the variation in fluid sources and chemistry between IOCG/IOA systems with similar styles of mineralization.

#### REFERENCES

Audétat, A. and Pettke, T., (2003). The Magmatic-Hydrothermal Evolution of Two Barren Granites: A Melt and Fluid Inclusion Study of the Rito Del Medio and Canada Pinabete Pultons in Northern New Mexico (USA). Geochimica et Cosmochimica Acta. Vol. 67, P 97-121

Barton, M.D. (2014), Iron oxide (-Cu-Au-REE-P-Ag-U-Co) systems: Treatise on Geochemistry, 2nd edition, Volume 11, Chapter 23, Elsevier, p. 515-541.

Johnson, D.A. and Barton, M.D., (2000). Time-Space Development of an External Brine Dominated, Igneous-Driven Hydrothermal System: Humboldt Mafic Complex, Western Nevada. Society of Economic Geologists Guidebook Series. Vol 32. P.127-145

Ootes L, Goff S, Jackso VA, Gleeson SE, Creaser RA, Samson IM, Evensen N, Corriveau L, and Mumin AH (2010) Timing and thermochemical constraints no multi-element mineralization at the Nori/RA Cu-Mo-U prospect, Great Bear magmatic zone, Northwest Territories, Canada. Mineralium Deposita 45: 549-566.

Rieger A, Marschik R, and Dı'az M (2012) The evolution of the hydrothermal IOCG system in the Mantoverde district, northern Chile: New evidence from microthermometry and stable isotope geochemistry. Mineralium Deposita 47: 359–369.

Yardley, B.W.D., (2005). Metal Concentrations in Crustal Fluids and Their Relationship to Ore Formation. Bulletin of the Society of Economic Geologists. Vol 100. P.613-632

# Formation conditions of the Casting Copper skarn, NV, based on spectroscopic analysis and elastic modeling of mineral inclusions

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Fluid inclusion thermobarometry is a useful tool for estimating the formation temperature-pressure conditions at the time the fluid was entrapped, e.g. according to isochoric modeling of inclusions based on microthermometry (Roedder and Bodnar, 1980). However, thermobarometry based on fluid inclusions is sometimes equivocal or affected by post-entrapment modifications, and in some cases suitable inclusions are lacking. *Mineral* inclusions (i.e., crystallites of minerals enclosed within larger grains) provide an alternative thermobarometric method, according to the degree of stresses built up in mineral inclusion-host pairs.

As rocks are exhumed from Earth's interior to Earth's surface, the accompanying decrease in temperature and pressure cause minerals in the rock to expand or contract according to the compressibility and thermal expansivity of each phase. When crystallites of minerals are completely encapsulated within a rigid host crystal, the elastic differences between the inclusion and host can cause the inclusion to either build up pressure (expansion greater than that of the host), or to develop tensile stress (expansion less than that of the host). Raman spectroscopic analysis can be used to quantify the pressure in mineral inclusions, as the magnitude of the Raman shift for characteristic molecular vibrations is proportional to pressure (e.g., Comodi et al., 2001). The measured peak shift and associated inclusion pressure can be used as a basis for elastic modeling to estimate the original pressure conditions under which the mineral inclusion was enclosed, and thus, the conditions at which the rock formed (e.g., Ashley et al., 2014).

In this study, Raman spectroscopic analysis of mineral inclusions was used to assess the formation conditions of hydrothermal garnet at the Casting Copper skarn, Yerington District, NV. Casting Copper is a classic skarn locality, and the skarn assemblage consists predominately of salite pyroxene plus andradite garnet with minor calcite. Skarn formation is associated with the emplacement of porphyry-type mineralization in the Yerington district. Casting Copper has been characterized in detail in previous studies, and Einaudi (2000) reported estimated formation depths based on paleostratigraphy and structural reconstruction of 2-3 km. In the present study, we used Casting Copper as a test locality for applying mineral-inclusion barometry to metasomatic/hydrothermal rocks, and for combining mineral-inclusion analysis.

To estimate the depth of formation of the Casting Copper skarn, we collected samples of andradite garnet from Casting Copper and conducted petrographic and Raman spectroscopic analyses of mineral inclusions in the garnet. Casting Copper garnets contain abundant apatite and calcite inclusions. Whereas calcite is visible in hand sample, apatite only occurs as inclusions in the garnet. SEM imaging was used to reveal garnet zonation, as well as to investigate how the distribution of inclusions varies between zones. These results showed that garnet cores contain abundant carbonate, pyroxene and iron-oxide inclusions. In addition, both garnet cores and rims contain micron-scale apatite inclusions. Garnet-hosted apatite inclusions from Casting Copper retain significant internal pressures, which are detectable and quantifiable by Raman spectroscopy. Our ongoing focus is to constrain formation conditions using elastic modeling, and to combine these results with microthermometry of garnet-hosted fluid inclusions.

#### REFERENCES

Ashley, K.T., Caddick, M.J., Steele-MacInnis, M., Bodnar, R.J., and Dragovic, B. (2014), Geothermobarometric history of subduction recorded by quartz inclusions in garnet. Geochemistry, Geophysics, Geosystems. 15, 350-360.

Comodi, P., Liu, Y., and Frezzotti, M.L. (2001), Structural and vibrational behavior of fluorapatite with pressure. Part II: in situ micro-Raman spectroscopic investigation. Physical Chemistry of Minerals. 28, 225-231.

Einaudi, M.T. (2000), Skarns of the Yerington District, Nevada: A triplog and commentary with applications to exploration. Society of Economic Geologists Guidebook Series. 32, 101-125. Roedder, E., and Bodnar, R.J. (1980), Geologic pressure determinations from fluid inclusion studies. Annual Review of Earth and Planetary Sciences. 8, 263-301.

# Fluid inclusions in bedded halite and gypsum as paleoenvironmental indicators

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Unaltered primary fluid inclusions are direct remnants of past fluids. As such, their analyses can provide data about a variety of types of past liquids and gases (Goldstein and Reynolds, 1994; Roedder, 1984). Fluid inclusions in minerals that precipitate from surface and near-surface water, such as those in caves, lakes, lagoons, and oceans, are excellent samples by which to interpret paleoenvironmnetal conditions (Goldstein, 2001; Lowenstein and Brennan, 2001). In particular, bedded halite and bedded gypsum grow quickly from saline surface waters. Their rapid growth results in entrapment of abundant, large, primary fluid inclusions. The goal of this abstract is to provide an overview of the analytical methods and types of paleoenvironmental interpretations resulting from recent fluid inclusion studies of bedded halite and gypsum.

Petrography is the foundation of any study of fluid inclusions in halite and gypsum. Distinct crystal types, sizes, and orientation exist in bedded halite and gypsum. Comparative sedimentology, using observations of halite and gypsum growth in modern saline surface waters, as well as in the laboratory, shows the influence of some specific environmental conditions (e.g., Arthurton, 1973; Shearman, 1970). For example, chevron halite crystals only grow in shallow surface waters less than ~0.5 meters deep Fluid-inclusion assemblages help define crystal types, showing growth bands and growth directions.

Primary fluid inclusions in halite and gypsum are typically abundant and range from less than 30 to over 100 microns in size. Although halite and gypsum are most commonly clear, optical clarity is not as high as in some other inclusion hosting minerals, such as quartz and fluorite. Provided burial at moderate depths, inclusions can remain well preserved in halite for hundreds of millions of years. In contrast, gypsum dehydrates to anhydrite at relatively shallow depths and low temperatures; as a result, only geologically recent gypsum contains unaltered primary fluid inclusions.

A variety of in situ methods have been developed in the past ~25 years to retrieve paleoenvironmental data from fluid inclusions in modern and ancient bedded halite. High magnification long-working distance objectives and improved transmitted light microscopy allow imaging of prokaryotes and algae (e.g., Lowenstein et al., 2011). UV-vis petrography shows that fluorescence can be used to document hydrocarbons and microorganisms (e.g., Conner and Benison, 2013). Homogenization of artificiallynucleated vapor bubbles in originally all-liquid inclusions results in past surface water temperatures and proxies for past air temperatures (e.g., Roberts and Spencer, 1995; Zambito and Benison, 2013). Freezing-melting runs can be used to determine water salinity and major ion composition (e.g., Davis et al. 1990) and to document pH (Jagniecki and Benison, 2010). Environmental SEM-EDS of frozen inclusions yields major elemental ratios (Lowenstein et al., 2001). Laser Raman spectroscopy can identify solids, gases, organic compounds, and solutes within inclusions (e.g., Jagniecki and Benison, 2010; Winters et al., 2013). In some cases, even pH of past waters can be determined with laser Raman spectroscopy of fluid inclusions in halite (Benison et al., 1998). Crushing of bubbles in fluid inclusions in halite can be used to estimate pressure of gases at time of entrapment (Benison, 2013; Goldstein and Reynolds, 1994). Ongoing efforts are attempting to analyse the composition of trapped atmosphere in ancient halites (N. Blamey, pers. comm.).

Fluid inclusion studies in gypsum are more limited than in halite, but still have benefitted from recent technological advances. Transmitted light and UV-vis petrography has been used to document microorganisms and organic compounds in Miocene and recent gypsum (Benison and Karmanocky, 2014). Freezing-melting behavior can trace salinity and major ion composition (Attia et al., 1995; Karmanocky and Benison, 2016; Natalicchio et al., 2014). Laser Raman microscopic analysis of inclusions in gypsum can provide useful compositional data, despite the strong background noise of the host gypsum spectra (Karmanocky and Benison, 2016).

Primary, unaltered fluid inclusions in bedded halite and gypsum represent amongst the best-preserved surface waters, air samples, and microorganisms from the past. By pairing analytical methods with

detailed fluid inclusion petrography, high-resolution records can be interpreted. Significant geological issues, such as past seawater composition, marine versus nonmarine deposition, fossil microorganisms, paleoweather and paleoclimate records, as well as extreme environments on Earth and Mars, have been addressed with these fluid inclusion studies.

#### REFERENCES

- Arthurton, R.S. (1973) Experimentally produced halite compared with Triassic layered halite rock from Cheshire, England. Sedimentology. 20. 145-160.
- Attia, O.E., Lowenstein, T.K., and Wali, A.M.A. (1995) Middle Miocene gypsum, Gulf of Suez: Marine or nonmarine?. Journal of Sedimentary Research. A65. 614-626.
- Benison, K.C. (2013) Acid saline fluid inclusions: Examples from modern and Permian extreme lake Systems. Geofluids. 13. 579-593
- Benison, K.C. and Karmanocky, F.J. III (2014) Could microorganisms be preserved in Mars gypsum? Insights from terrestrial examples. Geology. 42. 615-618.
- Benison, K.C., Goldstein, R.H., Wopenka, B., Burruss, R.C., and Pasteris, J.D. (1998) Extremely acid Permian lakes and groundwaters in North America. Nature. 392. 911-914.
- Conner, A.J. and Benison, K.C. (2013) Acidophilic halophilic microorganisms in fluid inclusions in halite from Lake Magic, Western Australia. Astrobiology. 9. 850-860.
- Davis, D.W., Lowenstein, T.K., and Spencer, R.J. (1990) Melting behavior of fluid inclusions in laboratory-grown halite crystals in the systems NaCl-H<sub>2</sub>O, NaCl-KCl-H<sub>2</sub>O, NaCl-MgCl<sub>2</sub>-H<sub>2</sub>O, and NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O. Geochimica et Cosmochimica Acta. 54. 591-601.
- Goldstein, R.H. (2001) Clues from fluid inclusions. Science. 294. 1009.
- Goldstein, R.H. and Reynolds, T.J. (1994) Systematics of fluid inclusions in diagenetic minerals. SEPM Short Course. 31. 199.
- Jagniecki, E.A. and Benison, K.C. (2010) Criteria for the recognition of acid-precipitated halite: Sedimentology. 57. 273-292.
- Karmanocky, III, F.J. and Benison, K.C. (2016) A fluid inclusion record of magmatic/hydrothermal pulses in acid Salar Ignorado gypsum, northern Chile: Geofluids. DOI: 10.1111/gfl.12171.
- Lowenstein, T.K. and Brennan, S.T. (2001) Fluid inclusions in paleolomnological studies of chemical sediments. In Last, W.M. and Smol, J.P. (eds.) Tracking environmental change using lake sediments. 2. Physical and Geochemical Methods. Kuver Academic. 190-216.
- Lowenstein, T.K., Schubert, B.A., and Timofeeff, M.N. (2011) Microbial communities in fluid inclusions and long-term survival in halite: GSA Today. 21. 4-9.
- Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A., and Demicco, R.V. (2001) Oscillations in Phanerozoic seawater chemistry: Evidence from fluid inclusions. Science. 294. 1086-1088.
- Natalicchio, M., Dela Pierre, F., Lugli, S., Lowenstein, T.K., Feiner, S.J., Ferrando, S., Manzi, V., Roveri, M., and Clari, P. (2014) Did Late Miocene (Messinian) gypsum precipitate from evaporated marine brines? Insights from the Piedmont Basin (Italy). Geology. 42. 179-182.
- Roberts, S.M. and Spencer, R.J. (1995) Paleotemperatures preserved in fluid inclusions in halite. Geochemica et Cosmochimica Acta. 59. 3929-3942.
- Roedder, E. (1984) Fluid Inclusions. Mineral. Soc. Amer. Reviews in Mineralogy. 12. 644.
- Shearman, D. (1970) Recent halite rock, Baja California, Mexico. Inst. of mining and Metallurgy. 79. 155-162.
- Winters, Y.D., Lowenstein, T.K., and Timofeeff, M.N. (2013) Identification of Carotenoids in Ancient Salt from Death Valley, Saline Valley, and Searles Lake, California Using Laser Raman Spectroscopy. Astrobiology. 13. 1065-1079.
- Zambito, J.J. and Benison, K.C. (2013) Extremely high temperatures and paleoclimate trends recorded in Permian ephemeral lake halite. Geology. 41. 587-590.

# Cathodoluminescence and fluid inclusion investigations in quartz: Preliminary results from the Yellow Pine Au-Sb deposit, Idaho

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Deposits in the historic Yellow Pine mining district in central Idaho have been mined for Au, Ag, Sb, and W. Ore occurs in breccia zones along NE-striking faults that transect Cretaceous quartz monzonite, alaskite, and pegmatite dikes, and metamorphosed Lower Paleozoic rocks in a roof pendant of the Idaho batholith. The igneous rocks are variably silicified, K-metasomatized, sericitized, sulfidized, argillized, or carbonatized. Veining took place in stages that include deposition of early milky quartz veins ± brassy pyrite, fine-grained dark pyrite and arsenopyrite ± quartz veinlets, stibnite-quartz veins, and pink dolomite or calcite veinlets. Gold resides in pyrite and arsenopyrite that occurs in veinlets and disseminations Early surveys completed by Cookro et al. (1988) described igneous quartz as milky to cloudy in appearance due to its wispy network of different overprinting fluid inclusion populations, whereas hydrothermal quartz intergrown with ore minerals contain fluid inclusions more similar to those encountered in shallow epithermal environments.

Investigations are currently underway to determine the paragenetic sequence of quartz growth and its relation to ore pyrite and stibnite, the P-T-X conditions of hydrothermal fluids through progressive stages of mineralization, the paleodepth of mineralization, and the origin and types of deposits in the district. Herein we present preliminary results from the study of quartz sampled along 270 meters of a drillhole through the center of the Yellow Pine deposit. Samples selected for initial examination include a suite of quartz-pyrite and quartz-stibnite veins hosted in sericite-altered monzonite and alaskite. Optical petrography was aided by SEM-Cathodoluminescence (CL) imaging to differentiate crosscutting quartz types and associated fluid inclusion assemblages for further characterization by microthermometry and laser Raman spectroscopy.

In ore zones, igneous quartz phenocrysts have homogenous to mottled intermediate-intensity CL, with faint ghosts of earlier textures that have been lost to recrystallization. Healed microfractures cutting the phenocrysts are distinguished by their CL intensity and fluid inclusion assemblages. Early patches of quartz with mottled dark CL rarely contain secondary assemblages of 3-phase aqueous carbonic fluid inclusions that are thought to represent pre-ore fluids that formed at greater depth. These inclusions are equant to rectangular in shape and contain visible *liquid* H<sub>2</sub>O, *liquid* CO<sub>2</sub>, and *vapor* CO<sub>2</sub> at room temperature; *liquid* H<sub>2</sub>O fills approximately 40-60 vol % of the inclusions. Later through-going cracks and hairline fractures are filled by dark-CL quartz that contains inclusions of pyrite  $\pm$  arsenopyrite along with secondary assemblages of 2-phase liquid-rich fluid inclusions that are equant to irregular in shape with ~10-20 vol % vapor. This dark-CL quartz is crosscut and offset by microveinlets of quartz with euhedral, inwardly oriented, intermediate- to dark-CL growth zones. These microveinlets lack fluid inclusions, but often contain pyrite mineral inclusions. The last stage of quartz has bright luminescence and fills dense fracture networks that cross cut all of the earlier quartz types. Stringers of bright-CL quartz contain stibnite needles and secondary trails of irregular shaped, liquid-rich inclusions with 0-10 volume % vapor.

In hydrothermal quartz veins, igneous quartz served as the nucleation site for dark- to intermediate-CL quartz crystals with oscillatory growth zones. Large quartz crystals on the margins of stibnite veins exhibit dull-CL cores with lobate contacts against later zoned quartz. Smaller crystals of euhedral quartz encapsulated in vein stibnite show similar CL zonation. Dark-CL growth zones contain abundant sericite mineral inclusions, which are accompanied by pyrite and arsenopyrite inclusions in later zones. The darkto intermediate-CL quartz veins are cross cut and overgrown by quartz with bright luminescence. Large crystals of bright-CL quartz rarely contain sericite mineral inclusions along growth zones, but are otherwise devoid of fluid inclusions. In places, the bright-CL quartz has a narrow rim of dark-CL quartz.

Raman peaks at 1289 and 1392 cm<sup>-1</sup> measured in 3-phase inclusions associated with early recrystallized igneous quartz confirm the presence of CO<sub>2</sub> and the absence of CH<sub>4</sub> in pre-ore fluids (Burke, 2001, and references therein). Raman peaks at 1292, 1392, and 2919 cm<sup>-1</sup> in secondary and pseudo-secondary liquid-rich inclusions in subsequent dark-CL quartz contain CO<sub>2</sub> and CH<sub>4</sub>. These inclusions homogenize to liquid from 175-207°C and 199-233°C, respectively, and have maximum salinities based on Tm<sub>ice</sub> of 6 to 7 wt % NaCl equiv. (Steele-MacInnis et al., 2012). Although the Th range of liquid-rich inclusions in later hydrothermal quartz overlaps that of inclusions analyzed in the igneous quartz, no CO<sub>2</sub> or CH<sub>4</sub> was detected in them. Rare secondary two-phase liquid-rich inclusions associated with intermediate zoned quartz yield homogenization temperatures of 180-210°C and salinities of 9 wt % NaCl equiv (Steele-MacInnis et al., 2012). Pressures of homogenization ranging from 9 to 28 bars for inclusions in hydrothermal quartz suggest that economic mineralization likely formed within a shallow epizonal environment. Liquid-rich inclusions in bright-CL quartz are too small to measure, however their irregular shape and low and variable volume % vapor is indicative of formation at low temperatures (< 200°C). Studies of these samples are ongoing, with the aim of identifying additional inclusions in ore-related intermediate- and bright-CL quartz for analysis.

#### REFERENCES

Burke, E.A.J., 2001, Raman microspectrometry of fluid inclusions: Lithos, v. 55, no. 1-4, p. 139–158.

- Cookro, T.M., Silberman, M.L., and Berger, B.R., 1988, Gold-Tungsten-Bearing Hydrothermal Deposits in the Yellow Pine Mining District, Idaho, *in* The Geological Society of Nevada: Bulk Mineable Precious Metal Deposits of the Western United States Symposium Proceedings, Reno, Nevada, p. 577–624.
- Steele-MacInnis, M., Lecumberri-Sanchez, P., Bodnar, R.J., 2012. HOKIEFLINCS\_H2O-NACL: A Microsoft Excel spreadsheet for interpreting microthermometric data from fluid inclusions based on the PVTX properties of H2O-NaCl. Computers & Geosciences, v. 49, p. 334-337.

# Fluid inclusion evidence for acid saline lake systems in the modern, Permo-Triassic, and Neoproterozoic

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Modern acid saline lakes in Western Australia and Chile provide provocative data about extreme surface water chemistry and its relationships to brine evolution, water-rock interactions, climate, and extremophilic life, both on Earth and on Mars. Ancient extremely acid saline environments in the rock record have recently been documented. The purpose of this abstract is twofold: (1) to describe various clues about acidity from fluid inclusions in bedded halite and gypsum; and (2) to report preliminary data suggestive of low pHs from the Triassic Mercia Mudstone of Northern Ireland and the Neoproterozoic Browne Formation of Australia.

Modern acid saline lakes in Western Australia and Chile precipitate halite and gypsum. Primary fluid inclusions, easily distinguished along growth bands, are large (some more than 100 microns long) and abundant. Modern parent waters have been analysed and allow for fluid inclusions in the halite and gypsum to serve as "knowns". In addition, we use fluid inclusions in synthetic halite grown from simple acid brines as standards for comparison. Acid fluid inclusions in synthetic halite and/or in natural modern halite and gypsum have the following characteristics: (1) have Raman peaks for bisulfate (when pH is less than ~1.5 (Benison et al., 1998); (2) commonly will not freeze; when they do freeze, they have distinct "fuzzy borders" upon warming (Benison, 2013; Jagniecki and Benison, 2010); (3) have elevated concentrations of Al, Fe, and/or Si (Benison and Goldstein, 2002); and (4) may contain H<sub>2</sub>SO<sub>4</sub> (Karmanocky and Benison, 2016). Primary unaltered fluid inclusions in bedded halite in the Permian Opeche Shale (North Dakota) and Nippewalla Group (Kansas) show evidence of extremely acid saline Permian environments (Benison et al., 1998).

Our observations of the Triassic Mercia Mudstone of Northern Ireland and the Neoproterozoic Browne Formation of Australia suggest that the their depositional waters may have been acidic. Both units are primarily composed of red bed siliciclastics and bedded and early depositional halite and gypsum/anhydrite. Sedimentary, mineralogic, and diagenetic features are strikingly similar among the Nippewalla, Opeche, Mercia, and Brown strata. Preliminary freezing-melting and laser Raman studies of the fluid inclusions in the Mercia and Browne halite indicate that they are not typical neutral-alkaline saline inclusions. They are reluctant to freeze and they have Raman spectra that include bisulfate and match some synthetic and modern natural acid inclusions. Further studies are needed to refine the compositions of these inclusions.

#### REFERENCES

Benison, K.C. (2013) Acid saline fluid inclusions: Examples from modern and Permian extreme lake Systems. Geofluids. 13. 579-593.

Benison, K.C. and Goldstein, R.H. (2002) Recognizing acid lakes and groundwaters in the rock record. Sedimentary Geology. 151. 177-185.

Benison, K.C., Goldstein, R.H., Wopenka, B., Burruss, R.C., and Pasteris, J.D. (1998) Extremely acid Permian lakes and groundwaters in North America. Nature. 392. 911-914.

Jagniecki, E.A. and Benison, K.C. (2010) Criteria for the recognition of acid-precipitated halite: Sedimentology. 57. 273-292.

Karmanocky, III, F.J. and Benison, K.C. (2016) A fluid inclusion record of magmatic/hydrothermal pulses in acid Salar Ignorado gypsum, northern Chile: Geofluids. DOI: 10.1111/gfl.12171.

#### Defining the PTX of fluids associated with greisen and vein formation at the East Kemptville Sn-Cu-Zn-Ag(-In) deposit, Nova Scotia, Canada

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The East Kemptville Sn-Cu-Zn-Ag(-In) deposit in southwest Nova Scotia, Canada, was previously mined (1985-1992) but remains a potential metal resource of value to the technology sector. Renewed interest in the deposit has provided an opportunity to further characterize and study the magmatic-hydrothermal evolution of this deposit, thereby contributing to exploration strategies for similar granitoid-related deposits, both locally and globally. The greisen-style deposit hosts cassiterite (Sn), as well as pyrrhotite, sphalerite and lesser chalcopyrite that represent the Cu-Zn-Ag(-In) resource. The mineralization is hosted by the highly evolved East Kemptville topaz-muscovite leucogranite (EKL). The EKL is a highly fractionated portion of a muscovite-biotite leucomonzogranite, the Davis Lake pluton, which is one of several differentiated granites in the large (7800 km<sup>2</sup>) Late Devonian (375 Ma) South Mountain Batholith (SMB) that intruded a ~10-km thick sequence of Cambro-Ordovician meta-sandstones and meta-siltstones/slate. The SMB is a composite suite of crustally derived intrusions emplaced during the waning stages of deformation related to the Neo-Acadian Orogeny.

In the deposit area, the EKL is pervasively sericitized, and plagioclase has a near end-member albite composition. Two greisen alteration types are identified: one is massive, and the other is zoned (Richardson 1988; Halter et al. 1995), with the latter interpreted as a single, evolving greisen event leading to phase changes in the leucogranite, from K-feldspar to albite, albite to sericite, and sericite to topaz. Prolonged greisenization is interpreted to have resulted in an increase in the pH of the hydrothermal fluid and deposition of cassiterite (Halter et al., 1996). Fluid inclusion assemblages (FIAs) within quartz in each stage of the paragenesis were studied using microthermometry and decrepitate evaporate mound analysis, to determine the pressure-temperature-composition (PTX) conditions of the mineralizing fluid. The FIAs vary throughout the paragenesis, from L-V-H(±s; early) to L-V to L-V-CO<sub>2</sub> (late; X<sub>CO2</sub><0.5). The FIAs show two interesting results: 1) hydrohalite is the last solid phase to melt during heating from low temperatures, constraining fluid salinity to 23-26 wt % eq. NaCl (Bodnar, 2003), and 2) first melting temperatures in the greisen FIAs are depressed to around -37°C, indicative of a divalent cation in the greisen fluid (Fig.1). Microthermometrc data for greisen FIAs yield two dominant homogenization temperature (T<sub>H</sub>) ranges of 240-260°C and 290-350°C. The isochores derived from the latter temperature range, for a ~25 eq. wt % NaCl fluid, correlate to a maximum P-T of 600-650°C and ca. 3.5 kbars, consistent with the conditions of SMB emplacement and previous studies at the deposit (Halter et al., 1995; Kontak et al., 2001); cooler T<sub>H</sub> data correlate to a later stage within the greisen event near 500°C at a similar pressure. Decrepitate mound analysis, conducted on the same samples as thermometry, show a population dominated by NaCl, but also the presence of significant K in the greisen fluid, and Fe(±Mn) values that vary from ~15-0 wt % (relative to K and Na), consistent with the concentration predicted from microthermometry (Fig. 1). Both the variable K and Fe(±Mn) are indicative of chemical exchange between the host rock and the exsolved fluid (i.e., in the greisen). In addition, the early stage fluids are S-rich, with Na:S mass ratios near 1.

These initial findings, combined with our earliler work, indicate that a mineralizing fluid of moderate salinity was exsolved from an evolved melt at high pressure and temperature, ca. 3.5-4 kbars and  $650^{\circ}$ C. This is unusual, as most greisen-style Sn deposits developed in lower P settings (<1 kbar). During incipient greisen formation, the mineralizing fluid contained a significant amount of S and Fe(±Mn), but by the time of cassiterite and sulfide precipitation had lower Fe(±Mn) concentrations and had gained significant K. Late-stage barren veins contain Fe(±Mn) (Fig.1) as well as a minor amount of CO<sub>2</sub>, likely derived from the metasedimentary wall rocks, but are relatively depleted in S. Evaporate mound analysis confirms there is a consistent change in the fluid at each stage of the paragenesis. Integration of data

from mound analysis and microthermometry will be used in conjunction with other analytical methods (LA-ICPMS, laser Raman) to further characterize the fluids, in particular the concentrations of trace elements in the fluids. These data will provide the basis on which the chemical evolution of the system will be modelled, from initial fluid ingress to its modification by fluid-rock interaction through the deposit paragenesis, culminating in formation of the Sn-Cu-Zn-Ag(-In) mineralization.



Fig. 1. Ternary diagram for H<sub>2</sub>O-NaCI-FeCl<sub>2</sub> system (left; after Lecumberi-Sanchez et al. 2015) with East Kemptville FIAs plotted based on temperatures of ice melting ( $Tm_{ice}$ ), and hydrohalite melting ( $Tm_{HH}$ ). Decrepitate mound data (right), as determined using the SEM-EDS, show the proportions of the dominant cations in the mounds in a Na-K-(Fe+Mn) ternary. The FeCl<sub>2</sub> weight percent in a FeCl<sub>2</sub>-NaCI-H<sub>2</sub>O system predicted from microthermometry (~15 wt %, left) is verified from the Na:Fe(±Mn) in evaporate mound analyses (right).

#### REFERENCES

- Bodnar, R.J. (2003) Interpretation of data from aqueous-electrolyte fluid inclusions. *In* Fluid Inclusions: Analysis and Interpretation. Mineralogical Association of Canada Short Course Series Vol. 32, 81-100.
- Halter, W. E., Williams-Jones, A. E., & Kontak, D. J. (1996) The role of greisenization in cassiterite precipitation at the East Kemptville tin deposit, Nova Scotia. Economic Geology, 91(2), 368-385.
- Halter, W. E., Williams-Jones, A. E., & Kontak, D. J. (1995) Origin and evolution of the greisenizing fluid at the East Kemptville Tin Deposit, Nova Scotia, Canada. Economic Geology, 93, p. 1026-1051.
- Kontak, D.J., Dostal, J., Ansdell, K., Halter, W., Martin, R.F. & Williams-Jones, A.E. (2001) The nature and origin of pegmatite in a fluorine-rich leucogranite, East Kemptville, Nova Scotia. Transactions of the Royal Society of Edinburgh: Earth Sciences (C.F. Davidson Memorial Lecture, 1997), 92, p. 173-2000.
- Lecumberri-Sanchez, P., Steele-MacInnis, M., Bodnar, R.J. (2015) Synthetic fluid inclusions XIX. Experimental determination of the vapor-saturated liquidus of the system H2O-NaCI-FeCI2. Geochemica et Cosmochinica Acta, 148, 34-49.
- Richardson, J.M. (1988) Field and textural relationshiops of alteration and greisen-hosted mineralization at the East Kemptville tin deposit, Davis Lake Complex, southwest Nova Scotia. Canadian Institute of Mining and Metallurgy Special Volume 39, p. 265-279.

# It's like déjà vu all over again: Parallels in the evolution of fluid and melt inclusion research.

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The presence of fluid (FI) and melt inclusions (MI) in minerals has been known for centuries, and their description and interpretation in terms of physical and chemical processes is considered by many to have begun with the classic work of Sorby (1858). Today, we have a reasonably solid understanding of the limitations and potential pitfalls associated with studying FI and MI, and this understanding represents the accumulation of much knowledge over the past 150 years.

During the early to mid twentieth century, most of the significant FI research was being conducted in the Soviet Union. The leading researcher at that time was Nikolai Porfirievich Ermakov at the Moscow State University, who is referred to in the former Soviet Union (FSU) as "the founder of thermobarogeo-chemistry". Indeed, it was Ermakov and his students and followers who made some of the most significant quantitative applications of fluid inclusions in ore deposits studies. Unfortunately for those in the West, the publications were in Russian and not always available to researchers outside of the FSU, limiting the international impact of this research. Studies conducted in the FSU up to the middle of the 20<sup>th</sup> century were summarized in two publications entitled *"Criteria for determining the genesis and medium [fluid] of ore formation"* published in 1949, and *"Research on the nature of mineral forming solutions"* published in 1950. The latter publication was translated into English by V. P. Sokoloff (with Ermakov becoming Yermakov) and edited by Edwin Roedder (Yermakov, 1965). This publication helped to generate interest in Western countries in fluid inclusions.

During the early days of Western FI research, some workers attempted to use FI to address problems that were beyond the scope of what FI data can provide, and most were also unaware of potential reequilibration associated with FI. This, in turn, led many to distrust FI and the information that they provided. Thus, Kennedy (1950), in discussing the observation that fluid inclusions often indicated a different P-T history than other geothermobarometers, wrote that "*It is our fundamental assumptions in the use of vacuoles [fluid inclusions] in geologic thermometry that need revision"*. Similarly, Skinner (1953) subjected Brazilian quartz to high temperatures and documented that water was lost from the inclusions and concluded (p. 550) "*When evidence from liquid inclusions is at variance with other lines of geologic evidence, as is often the case, it would seem pertinent to consider the possibility that the vacuoles indicate later and different conditions from those operative at the time of formation"*. At about this same time F. Gordon Smith (1950) published a paper in which he invoked sparse FI data to estimate the direction and velocity of fluid flow in the McIntyre Mine, Canada. The conclusions were not generally accepted and led many to be dubious of the validity of FI studies in general.

Led by dedicated and careful workers, including Ed Roedder in the US and George Deicha and Bernard Poty in France, FI microthermometry gradually began to gain acceptance as a valid method of geothermobarometry starting in the 1960s. A new generation of researchers began to address many of the fundamental problems associated with fluid inclusion research, including experimental studies to determine PVTX properties of more complex fluids and studies to better understand the process of FI reequilibration. Today, FI offer the most reliable and precise method of constraining the PTX history of fluid mediated geologic processes, assuming that proper protocols are followed during data collection and interpretation – the most important among these the collection of FI data within the Fluid Inclusion Assemblage (FIA) framework.

Melt inclusion research has followed a similar evolution to that of fluid inclusions. Even though Sorby (1858) described different types of MI in detail 150 years ago, their study did not begin in earnest until about the 1970s, led by workers including Fred Anderson (Anderson, 1973; 1974) and Ed Roedder (1972) in the US, Vladimir Sobolev (1975) in the Soviet Union, and Roberto Clocchiatti (1975) in France. Much of the early interest in melt inclusions was driven by studies of MI in lunar samples returned by the US Apollo missions. The recognition that MI provide the best samples of pre-eruptive melt in a volcanic system led to a rapid increase in the number of studies reporting data from MI in the late 1980s and

continuing into the 1990s and today. As with the early days of FI research, many workers collected and reported data from MI without consideration of possible post-entrapment processes that might modify the MI composition. As happened with FI in the 1950s, presentation of data from MI that were at odds with other, more reliable and robust data on volcanic systems led some to question the validity of MI data. During the past few decades our understanding of these processes has improved and we are now able to anticipate and avoid many potential problems associated with MI analyses, or to correct for post-entrapment modifications. Today, MI are gaining a reputation as providing the most reliable information on the pre-eruptive volatile contents of magmas.

REFERENCES

- Anderson, A.T., Jr. (1973) The before-eruption water content of some high-alumina magmas. Bull. Volcanology 37, 530–552.
- Anderson, A.T., Jr. (1974) Evidence for a picritic, volatile-rich magma beneath Mt. Shasta, California. Journal of Petrology 15, 243–267.
- Clocchiatti, R. (1975) Les inclusions vitreusesdes cristaux de quartz. Étude optique, thermooptique et chimique. Applications geologiques. [Glass (melt) inclusions in quartz. Optical, microthermometric and chemical study. Geologic applications] Memoires de la Société Géologique de France, LIV, 122, 1–96 [in French].
- Kennedy, G.C. (1950) "Pneumatolysis" and the liquid inclusion method of geologic thermometry. Economic Geology, 45, 533-547.
- Roedder, E. (1972) Interpretation of silicate melt inclusions in lunar, terrestrial and meteoric minerals. Proceedings of COFFI, 1969, 21-22.
- Skinner, B.J. (1953) Some considerations regarding liquid inclusions as geologic thermometers. Economic Geology, 48, 541-550.
- Smith, F.G. (1950) A method for determining the direction and flow of hydrothermal solutions. Economic Geology, 45, 62-69.
- Sobolev, V.S. and Kostyuk, V.P. (1975) Magmatic crystallization based on a study of melt inclusions.

Fluid Inclusion Research 9, 182–253 (translated from original publication in Russian).

Sorby, H.C. (1858) On the microscopical structure of crystals, indicating the origin of minerals and rocks. Quarterly Journal of the Geological Society of London, 14, 453- 60.

## Physicochemical conditions of ore formation at the Samolazovskoye gold deposit, Central Aldan

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Thermobarogeochemical techniques were used to study physicochemical conditions of ore formation at the Samolazovskoye gold deposit located in the Central Aldan ore (Au-U) region in the Southern Yakutia. It is confined to the Yuhtinskiy alkaline massif of the Late Mesozoic age (K<sub>1</sub>). The massif is composed of alkali and calc-alkaline syenites, nordmarkites, syenite- and granosyenite-porphyries, kersantite dykes and stocks of alkaline basic rocks. The latest magmatic formations are explosive breccias with syenite-porphyry cement (<127 Ma, U-Pb method). Two different age stages of mineralization are established: 1) the early – poorly auriferous skarn stage with pyrite-chalcopyrite mineralization (130 Ma), and 2) the main productive Au-Mo-polymetallic stage (<127 Ma) manifested after explosive breccias. Four stages of vein mineralization are distinguished: 1) early quartz-fluorite (Q + FI), 2) pyrite-chalcopyrite (Py-Chp), 3) pyrite, molybdenite (Py-Mo), and 4) gold-polymetallic (Au -Pb-Zn) (pyrite, gray ores, galena, sphalerite, chalcopyrite, bornite, cattierite, sulvanite, vanadinite, roscoelite, Hg-gold, silver, etc.). Uranium mineralization is represented by uraninite, coffinite with quartz, carbonates and fluorite. Geochemical specifics of ores at the Samolazovskoye deposit is characterized by the following series of elements: Au, F, Pb, Mo, As, V, Co, Sb, Hg that corresponds to the mineral composition of ores.

Primary and primary-secondary fluid inclusions in quartz of all stages have been studied. They differ substantially in phase composition: Q-CaF<sub>2</sub> stage (L + V, L + V + CO<sub>2</sub> and L + V + 2-5 min. phases), Py-Chp (L + V, L + V + CO<sub>2</sub> and L + V + 2-3 min. phases +/- Chp), Py-Mo (L + V, L + V + CO<sub>2</sub>), Au-Pb-Zn (L + V). Analysis of mineral phases by Raman spectroscopy showed that thenardite predominates by volume among them. Of minor amounts are the soluble phases: syngenite (K<sub>2</sub>Ca(SO<sub>4</sub>)  $_2$ ·H<sub>2</sub>O), halite, cyanochlorite (K<sub>2</sub>Cu(SO<sub>4</sub>)·6H<sub>2</sub>O), hexahydrite (MgSO<sub>4</sub>·6H<sub>2</sub>O), and native sulfur (S°). The insoluble, most

probably, xenogeneic phases such as mendozite NaAl(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, fluorellestadite \_  $Ca_{10}(SiO_4)_3(SO_4)_3F_2$ , gypsum. siderite pickeringite  $MgAl_2(SO_4)_4 \cdot 22H_2O$ have been also established. The gas phase composition of inclusions contains (in mol %): CO<sub>2</sub> -100 - 0,  $N_2$  – 8.6-0 and  $H_2S$  <0.1. The  $SO_4^{2-}$  and  $HCO_3$  ions predominate in the solutions of all types of inclusions allowing to attribute such solutions to a water-salt system Na<sub>2</sub>SO<sub>4</sub> - NaHCO<sub>3</sub> - H<sub>2</sub>O and interpret the results of cryometric analysis of sulfate-sodium bicarbonate solutions of two-phase (L + V) inclusions. Using the handbook of solubility (1), we constructed a diagram for this system for temperature <40<sup>°</sup> C and Na<sub>2</sub>SO₄ aqueous



Fig. 1. Diagram of the Na<sub>2</sub>SO<sub>4</sub> – NaHCO<sub>3</sub> - H<sub>2</sub>O salt system

#### Pan-American Current Research on Fluid Inclusions (PACROFI-XIII) University of Missouri—Columbia, May 24-26, 2016, Abstract Volume concentration <35 wt.% (Fig. 1).

Based on the data of cryometric analysis (the eutectic temperatures are  $5^{\circ}$  C, the dissolution temperatures of crystallohydrate Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O are +2° - (+13° C), we calculated the concentrations of the main salt components for solutions of inclusions in quartz of quartz-fluorite and Au-polymetallic stages: Na<sub>2</sub>SO<sub>4</sub> – from 3% to 8,3%, NaHCO<sub>3</sub> – from 6% to 5,5%. Their total concentration is in the range from 9 to 13.8 wt.%. The inclusions containing mineral phases dissolving at temperatures 240-380°C have higher contents of salt components. Their concentration may be as much as 50 wt.% and even more. The homogenization

temperatures of inclusions in quartz of the quartz-fluorite stage range from 380 to 270° C, while those of pyritemolybdenite stage from 300 to 260°C and Au-polymetallic stage from 310 to 250°C.

Concentrations of ore elements in fluid inclusions were determined using LA-ICP-MS method (Table 1). The obtained data showed that: 1) the composition and concentration of ore elements in the solutions of inclusions fluid differ significantly; 2) the solutions of high-temperature quartzfluorite stage are characterized by high concentrations of B, V, Co, Ni, Zn, As, Te, Cs, and Ba; 3) solutions of pyritethe molybdenite stage are enriched in Ti, Co, Ni, Nb, and Mo; 3) the solutions of

	Stages					
Elements	1 Q-FI	Py-Mo	2 Q-FI	Zn	Pb-Zn	Pb-Zn
В	36500		300	240	320	200
Na	56000	58000	170000	170000	28000	56000
Mg	4900	20	330	270	180	170
K	19000	11000	23000	13000	7550	5100
Ca			1600	3000	270	9700
Ti		5900	110	160	140	30
V	210	30	130	40	90	70
Mn	4000		990	4500	170	80
Fe	550		1583	1300	180	130
Co	260	80		2		10
Ni	6400	1600	250	70	60	30
Cu	490	30	20	60	16	5
Zn	7200	410	210	40	70	5
As	370			70	260	210
Rb	210	40	2400	2300	1300	670
Sr	670		1824	3900	250	270
Y			50	25	2600	7
Nb		130			30	
Мо	3	300		10	100	25
Ag					60	2
Sb			60	40	30	70
Те	2600		170	242	50	270
Cs	200		230	210	80	60
Ва	750	40	1100	2900	60	30
w		30	150	220	40	30
U			80	20	15	20

Au-polymetallic stage have high concentrations of Ca, As, Sb, Te, Ag, Rb, Ba, and Sr. In general, the geochemical specifics of solutions of each stage correlate with the predominant ore components in corresponding mineral assemblages.

Table 1. Results of LA-ICP-MS Analysis.

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#### REFERENCES

1) V.A. Koz (1973) The Handbook of experimental data on the solubility of multicomponent water-salt systems. Chemistry. Volume 2. Page 568.

#### 3D multiphoton, multimodal microscopy of fluid inclusions

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Following our initial results [1], we have continued to explore the potential of multiphoton methods to image fluid inclusions (FI) in 3 dimensions. 3D images of inclusions yield new information on the size, shape, and distribution of inclusions in a host crystal providing new opportunities to resolve questions of the timing of trapping and identification of inclusion assemblages

Multiphoton microscopy is a type of laser scanning confocal microscopy (LSCM) but it has distinct advantages over conventional fluorescence LSCM. Unlike LSCM, multiphoton responses are generated only in the focal volume of the objective, yielding high contrast images without confocal pinholes. . Multiphoton microscopes used in biomedical research can routinely image samples with two or more simultaneous modes (multimodal imaging), most commonly with second harmonic generation (SHG) and two-photon excitation fluorescence (TPEF).SHG can image non-fluorescent aqueous inclusions at the same time that TPEF creates images of fluorescent hydrocarbon inclusions, unlike conventional LSCM [2] that can only image hydrocarbon inclusions. Systems capable of imaging with coherent Raman scattering, either coherent anti-Stokes Raman scattering (CARS) or stimulated Raman scattering (SRS), can create images in all three modes simultaneously. CARS and SRS can create chemically specific images based on the C-H stretch of hydrocarbons or the O-H stretch of water. Although imaging is possible with conventional scanning confocal Raman systems, multiphoton methods are orders of magnitude faster. The disadvantage of multiphoton microscopy is that it requires ultrafast (picosecond, or femtosecond) pulsed lasers making microscopes more complex and expensive than conventional LSCM.

SHG response occurs in non-centrosymmetric materials, such as quartz, or where symmetry is broken at the interface between gas and liquid, or between fluid and solid. Figure 1a shows a 3D gray-scale image of 2-phase aqueous inclusions (gas-rich and water-rich) in fracture-filling diagenetic quartz created with SHG. The maximum intensity Z projection in Fig. 1b shows all the inclusions within the 3D volume. The 3D object counter in ImageJ [3] identifies 37 inclusions ranging in volume from 0.5 to 7232  $\mu$ m<sup>3</sup> with log-normal size distribution. In some quartz samples SHG images of quartz is dominated by Brazil and Dauphiné twins making detailed observations of FI difficult as shown in Figure 2. In this case, the 2-phase aqueous inclusions appear as holes in the SHG response from the Brazil twins. However, Dauphine twins in quartz can be induced by deformation. The unique ability of SHG to simultaneously image twins and inclusions in quartz in 3D may provide new information on trapping and re-equilibration of inclusions that is not possible with 2D imaging methods like EBSD [4].

TPEF images of hydrocarbon inclusions are the same as those from conventional LSCM. However, the simultaneous generation of SHG and TPEF allows imaging of fluorescent oil and aqueous inclusions in the same FOV as shown in Figure 3. CARS and other coherent Raman scattering processes can produce chemically specific images, with contrast based on Raman active molecular vibrations. We have shown that CARS can image methane rich gas, oil, and aqueous inclusions based on the C-H stretching vibration of hydrocarbons and the O-H stretch of water in the 2700 to 3600 cm<sup>-1</sup> region [1]. A new microscope using stimulated Raman scattering (SRS) allows imaging over a wide spectral range, 400 to 4000 cm<sup>-1</sup>, so that we can image host minerals (silicates, carbonates, sulfates, phosphates) as well as inclusion fluids[5].

#### REFERENCES

[1]Burruss, R. C, Slepkov, A.D., Pegoraro, A. F., and Stolow, A., 2012, Unraveling the complexity of deep gas accumulations with multimodal CARS microscopy, Geology, v.40, pp. 1063-1066.

[2]Pironon, J., Canals, M., Dubessy, J., Walgenwitz, F., and Laplace-Builhe, C., 1998, Volumetric reconstruction of individual oil inclusions by confocal scanning laser microscopy, European Journal of Mineralogy, v. 10, pp. 1143-1150.

[3]Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2014.

[4]Fall, A., Ukar, E., Marrett, R., and Laubach, S. E., 2015, Dauphiné twin planes in quartz trap fluid inclusions and indicate paleostress in deeply buried sandstones, ECROFI-XXIII, Extended Abstracts Volume, pp. 61-62.

[5]Houle, M-A., Burruss, R. C., Ridsdale, A., Moffat, D. J., Légaré, F., and Stolow, A., 2016 in review, Rapid 3D chemical-specific imaging of minerals using stimulated Raman scattering (SRS) microscopy, Journal of Raman Spectroscopy

[6]Pologruto, T. A., Sabatini, B. L., and Svoboda, K. 2003, ScanImage: flexible software for operating laser scanning microscopes, Biomedical Engineering OnLine, 2:13.

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**Figure 1:** 3D image volume, 170 x 170 x 110  $\mu$ m<sup>3</sup>. SHG, 2-phase gas-water and gas-rich FI in quartz. a) 3D volume, inclusions in gray, transparent background. b) Z projection of all image slices. Olympus FemtoCARS FV1000, 25x, 1.05 N.A. water immersion objective. Image processing with ImageJ [3].



a.

**Figure 2:** SHG image of epithermal quartz showing multiple Brazil twins with holes where 2-phase aqueous inclusions occur. 170 x 170 x 150  $\mu$ m<sup>3</sup> volume, Olympus FemtoCARS FV1000 microscope 25x, 1.05 N.A. water immersion objective. Image processing with ImageJ [3].



**Figure 3:** 3D distribution of oil inclusions (TPEF, green) and aqueous inclusions (SHG, red) in fracture filling quartz. 250 x 250 x 74  $\mu$ m<sup>3</sup> volume. USGS built microscope, 20x 0.7 N.A. objective, ScanImage acquisition [6], image processing with ImageJ [3].
### An investigation into the genesis of the Zaccar iron deposit with special reference to its fluid inclusions (MILIANA, AIN DEFLA, ALGERIA).

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The Zaccar metasomatic-type iron deposit in northwestern Algeria is hosted in Jurassic carbonate sequences proximal to Neogene volcanic rocks. The deposit consists of iron carbonates and oxides. Country Jurassic limestone is partly replaced by the original epigenetic metasomatic ore of ankerite and siderite, associated with minor pyrite, chalcopyrite, galena, and barite. Abundant hematite was formed by supergene enrichment of iron carbonates controlled by ground water level at low to medium temperature. Betier et al. (1952) suggests that temperature of formation of iron carbonate of Zaccar range from 90°C to 100°C, which is similar to other iron carbonate formations in Eastern Algeria (Ouenza and Boukhadra deposits). The emplacement of Miocene volcanic formation is followed by another type of iron mineralization i.e. namely specularite which crosscuts former mineralization of iron and polymetallic ore. The microthermometry study of primary fluid inclusion trapped in quartz associate to specularite shows the existence of cavities with dominant of aqueous phase, a bubble of gas and cube of halite; visually estimated vapor to liquid ratios in all samples range from 5 to 10 Vol. % without large variation (fig.1).



Fig.1. Fluid inclusions trapped in quartz.

Most of the fluid inclusions homogenize into liquid phase at a temperature ranging from 270° to 290°C before dissolution of halite. The dissolution temperature of halite ranges from 300° to 320°C. Thus, the "300° to 320°C + ca. 10°C" was applied to calculate salinity from the dissolution temperatures of halite crystals according to Sterner and Bodnar (1988). In this case, salinities of mineralizing fluids range from 38 to 40 wt% NaCl eq.

The plotting of measurement into the "Magmatic-Meteoric Mixing" fields (Beane1983) (Fig.2) indicates that specularite was formed by hydrothermal activity related to Neogene volcanism, evolved from the mixing of magmatic and meteoric waters.





• Betier G, Glangeaud L, Jouhand M, Duplan L, Juston F (1952) Etude sur les gisements de fer de l'Algérie. Introduction à l'étude des gisements de fer. In Blondel Symposium sur les gisements de fer du monde. XIXe Congr. Geol. int. Alger 35-46.

• Beane RE (1983) The magmatic-meteoric transition. Geothermal Resource Council, Special Report no. 13: 245-253.

• Sterner SM and Bodnar RJ (1988). Synthetic fluid inclusions, VII. Re-equilibration of fluid inclusions in quartz during laboratory-simulated metamorphic burial and uplift. J. metamorphic. Geol, 7: 243-260.

#### Iron and oxygen isotope signatures of the Pea Ridge and Pilot Knob magnetite-apatite deposits, southeast Missouri, USA.

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The Pea Ridge and Pilot Knob magnetite-apatite (IOA) deposits of southeast Missouri, USA, share many similarities with Kiruna-type (IOA) deposits, including, inter alia, similar bulk chemical compositions and a spatial and temporal relationship to coeval host volcanic terrane. The high-grade massive magnetite ore zones in the Missouri deposits contain magnetite that has cores that are texturally similar to igneous phenocrysts; the cores contain polymineralic inclusions and are surrounded by inclusion-free magnetite rims. Primary fluid inclusions in guartz indicate high salinity (54 to 60 wt. % NaCl eg.) ore fluids trapped at temperatures of 480 to >530 °C, and cross-cutting relationships between the ore bodies and igneous host rocks have been interpreted to indicate a magmatic origin for the deposits. However, igneous and hydrothermal features have led to debate as to whether magnetite crystallized from a melt, precipitated from a magmatic-hydrothermal fluid, or precipitated from a fluid of crustal origin. We report new O and Fe stable isotope ratios for magnetite samples from the high-grade massive magnetite of the Pea Ridge and Pilot Knob deposits and compare these stable isotope data with other iron oxide - apatite deposits. The δ18O values of magnetite from Pea Ridge (n=12) and Pilot Knob (n=3) range from 1.0 to 7.0‰ and 3.3 to 6.7‰, respectively. The δ56Fe values of magnetite from Pea Ridge (n=10) and Pilot Knob (n=6) samples range from 0.03 to 0.35‰ and 0.06 to 0.27‰ respectively. The  $\delta$ 18O and the  $\delta$ 56Fe values are consistent with magnetite that crystallized from a silicate melt and magnetite that grew in equilibrium with a magmatichydrothermal aqueous fluid (typical igneous  $\delta$ 56Fe ranges 0.06 to 0.49‰). We propose that the  $\delta$ 18O and δ56Fe data for the Pea Ridge and Pilot Knob magnetite – apatite ore deposits fit the floatation model recently presented by Knipping et al. (2015), which invokes floatation of a magmatic magnetite-fluid suspension and offers a plausible explanation that combines the igneous (i.e., magnetite contains up to ~15.93 wt.% TiO2) and hydrothermal features of the deposits. In this model, igneous magnetite would have an O-isotope signature consistent with the upper range of δ18O values (i.e., 4.5‰ to 7‰) measured in the current study, and magnetite that grew from a magmatic-hydrothermal aqueous fluid at sub-solidus temperatures and/or lower evolved  $\delta$ 180 would have O-isotope signatures consistent with the lower range of 518O values (i.e., 1‰ to 4‰) reported here.

#### REFERENCES

- Knipping, J.L., Bilenker, L.D., Simon, A.C., Reich, M., Barra, F., Deditius, A.P., Lundstrom, C., Bindeman, I., and Munizaga, R., (2015) Giant Kiruna-type deposits form by efficient flotation of magmatic magnetite suspensions. Geology. 43. 491-594.
- Nold, J.L, Davidson, P., and Dudley, M.A., (2013) The Pilot Knob magnetite deposit in the Proterozoic St. Francois Mountains terrane, southeast Missouri, USA: A magmatic and hydrothermal replacement iron deposit. Ore Geology Reviews. 53. 446-469.
- Nold, J.L., Dudley, M.A., and Davidson, P., (2014) The Southeast Missouri (USA) Proterozoic iron metallogenic province Types of deposits and genetic relationships to magnetite-apatite and iron oxide-copper-gold deposits. Ore Geology Reviews. 57. 154-171.
- Weis, F., (2013) Oxygen and iron isotope systematics of the Grängesberg mining district (GMD), Central Sweden. Diss. Uppsala Universitet.

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Figure 1: Magnetite  $\delta^{18}$ O values from Pilot Knob and Pea Ridge ore bodies compared to other volcanically hosted iron oxide – apatite ore deposits.



Figure 2: Magnetite δ56Fe values from Pilot Knob and Pea Ridge ore bodies compared to magnetite from other IOA ore deposits, igneous magnetite, magmatic-hydrothermal magnetite, and low-temperature hydrothermal magnetite.

## Are Trace and Minor MVT Occurrences Related to the Ore Deposits of the Mississippi Valley, U.S.A.?

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For hundreds of years MVT deposits like those of the Mississippi Valley U.S.A. have been among the most important sources of metals for American industry (Fig. 1). This class of ore deposits includes the Viburnum Trend ore body of Missouri, measuring ca. 50 km north to south, making it the World's single largest lead ore body. In western Missouri the even more widespread Tri-State district, active ca. 1840-1967 which was particularly valued during WWII, and is now defunct has become an environmental catastrophe (In fact it is U.S. Environmental Protection Agency superfund site today). In both places MVT ores were emplaced mainly during the Late Paleozoic judging from available age determinations and modelling studies that attribute the deposits to migrating basinal brines set in motion by gravity-driven flow that resulted from Alleghenian tectonism. It is not surprising that widespread sporadic trace and minor occurrences of sphalerite, the subject of this effort, would occur in the Paleozoic country rocks between the ore deposits. As is the case for the ores, the trace occurrences are commonly associated with epigenetic calcite, dolomite and crystalline kaolinite or dickite. Most of our trace occurrences are found in Pennsylvanian beds. Our challenge has been to determine whether or not these traces of MVT ores are directly related to the main ore districts or not.

The greater Mississippi Valley, the type location for MVT deposits, is characterized by substantial deposits of lead, zinc, barite, and, in some cases, copper or even cobalt. Trace and minor occurrences of sphalerite occur sporadically in the flat-lying Paleozoic country rocks, surrounding the main ore deposits such as Missouri's Old Lead Belt, the newer world-class Viburnum Trend, the now defunct Tri-State district. Judging from the few available age determinations and current determinations from modeling studies formed mainly during the Late Paleozoic. The ZnS occurrences are commonly associated with epigenetic calcite, dolomite, and either dickite or kaolinite depending upon the location. All of these are found in a variety of settings including joint fillings, minor faults, cavities in fossils and the ground masses of both carbonate land silicicastic Paleozoic strata. Primary fluid inclusions in the ZnS from the trace occurrences generally resemble those in the MVT ores. However recent work has disclosed important differences from the ores, for example, slightly lower mean homogenization temperatures and lower salinities in the trace occurrences which may permit exploration teams to distinguish proximity to viable ore deposits.

It is not clear whether the bulk of the trace ZnS-hosted inclusions are derived from the main MVT mineralization events(s) or not but, if they are, it seems that they represent spent fluids remaining after ore deposition. However two locations differ from the other trace and minor occurrences - The Jumbo mine and unmined Prescott deposit which have been are relatively minor occurrences economically but both have geochemical characteristics that are indistinguishable from the main MVT ore deposits. One of these deposits, the Jumbo, has been mined and takes the general form of a vertical pipe that is more than 100 m tall. The other has not been well exposed, but probably is also a pipe. These may be representative of key pathways for transmission of ore depositing fluids. It is possible, but by no means

proven, that these two unusual deposits were deposited along the main pathways of the MVT fluid migration. Their presence suggests that the main MVT deposits are largely a product of focused flow rather than diffuse pervasive migration.



Fig. 1. Trace occurrences of ZnS (\*) with mining districts shown in darker gray. The deposits of the Central MO and Tri-State districts are shown as clusters of ellipses.

## A new technology for exploration for precious metal deposits: application of a portable fluid inclusion crushing stage.

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The search for mineral deposits is high risk, time consuming and expensive. Any technique or technology than can help the explorationist to inexpensively and quickly discriminate between areas with high potential for economic mineralization and those with lower potential provides a competitive advantage to those applying the technology. This study describes a tool that may be applied in exploration for Au-rich veins that have been the source of many of the great placer districts worldwide. These kinds of orogenic gold deposits are commonly located in metamorphic terrains, are associated with deformed mid-crustal blocks and hosted by greenschist to upper amphibolite facies rocks (Goldfarb et al., 1998). They display evidence of fluids at supralithostatic pressures that form fluid inclusions that can be easily identified by thin-section petrography or any equivalent microscopy technique; however, there are more time-efficient methods for field based exploration such as the fluid-inclusion crushing-stage which is able to qualitatively verify the presence of high-pressure CO<sub>2</sub> and other volatiles in fluid inclusions (Deicha, 1950; Roedder, 1970; Diamond and Marshall, 1990). Recognizing the need of have a fast fieldbased analysis, in this study we are developing and building a portable fluid-inclusion crushing stage using a 3D printer (Fig. 1). The crushing stage will be used to study the fluid inclusions in different host minerals (e.g. quartz, feldspar) in the exploration for Au-rich vein deposits in the metamorphic basement in Chile, especially in areas of little or non-existent outcrop.



## Fig. 1. Portable Fluid-inclusion crushing stage, developed using 3D CAD modeling programs (A) and built with a 3D printer (B).

#### REFERENCES

- Diamond, L.W. and Marshall, D.D., 1990. Evaluation of the fluid-inclusion crushing-stage as an aid in exploration for mesothermal gold-quartz deposits. Journal of Geochemical Exploration, 38(3): 285-297.
- Deicha, G. (1950). Essais par écrasement de fragments minéraux pour la mise en évidence d'inclusions de gaz sous pression. Bull. Soc. fr. de Minér. 73. 439-445.
- Goldfarb, R. J., Phillips, G. N., & Nokleberg, W. J. (1998). Tectonic setting of synorogenic gold deposits of the Pacific Rim. Ore Geology Reviews. 13(1). 185-218.
- Roedder, E. (1970). Application of an improved crushing microscope stage to studies of the gases in fluid inclusions. Schweiz. Mineral. Petrogr. Mitt. 50(1). 41-58.

# Representative CO<sub>2</sub>, H<sub>2</sub>O, and S Concentrations of Volcanic Silicate Melt Inclusions

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Volatiles exsolving from silicate melts play an important role for a variety of geological processes such as the ascent of magmas and the magnitude of eruptions. But quantification of amount of volatiles in undegassed or partially degassed melts is a difficult task owing the inaccessibility of melts for direct *in situ* measurements at depth. Fortunately, crystals growing in magma reservoirs commonly trap samples of the surrounding parent melt. Igneous crystals function as vessels that ideally prevent the degassing of melt inclusions (MI) after trapping. If a MI is not modified after trapping, that MI provides the only direct measurement of volatiles of undegassed melt.

One of the common features of a MI dataset from a single rock sample is that major, trace, and volatile element concentrations are variable. In particular, MI volatile concentrations show the largest variations among all the elements. The volatile concentration variations can reflect different depths of MI entrapment since at vapour saturation pressure exerts a strong control on volatile solubility in silicate melts. Even if the magma is not volatile-saturated, a wide range in volatile concentrations can result from variations in temperature, oxidation state, and melt composition in the magma reservoir. The volatile variability in MI has been used by inclusionists to investigate chemical and physical magmatic processes. For instance, several studies show the magma dynamic noticing that deeper MI correlate with the degree of crystallization of volcanic system (Métrich and Wallace, 2008 and references therein). Other studies attempt to estimate the magmatic volatile input for the global volatile cycles (e.g., Wallace, 2005).

The optimistic view and use of MI to better understand the dynamics of magmas, depths of magma reservoirs, and global volatile input contrast with several other studies reporting that the variability in volatile contents of MI can be produced by modifications of MI after trapping. In fact, MI can be modified after trapping. The intensity of these modifications depend on (1) the amount of time a MI is kept at high T after trapping but before eruption and the difference of the trapping T and (2) the T at the eruption. Also, depending on cooling rate, MI could either preserve a homogenous glass ± bubble(s) (tephra samples) or heterogeneous multi minerals plus bubble(s) (lava samples). Thus, MI can be found in nature as glassy bubble-free, glassy bubble-baring or totally-partially crystallized. For this reason, either an inclusionist studies only glass bubble-free or bubble-bearing MI or may reheat MI in the lab.

The formation of a bubble after trapping of MI is promoted by (1) post entrapment crystallization (PEC) at the host/MI interface (2) by differential thermal contraction between melt and host, and (3) extensive diffusive-loss of volatiles from the MI. If MI contains a vapor bubble that formed after trapping any measurement of volatile in the glass of that MI most likely does not represent the volatile content of the melt surrounding the crystal during growth in the magma chamber. This is particularly important for originally volatile-saturated melts. In fact, it has been demonstrated that loss of volatiles into the vapor bubble after MI trapping can determine pseudo-degassing path if only the volatile content of the glass is considered (Steele-MacInnis et al., 2011). Recently, several researchers reported methods to correct the original CO<sub>2</sub> concentration of trapped melt and pointed out that in many bubble-bearing MI most of the CO<sub>2</sub> is stored in vapor bubbles, not in the glass (e.g., Esposito et al., 2011). While it is now widely accepted that it is important to analyze the CO<sub>2</sub> content of the vapor bubbles, only recently liquid H<sub>2</sub>O was detected in vapor bubble of reheated MI from Vesuvius (Esposito et al., accepted). This discovery highlights the importance of analyzing H<sub>2</sub>O and S in addition to CO<sub>2</sub> in bubbles of MI to understand the type of magmatic vapor exsolving directly from natural undegassed silicate melts.

In this study, we review methods to assess the reliability of volatile contents of MI hosted in igneous crystals. In particular, we discuss the concept of melt inclusion assemblage (MIA, Bodnar and Student, 2006) that represents a group of MI which were trapped all at the same time, and thus, at the same physical and chemical conditions. For instance, a MIA consists of MI trapped along a growth zone of a phenocryst. Here, we provide new case studies of MIA included in volcanic phenocrysts and other examples from the literature highlighting the importance of petrography to study MI. In addition, we

highlight the importance of bubbles of bubble-bearing MI and methods to assess the original CO<sub>2</sub>, H<sub>2</sub>O, and S concentration of MI.

#### REFERENCES

Bodnar, R.J., and Student, J.J. (2006) Melt inclusions in plutonic rocks: Petrography and microthermometry. In J.D. Webster, Ed. Melt Inclusions in Plutonic Rocks, 36, p. 1-25. Mineralogical Association of Canada, Montreal, Quebec, Canada.

Esposito, R., Bodnar, R.J., Danyushevsky, L., De Vivo, B., Fedele, L., Hunter, J., Lima, A., and Shimizu, N. (2011) Volatile Evolution of Magma Associated with the Solchiaro Eruption in the Phlegrean Volcanic District (Italy). Journal of Petrology, 52, 2431-2460.

Esposito, R., La Madrid, H., Redi, D., Steele-MacInnis, M.J., Bodnar, R.J., Manning, C.E., De Vivo, B., Cannatelli, C., and Lima, A. (accepted) Detection of liquid H<sub>2</sub>O in Vapor bubbles of reheated melt inclusions: implications for magamatic fluid composition and volatile budgets of magmas? American Mineralogist.

Métrich, N., and Wallace, P.J. (2008) Volatile abundances in basaltic magmas and their degassing paths tracked by melt inclusions. Reviews in Mineralogy and Geochemistry, 69, 363-402.

Steele-MacInnis, M.J., Esposito, R., and Bodnar, R.J. (2011) Thermodynamic model for the effect of post-entrapment crystallization on the H<sub>2</sub>O-CO<sub>2</sub> systematics of volatile saturated silicate melt inclusions. Journal of Petrology, 52, 2461-2482.

Wallace, P.J. (2005) Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. Journal of Volcanology and Geothermal Research, 140(1), 217-240.

# Insights into MVT Ore Genesis from Fluid Inclusions in Trace Occurrences of MVT Mineralization

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The presence of Mississippi Valley-type Pb-Zn mineralization throughout the Paleozoic carbonates of the U.S. mid-continent records the pervasive movement of hot, saline fluids. These fluids typically only precipitated trace amounts of sulfide mineralization on the order of a few grams, but in rare instances formed deposits containing millions of tons of Pb and Zn. Mid-continent MVT ore deposits have been the focus of much research because they represent anomalously high metal concentrations that are much greater than average metal concentrations in the Earth's crust. As a result, much has been learned about the composition of the ore fluids and paths of their flow, sources of metals and sulfur, timing of mineralization, and structural controls on mineralization. Comparatively little research has so far been directed toward trace occurrences of MVT mineralization in the U.S. mid-continent or elsewhere in the world, making it difficult to recognize what aspects of the MVT mineralizing process were anomalous in the ore deposits, allowing them to reach their great size.

MVT ore deposits are characterized by homogenization temperatures mainly between 85 and 135° C and salinities mainly between 22 and 26 eq. wt. % NaCl. The ore-forming fluids have dolomitizing Ca/Mg ratios, high methane concentrations, and high K concentrations (Stoffel et al., 2008; Wenz et al., 2012; Pelch et al., 2015). Furthermore, many fluid inclusions in MVT ore deposits contain large amounts of Pb, which, if present as aqueous solute, would equate to up to 1000's of ppm. Analyses of MVT trace and minor occurrences from the U.S. mid-continent show that they precipitated from fluids that strongly resemble MVT ore fluids, but are, on average, slightly cooler and have a wider range of salinities (Fig. 1). Fluids that formed trace MVT occurrences are on the whole even more dolomitizing than mid-continent MVT ore fluids, but are similarly enriched in K relative to typical sedimentary brines. However, methane has only rarely been detected in fluid inclusions in trace MVT occurrences, and then only at lower concentrations than in MVT ore deposits. Pb has been detected less frequently in the fluid inclusions of trace MVT occurrences than MVT ore deposits, but when observed, apparent aqueous concentrations also range up to 1000's of ppm. The concentrations of Pb in the matrix of sphalerite in trace MVT occurrences are similar to those in MVT ore deposits. This suggests that trace MVT occurrences and MVT ore deposits in the U.S. mid-continent were precipitated from fluids containing similar concentrations of Pb. If Pb is a proxy for overall metal content, then metal content would not appear to have been a controlling factor in MVT deposit growth. Given the similarity in major element and Pb concentration between the fluids that formed trace MVT occurrences and MVT ore deposits, a more likely limiting factor in MVT deposit growth is the local abundance of reduced sulfur.

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Figure 1: Homogenization temperatures and salinities of fluid inclusions in trace MVT occurrences and major MVT ore districts in the U.S. mid-continent. Trace = trace occurrences, TRI = Tri-State, NARK = Northern Arkansas, CEMO = Central Missouri, SEMO = Southeast Missouri, IL-KY = Illinois-Kentucky.

#### REFERENCES

Pelch, M. A., Appold, M. S., Emsbo, P., & Bodnar, R. J. (2015) Constraints from fluid inclusion compositions on the origin of Mississippi Valley-type mineralization in the Illinois-Kentucky district. Economic Geology. 110(3). 787-808.

Stoffell, B., Appold, M. S., Wilkinson, J. J., McClean, N. A., & Jeffries, T. E. (2008) Geochemistry and evolution of Mississippi Valley-type mineralizing brines from the Tri-State and Northern Arkansas districts determined by LA-ICP-MS microanalysis of fluid inclusions. Economic Geology. 103(7). 1411-1435.

Wenz, Z. J., Appold, M. S., Shelton, K. L., & Tesfaye, S. (2012) Geochemistry of Mississippi Valley–type mineralizing fluids of the Ozark Plateau: A regional synthesis. American Journal of Science. 312(1). 22-80.

## Li, B, F, and CI controls on transition from magmatic to hydrothermal crystallization in low pressure pegmatite dikes

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In San Diego County, California, Li–Cs–Ta type pegmatite dikes occur in the Mesozoic Peninsular Ranges Batholith. Emplacement of the dikes occurred at low pressures (2–3 kbar) that allowed the formation of large miarolitic cavities (pockets). The pockets occasionally contain gem-quality, Li-bearing minerals, including elbaite tourmaline and spodumene. Two pegmatite suites were studied: the gem-bearing Himalaya and the more barren La Posta. Thermometric properties and compositions of fluid inclusions in quartz are used to deduce the roles that fluid-soluble elements, Li, B, Cl, and F, have in controlling the transition from magmatic to hydrothermal mineral paragenesis in the pegmatites to ultimately understand why some pegmatites in the San Diego County pegmatite district contain abundant, gem-quality, Li-bearing minerals in pockets, whereas others do not.

The inclusions measured in this study support highly undercooled crystallization of pegmatites. The highest measured, pressure-corrected homogenization temperatures ( $T_h$ ) of approximately 400 to 515 °C, were obtained for primary inclusions in the intermediate zone of a La Posta dike.  $T_h$ 's of primary inclusions in core of the pegmatite range from ~270 to 425 °C. Primary inclusions in the intermediate zone in center of the Himalaya pegmatite homogenized between 350 and 420 °C, whereas primary inclusions in a massive quartz core homogenized between 150 and 300 °C. The upper part of this temperature range is interpreted to represent the conditions that existed during the initial crystallization of minerals that line pegmatite pockets.

Laser-ablation ICP-MS was used to measure cation chemistry of fluid inclusions. Na<sup>+</sup>, B<sup>3+</sup>, and Li<sup>+</sup> are the most important cations in fluid inclusions in both pegmatites. Li concentrations are much higher in inclusions in the Himalaya pegmatite, up to 51 at% of all cations. In the La Posta pegmatite, only few primary inclusions contain Li. B content is high in both pegmatites, up to 65 at% of cations, and is likely present as  $H_3BO_3$ . In primary inclusions within the massive quartz in the core zone of the Himalaya pegmatite, Li, B, and Na occur in subequal concentrations. Cl<sup>-</sup>, F<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are the dominant anions in the inclusions. Together with  $H_3BO_3$ , these anions suggest that hydrothermal fluids that collected in pockets were acidic and promoted the growth of tourmaline and other minerals that are stable in acidic solutions in pocket walls of the Himalaya pegmatite.

In both pegmatites, Na and B dominate secondary inclusions. These inclusions reveal fluids stripped of Li and K by crystallization of lepidolite that occurs within fractures of primary minerals throughout the pegmatites, and sometimes as an alteration product in pockets. The lowering of alkali/H<sup>+</sup> ratios in the fluids stabilized clays, including kaolinite, that line the walls of pockets. Published data for Al solubility in hydrothermal fluids show that fluids that collected in centers of dikes could have carried sufficient Al to precipitate the amounts of clays seen in the pockets. Coeval crystallization of terminated quartz crystals with clays is consistent with its precipitation from the fluids. This study shows that clay precipitation in the pockets occurred as a distinct part of the pegmatite crystallization sequence, rather than as a secondary, supergene process.

#### Isotopic Identification of Multiple Contributors of Metal Ions in Mississippi Valley-Type Ore Deposits along the Cincinnati Arch:

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Mississippi Valley-Type (MVT) ores are economically-viable deposits of sulfide minerals, often dominated by sphalerite (zinc-sulfide) in carbonate facies, and galena (lead-sulfide) in siliciclastic facies. These deposits precipitate from migrating fluids, which carry base metals often complexed with chlorine ions within a basinal brine. This study identifies the contributing regions of the Burkesville MVT deposit, found in south-central Kentucky within the Middle-Tennessee ore district along the crest of the Cincinnati Arch, which is the anticlinal divide between the Appalachian Basin and the Illinois Basin. Current workers believe the metals were mobilized from the Appalachian Basin during multiple collisional orogenic events, with concurrent sulfide mineralization, dolomitization, and petroleum brine migration. Former industry workers from the area agree with this ore genesis mechanism, but believe the metals traveled with petroleum brines of the Illinois Basin during the Ouachita orogeny and the uplift of the Ozark Plateau. Results from this study of lead isotopes imply that the Burkesville deposit correlates strongly with the southern Appalachian Basin, but also suggests that there was some contribution from the Illinois Basin due to brine mixing or multiple paragenetic events. Isotopic ratios were obtained via analysis with a Nu-Plasma MC-ICP-MS. Ratios for <sup>206</sup>Pb/<sup>204</sup>Pb ranged from 19.63 to 19.81, ratios for <sup>207</sup>Pb/<sup>204</sup>Pb ranged from 15.71 to 15.81, and ratios for <sup>208</sup>Pb/<sup>204</sup>Pb ranged from 39.29 to 39.58. These results provide an explanation to the contradictory works of previous researchers, who sought to constrain the contributing basin of the Middle Tennessee district via trace-element and crystallographic analyses. This research has produced a new model for MVT ore formation near the Cincinnati Arch, in which the majority of the deposit precipitated from brines from the southern Appalachian Basin, but which either mixed with or was later altered by a higher-temperature brine originating from the Illinois Basin which contributed the higher concentrations of Cd, Cu, Ge, and Ga observed in the district today.

#### REFERENCES

- Anderson, W.H. (1991) Mineralization and hydrocarbon emplacement in the Cambrian-Ordovician Mascot Dolomite of the Knox Group in south-central Kentucky. Kentucky Geological Survey Report of Investigations. p. 9, 1-31.
- Baird, R.A., and Dennen, W.H. (1985) A geochemical survey of the top of the Knox Dolomite: implications for brine movement and mineralization in central Kentucky. Economic Geology. v. 80. p. 688-695.
- Goldhaber, M.B., Church, S.E., Doe, B.R., Aleinikoff, J.N., Brannon, J.C., Podosek, F.A., Mosier, E.L., Taylor, C.D., and Gent, C.A. (1995) Lead and sulfur isotope investigation of Paleozoic sedimentary rocks from the southern midcontinent of the United States: implications for paleohydrology and ore genesis of the southeast Missouri lead belts. Economic Geology. v. 90. p. 1875-1910.
- Harper, D.D. (2007) Dolomite Fronts And Associated Zinc-Lead Mineralization USA. Economic Geology. v. 102. p. 1345-1352.
- Heyl, A.V., Delevaux, M.H., Zartman, R.E., and Brock, M.R. (1966) Isotopic study of galenas from the Upper Mississippi Valley, the Illinois-Kentucky, and some Appalachian Valley mineral districts. Economic Geology. v. 61. p. 933-961.
- Kesler, S., Appold, M.S., Cumming, G.L., and Krstic, D. (1994) Lead isotope geochemistry of Mississippi Valley-Type mineralization in the central Appalachians. Economic Geology. v. 89. p. 307-321, 1492-1500.





Figure 1: <sup>208</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb and <sup>207</sup>Pb/<sup>204</sup>Pb vs. <sup>206</sup>Pb/<sup>204</sup>Pb data from the Burkesville, KY mine relative to the Elmwood and Young mines of TN (Moyers, 2015), as well as known values for deposits within the Southern Appalachian District, Central Appalachian District, KY-IL Fluorspar District, Upper MVT District, Central MO District, Tri-State District, Old Pb Belt, and Viburnum Trend (Heyl et al., 1966; Kessler et al., 1994; and Goldhaber et al., 1995).

#### Partitioning of Indium between Biotite and Felsic Melts

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Indium is a rare element present in Earth's crust at a concentration of  $\sim$  50 ppb, and is produced primarily as a by-product of zinc extraction. It is commonly used as indium tin oxide, a component of modern LCDs and smart phone screens due to the combination of its optical transparency and conductivity.

Biotite is an abundant phase in many felsic magmas and may sequester indium during magmatic crystallization. Experiments are being performed to determine the partition coefficient for indium between biotite and rhyolitic melts. Indium is added to all experiments in the form of indium-gold alloy. Experiments have been performed with the starting materials: aqueous chloride solution + natural biotite + rhyolite glass; aqueous chloride solution + glass, with added magnetite + enstatite + sanidine which react to yield biotite ± a natural biotite seed crystal. The starting materials are loaded into gold capsules, which are then placed inside René 41 cold seal pressure vessels that are run at 800°C and 1000 bars for durations of 7 days or more. In the first set of experiments, the partitioning of indium into biotite was found to be limited by indium's diffusion rate into biotite. Indium concentrations in biotite were consistently below the detection limits by EPMA (~25 ppm). In the second set of experiments, biotite up to 200 µm in length nucleated and grew. Indium was incorporated into biotite at concentrations of 2000 ppm  $\pm$  350 ppm ( $\pm$  1 $\sigma$ ) and melt of 500 ppm ± 45 ppm (± 1 $\sigma$ ) with a partition coefficient D<sup>bt/m</sup> ~4 ± 0.8 (± 1 $\sigma$ ). These preliminary results suggest that biotite is capable of sequestering indium in magmatic systems, reducing the indium available to partition into a potential proto-ore fluid. Biotite in granitic rocks is present at about 9 modal percent and can reach levels of ~30 modal percent or more. These modal proportions are equivalent to 10% up to 34% by mass, respectively. Using the mass fraction of biotite in felsic systems and the partition coefficient of indium between biotite and melt, the contribution of biotite to the bulk partition coefficient of indium is calculated to be 0.4 and up to 1.3.

By using a simple model we can estimate the proportion of indium sequestered by biotite before water saturation occurs in a magma. To a first order approximation, the proportion of indium sequestered in biotite during crystallization occurring before before water saturation can be estimated from the ratio of the initial to saturation water concentrations in the melt. This simple model suggests that up to 90% of indium can be sequestered in biotite for initial and final water saturations of melt at 6 wt% and 1 wt%, respectively. These preliminary results and our continued experimentation can provide insight into the behavior of indium in magmatic-hydrothermal systems and the development of exploration models.

#### Mineralizing fluids from the Alhué mining district, Chile.

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During the past half century numerous fluid inclusions studies of hydrothermal precious and base metal deposits were undertaken, and much of our understanding of the physical and chemical context of metal transport and deposition in hydrothermal environments evolved from these studies. The search for mineral deposits is a time consuming, risky and oftentimes very expensive process. Any technique that can help to quickly and inexpensively discriminate between areas with high or low potential for economic mineralization provides a significant competitive advantage during exploration. Here we present a quick and inexpensive model for explorationist at the Alhué mining district to discriminate between areas with high potential for economic mineralization.

The Alhué mining district is located within the Coastal Range of Central Chile, 24 kilometers east of the locality of Villa Alhué (Fig. 1A), and is characterize by more than 76 Au-Ag veins of hydrothermal origin with different thicknesses related to major and minor, normal and strike-slip faults trending N25°W and with significant displacement (Cotton, 1998). The veins that create the Alhué mining district formed during the Upper Cretaceous as a result of magma-driven fluid flow in a convecting hydrothermal system associated with a sub-volcanic arrangement in the context of a magmatic arc. Average metal content in this district reaches 5 ppm gold (Au), 23 ppm silver (Ag) and 0.1% copper (Cu) and the mineralized veins are hosted in volcanic and volcanoclastic rocks (andesites, dacites, tuffs and breccias of andesitic and dacitic composition) and brecciated granodiorites (Camus, 1990). In collaboration with staff from Yamana Gold Inc. more than 250 samples representing all the different mineralization styles were collected from outcrops, drill holes and underground workings. Thin sections of each sample were examined using a petrographic microscope and the mineral textures and fluid inclusion characteristics were recorded. The majority of the samples were assayed for Au, Ag, Zn, Cu, Pb, As, Sb and Mn. A more detailed study concentrating on a single vein will be conducted to unravel the complexities of fluid evolution related to ore deposition in the Alhué mining district.

Hydrothermal alteration is mainly characterized by quartz (most common gangue mineral), chlorite, epidote, actinolite, calcite, sericite, adularia with major contents of magnetite. Quartz shows a wide variety of textures reflecting the various crystallization mechanisms that operate in fluid-filled cracks. Most common quartz's textures are jigsaw, zonal, mosaic, crustiform, but also cockade, feathery and pseudo-acicular are present. Main sulfide-mineralization corresponds to sphalerite, galena, chalcopyrite and pyrite. Petrographic evidence shows primary and secondary Fluid Inclusion Assemblages (FIA's) and were classified as containing (1) only liquid-rich inclusions with consistent liquid-to-vapor ratios, (2) coexisting liquid-rich and vapor-rich inclusions with a broad range in liquid-to-vapor ratios, (3) assemblages consisting of only vapor-rich inclusions (Fig. 1B and C, 2B), (4) Halite-bearing fluid inclusions with solids (Fig. 2A), (5) Halite-bearing and iron-chloride fluid inclusions with solids (Fig. 2C). All the inclusions described are hosted in quartz. Spatial distribution of FIA's show a decreasing tendency of "flashing" processes with depth and a common presence of vapor-rich primary and secondary inclusions.

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Figure 1. Plan view of the Alhué mining district showing the general geology (A) (Modified from Nasi and Thiele, 1982). Photomicrograph showing quartz under plain transmitted light (B) and under crossed-nicols (C) of a primary FIA consisting of only vapor-rich inclusions, indicative of "flashing" or intense boiling of the hydrothermal fluid.



Figure 2. Photomicrograph showing quartz under plain transmitted light. Secondary FIA of Halitebearing with solids (A). Primary FIA consisting of only vapor-rich inclusions, indicative of "flashing" or intense boiling of the hydrothermal fluid (B). Secondary FIA halitebearing and iron-chloride FIA with solids (C).

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- Camus, F. (1990). The geology of hydrothermal gold deposits in Chile. Journal of Geochemical Exploration 36(1-3): 197-232.
- Cotton, W. B. (1998). Geology and Ore Deposits of the Maqui Vein, Alhué Mining District, Coast Range of Central Chile. MS thesis, University of Colorado.130 p

Nasi, C and Thiele, R. (1982). Estratigrafía del Jurásico y Cretácico de la Cordillera de la

Costa al sur del río Maipo, entre Melipilla y Laguna de Aculeo (Chile Central). Revista Geológica de Chile Nº 16 p. 81-99.

## Studies of Fluid Inclusion Temperatures and Salinities for Fluorite Crystals at the Okorusu Fluorspar Mine in North-Central Namibia

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The fluorspar ore deposits at Okorusu, Namibia are associated with an alkaline igneouscarbonatite complex nearly circular in plan view and with a diameter of about 8 km. A total of eight separate fluorspar orebodies have been mined or outlined by drilling. During its mining history from 1988 to 2014, Okorusu was a very significant producer of fluorspar for the chemical industry. At times, Okorusu, together with the Witkop mine in South Africa, have produced as much as 300,000 tons of fluorspar concentrate annually that constituted 20% of the western world's fluorspar consumption. In 2015 the Okorusu mine was placed under care and maintenance.

The Okorusu Alkaline Igneous-Carbonatite Complex comprises low hills of nepheline syenite and foyaite in the northern portion (Van Zijl, 1962). Early alkali-rich fluids streaming up the vent caused pervasive metasomatism resulting in fine-grained aegirine pyroxene sodic fenites that form Okorusu Mountain and other hills along the southern margin of the complex. The fenites were explosively brecciated and intruded by diopside pyroxene carbonatite and closely related coarse-grained pegmatitic carbonatite. Tinguaite and other dike-forming rock traverse the fenites and carbonatites. Late hydrothermal fluorite-depositing fluids were restricted to the southern portion of the complex.

Examinations of fluid inclusions in fluorite (Roedder, 1973; Bühn et al., 2002; Shivdasan, 2003: Shivdasan-Gebhardt and Hagni, 2008) at the Okorusu carbonatite-related fluorspar mine are evaluated to conclude that the main generation of purple and green fluorite deposition was 166-128°C. A younger generation of yellow fluorite, which was deposited on purple fluorite and is restricted to topographically high locations on Okorusu Mountain, was deposited at temperatures of 132-128°C. Secondary inclusions range greatly in temperatures. The salinities of the fluorite-depositing fluids ranged 5 to 1.5% NaCl equivalent.

Although fluorine was leached from carbonatites at depth at Okorusu, the fluorite-depositing ore fluids were introduced late in the history of the Okorusu Alkaline Igneous-Carbonatite Complex. Carbonatites are commonly rich in fluorine, and some carbonatites such as the recent carbonatite lavas at Ol Doinyo Lengai in Tanzania contain as much as 5% fluorite in their groundmass.

An early hydrothermal event that preceded the deposition of fluorite resulted in a series of mineral alterations of carbonatite pyrrhotite (Hagni, in press). That series consists of smythite, marcasite, fineand coarse-grained pyrite, secondary magnetite and hematite, chalcopyrite, and siderite. All of those minerals were subsequently altered, commonly pseudomorphically, to goethite during the introduction of the later fluorite-depositing hydrothermal fluids.

The fluorite ores at Okorusu are dominantly replacement deposits that replace especially carbonatites and marbles to a lesser extent. Carbonatite-replacement fluorspar ores are characterized by: 1) the presence of goethite pseudomorphs after diopside pyroxene, hexagonal pyrrhotite, and magnetite that were magmatic minerals originally present in the replaced carbonatite, 2) small areas of unreplaced carbonatite within the fluorspar ores, 3) lateral gradations into partly replaced and unreplaced carbonatite, and 4) elevated amounts of deleterious phosphorus. Marble-replacement fluorspar ores are characterized by: 1) banded textures, 2) gradation into marble units, 3) negligible amounts of phosphorus, and 4) elevated amounts of silica derived from sand grains in the marbles. Consideration of the tonnages of the fluorspar ore types indicates that 84% of the ores at Okorusu have formed by replacement of carbonatite, 15% by replacement of marble, and 1% by replacement and veining of fenite Hagni, 2011).

#### REFERENCES

- Bühn, B, Rankin, A. H., Schneider, J., and Dulski, P. (2002) The nature of orthomagmatic, carbonatitic fluids precipitating REE, Sr-rich fluorite: Fluid inclusion evidence from the Okorusu fluorite deposit, Namibia, Chemical Geology, vol. 186, pp. 75–98.
- Hagni, R. D. (2011) The replacement of carbonatite and marble by fluorspar ores and its relationship to beneficiation problems at Okorusus, Namibia, 10th International Congress for Applied Mineralogy, Norwegian Geological Survey. Trondheim, Norway, CD Rom, pp. 297-206.
- Hagni, R. D., in press, Early hydrothermal event in the fluorite ores at the Okorusu Alkaline Igneous-Carbonatite Complex, Namibia, Industrial Minerals Forum, Arizona Geological Survey.
- Roedder, E. (1973) Fluid inclusions from the fluorite deposits associated with carbonatite at Amba Dongar, India, and Okorusu, south west Africa. Institute of Mining and Metallurgical Transactions, Section B: pp. 35–39.
- Shivdasan, P. A. (2003) Petrology, geochemistry, and mineralogy of pyroxene and pegmatitic carbonatite and the associated fluorspar deposit at Okorusu alkaline igneous carbonatite complex, Namibia, unpublished Ph.D. dissertation, Univ. of Missouri-Rolla, Rolla, MO, 213 pp.
- Shivdasan-Gebhardt, P., and Hagni, R. D. (2008) Fluorspar deposits at Okorusu, Namibia with emphasis upon electron microprobe analyses of carbonatite minerals and fluorite fluid inclusion temperatures and salinities. In: Ninth International Congress for Applied Mineralogy, ICAM 2008 (pp. 631–641). Brisbane, Australia, the Australasian Institute of Mining and Metallurgy, Publication Series No 8/2008, Carlton Victoria, Australia.
- Van Zijl, P. (1962) The geology, structure and petrology of the alkaline intrusions of Kalkfeld and Okorusu and the invaded Damara rocks, In: Ph.D. dissertation, Universiteit van Stellenbosch, vol. 37, Ser. A, no. 4, pp. 241–324.



## Diagenetic history of deep-water carbonate mounds in the Mesoproterozoic Nanisivik zinc district, Nunavut

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The Mesoproterozoic (1.1 Ga) Borden Basin (Nunavut) contains strata of the Bylot Supergroup, including extremely large, deep-water dolostone mounds (Ikpiariuk Formation) whose distribution is controlled by syndepositional faults. The mounds formed as a result of fluid-venting (groundwater) along subaqueous faults during black shale deposition (Hahn et al., 2015). Large expanses of the mounds contain framework-forming microbial clots. Abundant primary void space in the Ikpiarjuk Formation's microbial mound framework contains several generations of early and late dolomite and other cement (Hahn, 2016). The early (synsedimentary) cements include several different types of calcium carbonate cements (high Mg calcite, herringbone calcite, aragonite) which precipitated in a sedimentary envrionment with elevated Mg/Ca. Numerous Zn-Pb sulphide showings in the basin, including the past-producing worldclass Nanisivik deposit (~17.9 Mt @ 9% Zn, 0.72% Pb; Sherlock et al., 2004), are controlled by stratigraphy and faults, and some of the showings are associated with the same faults as the Ikpiariuk Formation mounds. The late (post-seafloor) cements in the Ikpiarjuk Formation were studied to (a) decipher the mounds' diagenetic history and (b) establish whether metal-bearing fluids associated with the regional showings used the fault systems associated with the Ikpiariuk Formation as fluid conduits. This study, following the methods outlined in Mathieu et al. (2013, 2015), used in situ analytical approaches, including detailed petrography, SEM analysis, fluid inclusion microthermometry and evaporate mound analysis, in situ LA-ICP-MS analysis, and SIMS analysis of O isotopes. The Ikpiarjuk Formation contains at least six void-filling late cements (Fig. 1): inclusion-rich euhedral dolomite (ED), finely crystalline clear dolomite (FCD), hematite-bearing dolomite (HD), coarsely crystalline clear dolomite (CCD), quartz, replacive calcite (RC) and late calcite (LC). The average homogenisation temperatures of fluid inclusion assemblages in FCD, HD, CCD, and quartz are 110°C, 84°C, 117°C, and 154°C, respectively. Combined eutectic and ice melting (Tm(ice)) temperatures of FCD, HD, and CCD inclusions indicate the fluids are both Ca-rich and saline (i.e., 20 to 37 wt. % equiv. NaCl). In contrast, the Tm(ice) for guartz-hosted inclusions indicates a lower-salinity NaCl fluid (i.e., 14 wt.% equiv. NaCl) than preceding phases. Average  $\delta^{18}$ O values of dolostone, ED, FCD, CCD, guartz, RC and LC are +26.3%, +34.3‰, +35.4‰, +24.5‰, +26.6‰, +15.2‰ and +9.5‰, respectively. Dolostone, ED, and FCD all have PAAS-normalised REEY patterns with LREE<HREE, no La or Gd anomalies, and positive Y anomalies. Hematite-bearing dolomite has abundant hematite inclusions and rare inclusions of pyrite, sphalerite, and galena. Coarsely crystalline clear dolomite has a PAAS-normalised REEY pattern with significant LREE depletion, and MREE>HREE. Calcite displays LREE<HREE, with a strong negative Ce anomaly. The results suggest that five different fluids passed through the mounds. Fluid 1, responsible for precipitation of ED and a component of FCD, was Na-rich saline with an oxygen isotopic signature indicating it was probably sourced from seawater or slightly modified seawater ( $\delta^{18}O_{H2O} \sim 0 \pm 6\%$ ). Fluid 2, responsible for precipitating HD and which contributed to the precipitation of FCD, was probably reduced, hydrothermal, saline and Ca(-Mq)-bearing, contained elevated Fe and Mn, was metal-bearing (hematite?, pyrite, sphalerite, galena), and had very heavy  $\delta^{18}O_{H2O}$  values (~13‰). Fluid 3, responsible for precipitating CCD through mixing with fluid 2, was reduced, hydrothermal, saline and K-bearing, and has oxygen isotopic values indicating a modified seawater source (~6‰). Fluid 4, responsible for precipitating guartz, was hydrothermal and contained elevated Na and little Ca+Mg, and an oxygen isotopic signature indicating a modified seawater source (~6‰). Fluid 5, responsible for precipitating RC and LC, was an oxygenated meteoric water that was undersaturated with respect to dolomite. The fluid-flow history through the Ikpiariuk Formation mounds shares some compositional similarities with fluids that generated the Nansivik Zn-Pb deposit, and the timing of precipitation of HD may be related to the ore-forming event at Nanisivik. Precipitation of ED, and partly FCD, occurred during shallow burial

through autocementation. Fluids associated with FCD, HD, and CCD may have been mobilised during faulting contemporaneous with deposition of the upper Bylot Supergroup, because this interval was the most tectonically active time in the region's Mesoproterozoic to Recent history. Quartz was derived from seawater that had been modified through water-rock interaction, the timing of which is poorly constrained. Replacive calcite and calcite precipitated from high-latitude oxidised meteoric water at some point post-Mesozoic.



Figure 1: A)Representative diagram of the various depositional and diagenetic components of the Ikpiarjuk Formation mounds. B) Close-up diagram of inset box in (A). ED is euhedral dolomite, FCD is finely crystalline clear dolomite, HD is hematite-bearing dolomite, CCD is coarsely crystalline clear dolomite, and RC is replacive calcite. C) The relative timing of each phase is shown, with proposed absolute timing of each event.

#### REFERENCES

Hahn, K., Turner, E.C., Babechuk, M.G., andKamber, B.S.(2015) Deep-water seep-related carbonate mounds in a Mesoproterozoic alkaline lake, Borden Basin (Nunavut, Canada). Precambrian Research. Vol. 271. 173-197

Hahn, K.E. (2016) Sedimentology, stratigraphy, geochemistry and diagenesis of giant lacustrine carbonate seep mounds (Ikpiarjuk formation), Mesoproterozoic Borden Basin, Nunavut, arctic Canada. Unpublished Ph.D. thesis. Laurentian University, Sudbury, Canada. 310p.

Mathieu J., Kontak, D.J., and Turner, E.C. (2013) A fluid inclusion study of diagenetic fluids in Proterozoic and Paleozoic carbonate rocks, Victoria Island, NWT. Geofluids. Vol. 13. 559-578.

Mathieu, J., Kontak, D.J., Turner, E.C., Fayek, M., and Layne, G (2015) Geochemistry of Phanerozoic diagenesis on Victoria Island, NWT, Canada. Chemical Geology. Vol. 415. 47-69.

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Sherlock, R.L., Lee, J.K.W., and Cousens, B.L. (2004) Geologic and Geochronologic Constraints on the Timing of Mineralization at the Nanisivik Zinc-Lead Mississippi Valley-Type Deposit, Northern Baffin Island, Nunavut, Canada. Economic Geology. Vol. 99. 279-293

# Cathodoluminescence imaging and fluid inclusions of the Reef deposit, a Paleoproterozoic Au-Cu occurrence in central Wisconsin, USA.

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The Reef deposit, Located within the Wausau Volcanic complex (WVC), a subregion of the Pembine-Wausau volcanic subterrane (PWST), is a vein hosted Au-Cu occurrence historically calculated to contain ~454,600 tons grading 0.262 opt gold, 0.25 opt silver and ~0.28% copper located approximately 15 miles east of Wausau, Wisconsin. The PWST is also known to contain many volcanogenic massive sulfide (VMS) deposits within the Ladysmith-Rhinelander volcanic complex (LRVC) which is adjacent to the North of the WVC, several of which are considered to be economically viable to mining (DeMatties 1994). The Reef deposit has been described in the past as a lode gold or shear-zone hosted gold deposit (Dematties, 1994) separating it genetically from the VMS deposits to the north, along with a physical separation of the hosting terrane (WVC vs. PWVT). The Reef deposit has also been described as the root zone of a Cu-Zn or Zn-Cu VMS deposit (Scott 1988) and although there are no known VMS deposits of economic interest, the WVC is known to host minor VMS mineralization (DeMatties 1994).

The Reef deposit consists of seven mineralized zones which consist of Au-Cu bearing quartz-sulfide veins hosted in primarily basaltic material (mafic metavolcanics and gabbroic intrusions) (Kennedy and Harding, 1990). Whilst ore zones of quartz-sulfide veins are also cross-cut by similar gabbroic intrusives it is unclear when the Au mineralization was deposited. The zones trend northeast, dip to the northwest and are closely associated with felsic intrusions (Kennedy and Harding 1990). Felsic dikes and sills are intermingled with the host gabbro intrusives as a swarm of granophyric to porphyritic, locally aplitic units. The deposit area is flanked to the west and northwest by dominantly basalt of massive and pillowed flows and mafic tuff. Felsic intrusions flanking the deposit are concentrated in the western and southeastern areas adjacent to the deposit. Kennedy and Harding (1990) report a serpentinized peridotite that occurs



Figure 1: Cathodoluminescence image of quartz with multiple dark bands representing healed fractures. Distinctive trail of dark patches in center of image is anomalous because there is no dark CL band linking the dark patches.

directly adjacent to the west of the deposit area.

Cathodoluminescense (CL) images of quartz veins are being utilized to identify assemblages of fluid inclusions: (1) secondary trails with dark CL patches tied to a linear dark band marking the original healed fracture, and (2) secondary trails of dark CL patches with no darker CL fracture band (Fig. 1). Inclusions in setting (1) can be broken into long curvilinear (conchoidal fracture) trails and jointed angular trails. Scheelite overgrowths are observed to correspond to dark patches in guartz (Fig. 2). Other curious CL signatures include dark CL patches along guartz crystal boundaries (often internally zoned) and banded guartz growth coincident with sulfides in large healed fractures.

Fluid inclusion trails are observed to contain inclusions with variable vapor fill, often suspected to contain 2 or 4 modes of fill, and other trails are observed to contain only inclusions with no visible vapor bubbles. These inclusions are found to have dark patches (in CL) surrounding them formed through morphological ripening of the inclusions. This process is only possible with the presence of liquid H<sub>2</sub>O either in trace amounts currently not visible, completely filling the inclusions (no vapor) or water was there prior to evacuation (Lambrecht and Diamond 2015).

Fluid inclusion assemblages will be further examined using microthermometry to qualitatively identify fluid species and quantitatively identify trapping conditions. Trace element mapping of quartz by electron microprobe will reveal insights into vein quartz formation including estimates for temperature of deposition (Rusk et al 2008).



Figure 2: Cathodoluminescence images of scheelite in quartz. (a,b) lower brightness setting to see the zoning in scheelite. (c,d) higher brightness setting to observe CL in the host quartz. White arrows highlight bright overgrowths on scheelite which correspond to dark patches in quartz (highlighted by black arrows).

#### REFERENCES

Dematties, T.A. (1994) Early Proterozoic volcanogenic massive sulfide deposits in Wisconsin: an overview, Economic Geology, v. 89, pp. 1122-1151.

Kennedy, L.P., and Harding, T.A. (1990) Summary report of the Reef joint venture Marathon County, Wisconsin, Noranda Exploration Inc., 63 pp.

Lambrecht, G.L., and Diamond, L.W. (2014) Morphological ripening of fluid inclusions and coupled zone-refining in quartz crystals revealed by cathodoluminescence imaging: Implications for CL-petrography, fluid inclusion analysis and trace-element geothermometry, Geochimica et Cosmochimica Acta, vol. 141, pp. 381-406.

Rusk, B.G., Heather, A.L., Reed, M.H. (2008) Trace elements in hydrothermal quartz: Relationships to cathodoluminescent textures and insights into vein formation, Geology, vol. 36, pp. 547-550.

Scott, W.P. (1988) A volcanic hosted gold occurrence in Marathon County, Wisconsin, A thesis submitted in partial fulfillment of the requirements for the degree of master of science geology, University of Wisconsin-Madison, 99 pp.

#### Geochemistry of fluid inclusions in the Vazante hypogene non-sulfide Zn and the Morro Agudo Irish-type Zn-Pb Deposits, Minas Gerais, Brazil.

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#### ABSTRACT

The Vazante and Morro Agudo deposits are the two largest ore deposits in the Vazante-Unaí Zn-Pb trend, southeast-central, Brazil. The two deposits also represent two strongly contrasting styles of mineralization in the trend. The Vazante deposit is an example of hypogene non-sulfide zinc mineralization dominated by willemite. The Morro Agudo deposit is an example of Irish-type Zn-Pb sulfide mineralization dominated by sphalerite and galena. Both styles of mineralization are hosted in Proterozoic shaley dolostones, with non-sulfide mineralization occurring in the south and sulfide mineralization concentrated in the north. The close proximity of these contrasting styles of mineralization to one another in similar geologic settings raises the question of whether the deposits are genetically related or products of unrelated events and processes. The purpose of the present research was to seek an answer to this question from the compositions and homogenizations temperature of fluid inclusions. The focus of the study was on fluid inclusions hosted by sphalerite from the Vazante and Morro Agudo deposits, as sphalerite is an ore mineral present in both deposits and because willemite, though transparent, was not found to preserve any primary fluid inclusions.

Most primary fluid inclusions (~ 80%) in the Vazante deposit and nearly all primary fluid inclusions in the Morro Agudo deposit consist of aqueous liquid and vapor in variable proportions, whereas most secondary fluid inclusions (~90%) in both deposits consist of a single aqueous liquid phase, with the remainder consisting of aqueous liquid + vapor. A small percentage of Vazante fluid inclusions contain rhombohedral crystals, most likely carbonate mineral accidentals.

Microthermometry results showed highly variable homogenization temperatures (T<sub>H</sub>) in both deposits, ranging from about 100 to 239 °C in Morro Agudo and from about 47 - 352 °C in Vazante. The huge variability in T<sub>H</sub> overall and within fluid inclusion assemblages suggests that fluid inclusions in both deposits have been affected by low grade metamorphism from the Brasiliano orogeny. Likewise, fluid inclusion salinities were found to be highly variable in both deposits, ranging from 4.8 to 23.2 equivalent weight percent NaCl in Morro Agudo and from 0.9 to 22 equivalent weight percent NaCl in Vazante. The wide range in salinities suggests mixing between a brine and a dilute fluid during ore formation. Fluid inclusion  $T_H$  and salinity were not found to correlate.

LA-ICP-MS analyses were performed on fluid inclusions in order to determine their elemental compositions. Elemental concentrations versus total salinity for liquid-vapor fluid inclusions from both deposits lie within the field of typical sedimentary basinal brines (Hanor, 1994), with the exception of K, which is significantly elevated for both deposits. Morro Agudo and Vazante fluid inclusions were found to have similar atomic K/Na ratios. However, Vazante fluid inclusions were found to have systematically lower Mg/Na Ca/Na, Sr/Na, and Ba/Na ratios, and to be overall more dilute than Morro Agudo fluid inclusions. Thus, the Vazante and Morro Agudo deposits appear to have formed from different fluids or from a fluid that evolved significantly with respect to composition as it traversed the Vazante-Unaí trend. Morro Agudo and Vazante fluid inclusions were found to have higher atomic Ba/Na, K/Na, and Mg/Na ratios but lower Ca/Na and Sr/Na ratios than Ozark MVT fluid inclusions. However, Vazante fluid inclusions were found to have similar atomic Ba/Na and Ca/Na ratios to Irish fluid inclusions. However, Vazante fluid inclusions were found to have higher atomic Ba/Na and Sr/Na ratios than Irish fluid inclusions.

Primary liquid-only fluid inclusions from the Vazante deposit were also analysed by LA-ICP-MS and found to be indistinguishable from liquid-vapor fluid inclusions in composition. This suggests not only that primary Vazante fluid inclusions have been partially thermally reequilibrated but that the Vazante zinc mineralization originally formed at relatively low temperature.

The fluid inclusion data do not provide clear evidence as to what factors promoted sphalerite precipitation in the Morro Agudo deposit versus willemite-dominated precipitation in the Vazante deposit. Ore formation in both deposits appears to have been associated with dilution of a brine, but the solubility of willemite and sphalerite are identically dependent on salinity. The solubility of sphalerite is more sensitive to temperature than that of willemite, but the temperature record provided by the fluid inclusions appears to have been altered by later thermal reequilibration, making the existence of cooling difficult to assess. The solubility of sphalerite. However, the fluid inclusion data in this study do not provide a clear indicator of pH or sulfide concentration. Willemite is very soluble in silica-saturated solutions, and thus can only precipitate from very Zn-rich fluids. Thus, a potentially profitable future direction of study would be to look for a difference in Zn concentrations in fluid inclusions in non-zinc ore minerals in the Vazante and Morro Agudo deposits.

#### REFERENCES

Hanor, J. S. (1994) Origin of saline fluids in sedimentary basins, in J. Parnell, ed., Geofluids: Origin and migration of fluids in sedimentary basins: Geological Society (London) Special Publication, v. 78, p. 151–174.

## Measuring fluorine concentrations of ore fluids in the Illinois-Kentucky district: An SEM-EDS analysis of fluid inclusion decrepitates.

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The U.S. midcontinent hosts several prominent Mississippi Valley-type (MVT) ore districts, most of which are dominated by Zn or Pb. However, the Illinois-Kentucky district is unique among midcontinent MVT ore districts in that it is composed predominantly of fluorite. This relative fluorite enrichment has long been hypothesized to be related to ultramafic igneous rocks that are abundant in Illinois-Kentucky but absent from other midcontinent MVT districts (Grogan and Bradbury, 1968). These ultramafic igneous rocks have been shown to be rich in F (Moorehead, 2013) and to be Permian (~270 Ma) in age (Zartman et al., 1967), making them coeval with the MVT mineralization based on direct <sup>147</sup>Sm/<sup>144</sup>Nd dates of fluorite of 272 ± 17 Ma (Chesley et al., 1994). Plumlee et al. (1995) used reaction path modeling to show that mixing of sedimentary brine with HF-rich fluid, assumed to have exsolved from magma in the Precambrian basement, could produce a fluorite-dominant mineral assemblage resembling what is observed in the Illinois-Kentucky district. Based on <sup>3</sup>He/<sup>4</sup>He ratios in fluid inclusions, Kendrick et al. (2002) determined that up to 6% of the ore fluid mixture in the Illinois-Kentucky district has a mantle-derived magmatic source. Pelch et al. (2015) measured the elemental composition of fluid inclusions in the Illinois-Kentucky ores and found them to be enriched in K and Sr relative to fluid inclusions in Ozark MVT ores, possibly reflecting the influence of K and Sr enriched ultramafic rocks in the Illinois-Kentucky district.

The evidence cited above supports the hypothesis that mixing of sedimentary brine with HF-rich fluid led to the formation of the fluorite-dominant Illinois-Kentucky ore. The purpose of the present study was to test this hypothesis further by measuring the F content of fluid inclusions hosted in sphalerite from the Illinois-Kentucky district through SEM-EDS analysis of fluid inclusion decrepitate salt mounds. For comparison, decrepitate salt mounds from several sphalerite-hosted fluid inclusions from the fluorite-absent Tri-State district were also analyzed. The decrepitate salt mounds were generated by heating the samples to ~500°C at a rate of ~50°C/min. Based on the fluid inclusion major element composition data of Pelch et al. (2015), F concentrations in the fluid inclusions could be calculated.

To calibrate the SEM-EDS analyses for F, standard solutions were produced with a major element composition near the average of sphalerite-hosted fluid inclusions analyzed by Pelch et al. (2015) and total F concentrations ranging from 20 to 3500 ppm. Droplets of the standard solutions were placed on thin sections of sphalerite and allowed to evaporate. The resultant salt mounds were then analyzed under the same conditions as the fluid inclusion decrepitate salt mounds. Analyses of evaporative salt mounds generated from the standard solutions showed the SEM-EDS to over-predict F concentrations systematically by about 0.5 to one log unit.

Fluid inclusions major cation concentrations determined from the SEM-EDS analyses were compared to data generated by LA-ICP-MS of Pelch et al. (2015), and showed agreement within 0.7 log units.

Results from the present study showed Illinois-Kentucky sphalerite-hosted fluid inclusions to be rich in F, with concentrations ranging from 100's to 1000's of ppm, significantly greater than the typical concentration of F in sedimentary brines (<10ppm). Such high F concentrations are consistent with a magmatic source.

In order for F concentrations to have been that high, the pH must have been between 1 and 2, about 2 to 3 units lower than what is considered typical for MVT ore fluids. A pH reduction of this magnitude would correspond to an orders of magnitude increase in metal-sulfide mineral solubility. Thus, the high F concentration in the Illinois-Kentucky ore fluid mixture may have simultaneously suppressed metal-sulfide mineral precipitation while promoting fluorite precipitation.

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Figure 1. SEM-EDS elemental maps of a fluid inclusion decrepitate mound on sphalerite from a sample collected near Hicks Dome in southern Illinois. Elevated levels of fluorine (a) can be seen within the decrepitate mound, which is defined by the presence of chlorine (b), calcium (c), and magnesium (d). Scale bar is equal to 5 µm.

#### REFERENCES

- Chesley, J.T., Halliday, A.N., Kyser, T.K., and Spry, P.G. (1994) Direct dating of Mississippi Valley-type Mineralization: Use of Sm-Nd in fluorite. Economic Geology. 89. 1192-1199.
- Grogan, R.M., and Bradbury, J.C. (1968) Fluorite-zinc-lead deposits of the Illinois-Kentucky mining district, in Ridge, J.D., ed., Ore deposits of the United States (Graton Sales Volume): New York, American Institute of Mining, Metallurgical and Petroleum Engineers. 1. 370-399.
- Kendrick, M.A., Burgess, R., Leach, D., Pattrick, R.A.D., (2002) Hydrothermal fluid origins in Mississippi Valley-type ore districts: Combined noble gas (He, Ar, Kr) and Halogen (CI, Br, I) analysis of fluid inclusions from the Illinois-Kentucky Fluorspar district, Viburnum Trend, and Tri-State districts, midcontinent United States. Economic Geology. 97. 453-469.
- Moorehead, A.J. (2013) Igneous intrusions at Hicks Dome, southern Illinois, and their relationship to fluorine-base metal-rare earth element mineralization. Master's Thesis, Southern Illinois University. 1-226.
- Pelch, M.A., Appold, M.S., Emsbo, P., and Bodnar, R.J. (2015) Constraints from fluid inclusion compositions on the origin of Mississippi Valley-type mineralization from the Illinois-Kentucky district. Economic Geology. 110. 787-808.
- Plumlee, G.S., Goldhaber, M.B., Rowan, E.L., (1995) The potential role of magmatic gases in the genesis of Illinois-Kentucky fluorspar deposits: Implications from chemical reaction path modeling. Economic Geology. 90. 999-1011.
- Zartman, R.E., Brock, M.R., Heyl, A.V., and Thomas, H.H. (1967) K-Ar and Rb-Sr ages of some alkalic igneous rocks from the central and eastern United States. American Journal of Science. 265. 848-870.

#### Fluid evolution at the North American Emerald Mine, Hiddenite, NC

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Emerald is a green gemstone variety of the beryl, in which color is defined by trace amounts of Cr and V. Genetic classification schemes of the emerald deposits, according to Zwaan (2006), are ambiguous and not useful in terms of the conditions of deposit formation. This is due to fact that gem quality emeralds can be formed in very different geological settings, in which only a few conditions have to be fulfilled. According to Zwaan (2006) these conditions defined are as: 1) availability of Be and Cr(V), 2) chemical and physical conditions at which beryl is stable and 3) sufficient free space for emeralds to grow.

During formation of emerald deposits, host rocks enriched in Cr (V) undergo alteration by the Be-enriched hydrothermal fluid. Evensen and London (2002) demonstrated preferential partitioning of Be into the magmatic-hydrothermal fluid during evolution of felsic magmas, while enrichment in Cr (V) is common for ultramafic rocks or their metamorphic equivalents. Thus, emerald formation occurs at conditions in which host rocks of ultramafic composition are being altered by a fluid derived from (or equilibrated with) felsic magma. These conditions can be fulfilled in environments associated with either (1) pegmatite or granite; or (2) thrust-shear zones in Cr (V)-bearing rocks

NAEM is located near Hiddenite, North Carolina and produced more than 60,000 carats of emeralds between 1995 and 2012, when the mine went on standby and operations were temporarily ended. The NAEM is located at the former Rist mine site that had produced emeralds since 1882, and is considered to be the most significant North American emerald locality. The emeralds are found in Alpine fissure-type quartz veins hosted by Silurian(?) migmatitic metasedimentary rocks interlayered with calc-silicate rocks that reached upper amphibolite facies (sillimanite grade). These rocks are part of the Brindle Creek thrust sheet (Cat Square Terrane) that overlies metasedimentary and meta-igneous rocks of Silurian to late Proterozoic age. Emeralds at the NAEM occur in cavities in close association with quartz, muscovite and carbonate. Fluid inclusions (FI) are abundant in emerald, quartz and carbonate minerals.



Fig. 1. Density variations in fluid inclusion assemblages (FIA) in different host minerals

FI in emeralds, carbonates and quartz were analysed to characterize fluid composition and its evolution. At room temperature, fluid inclusion assemblages (FIA) in emerald contain two L+V phases only. Raman analysis showed that the vapor phase is high density  $CO_2$  with an average density of ~0.74 g×cm<sup>-3</sup> (Fig. 1). Based on room temperature phase ratios, the fluid has a composition of ~80-90 mole%  $CO_2$  and 10-20 mole%  $H_2O$  (bulk density ~0.76 g×cm<sup>-3</sup>). FI in spatially associated quartz also contain L+V phases when observed at room temperature, and the vapor bubble contains  $CO_2$ . However, the density of the  $CO_2$  phase is much lower (~0.1 g×cm<sup>-3</sup>) bulk density of the FIAs ~0.2 g×cm<sup>-3</sup>) compared to FI in emerald. Carbonates in

most cases contain two fluid phases at room temperature, with CO<sub>2</sub> density estimated at ~0.73 g×cm<sup>-3</sup> (bulk density ~0.75 g×cm<sup>-3</sup>).

Salinity of the fluid in FI in carbonates was estimated to be ~ 3 wt. % NaCl eq. based on clathrate melting temperature. In some carbonate samples, a daughter phase interpreted to be graphite is present. The FI cannot be heated to homogenization owing to decrepitation from the high internal pressures generated in CO<sub>2</sub>-rich FI during heating. However, Ca/Mg partitioning data for coexisting carbonate minerals indicate a formation temperature of ~250°C. Assuming that the trapping temperature for the FI in emeralds is the same as the temperature of formation of the closely associated carbonates, PVTX data for the system H<sub>2</sub>O-CO<sub>2</sub> indicate a minimum pressure of formation of ~1.1 kbar. CO<sub>2</sub>-rich fluids are characteristic of medium-grade metamorphic environments, suggesting that emerald formation and regional metamorphism are related. The presence of graphite in the FI and as a free mineral phase in chromian-spodumene bearing cavities (Wise & Anderson, 2006) is evidence of the reducing conditions of the fluid. The 1 kbar pressure estimate is in the agreement with Wise and Anderson (2006), however no evidences of fluid boiling reported by Wise and Anderson was found during this study.

#### REFERENCES

Evensen, J. M., & London, D. (2002). Experimental silicate mineral/melt partition coefficients for beryllium and the crustal Be cycle from migmatite to pegmatite. Geochimica et Cosmochimica Acta, 66(12), 2239-2265.

Wise, M. A., & Anderson, A. J. (2006). The emerald-and spodumene-bearing quartz veins of the Rist emerald mine, Hiddenite, North Carolina. The Canadian Mineralogist, 44(6), 1529-1541.

Zwaan, J. C. (2006). Gemmology, geology and origin of the Sandawana emerald deposits, Zimbabwe. Scripta geologica, 131, 1-212.

#### Evidence for pressure cycling and fluid unmixing as relevant processes in gold deposits from fluid inclusion studies of Archean and Phanerozoic orogenic and intrusion-related settings in Canada

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Studies of quartz-hosted fluid inclusions (FI) suggest that a mixed aqueous-carbonic fluid with  $X_{CO2} = 0.1-0.2$  is the dominant fluid type in both orogenic (OR) and intrusion-related (IR) gold deposits (e.g., Bodnar et al. 2013). Furthermore, the occurrence of complementary aqueous- and carbonic-rich FI as distinct or mixed fluid inclusion assemblages (FIA) provide support for fluid unmxing. As unmixing may cause destabilization of Au transporting ligands, it is therefore considered important for gold deposition. That this process occurs in OR gold deposit settings is attributed to transient pressure cycling ( $\Delta P$ ; Sibson et al. 1988), as evidenced by both vein types (e.g., flat extensional and vertical fault fill) and vein textures (e.g., ribbon or crack seal). However, further evidence for transient  $\Delta P$  is documented at the micro-scale based on FI textures observed in both experimental runs (e.g., Sterner and Bodnar 1989, Tarantola et al. 2010) and natural settings (Diamond et al. 2015). Although these studies demonstrate that decrepitate textures and formation of neonate inclusions provide evidence for  $\Delta P$ , there has been little integration of such observations into ore deposit research. Herein are presented three examples where such textures are common in both OR and IR gold deposit settings. A further relevant aspect is that where decrepitates are abundant due to  $\Delta P$  (Plithostatic to Phyrostatic), we suggest that mixing of different FI populations with varying chemistry (e.g., X<sub>CO2</sub>) and density may compromise FI studies if not recognized.

The Archean Red Lake district, Ontario, is famous for its high-grade ore, hosted in highly deformed and altered (silica, carbonate, biotite) metavolcanic rocks; these deposits are considered to be of OR type. Previous work revealed the dominance of pure CO<sub>2</sub> FI (Chi et al. 2006). Our studies, using samples from five current operations (mines and development) confirm carbonic inclusions in all paragenetic stages, however here we also document decrepitates as pervasive features (Fig. 1A-D). Using isolated FIAs (n=80), a large range in density is noted based on Th<sub>CO2</sub> with values from -18°C to +30°C, but for any one FIA Th<sub>CO2</sub> is  $\leq$ 2-3°C; these data suggest a large  $\Delta$ P during vein formation. Furthermore, we suggest the CO<sub>2</sub>-rich fluid was generated due to decarbonisation reactions in previously carbonated mafic volcanic host rocks due to reaction with typical H<sub>2</sub>O-CO<sub>2</sub> fluids, as seen in other gold systems here and elsewhere.

The Archean gold deposits of the Timmins district, Ontario, include both OR and IR types with the Timmins West Gap Zone discussed. Here a syenite hosts a swarm of mineralized quartz veins with abundant FI (Fig. 1E) of H<sub>2</sub>O-CO<sub>2</sub> ( $X_{CO2} \le 0.2$ ; 5-12 wt. % eq. NaCl), CO<sub>2</sub> (Fig. 1F) and H<sub>2</sub>O (1-12 wt. % eq. NaCl) types. These distinct FIAs likely relate to a single fluid event through fluid unmixing. Abundant decrepitate clusters with neonates (Fig. 1G, H, I) provide further support for  $\Delta P$ ; in addition the variable fluid chemistries and densities of neonates indicate variable amounts of  $\Delta P$ . Cursory studies of OR deposits in the Timmins camp include the richly mineralized Dome and Hoyle Pond sites, both hosted by carbonate altered mafic metavolcanic rocks. As with Red Lake, the samples only contain CO<sub>2</sub> inclusions throughout the paragenesis. Formation of this CO<sub>2</sub>-rich fluid is considered to reflect the same process as proposed for the Red Lake fluid discussed above.

The well-known Meguma quartz vein gold deposits of Nova Scotia occur in Cambro-Ordovician metaturbidite rocks and represent a classic OR gold setting. Examination of vein samples from numerous districts indicates a similar vein fluid in all cases, a H<sub>2</sub>O-CO<sub>2</sub> type with X<sub>CO2</sub> = 0.1-0.2 (Fig. 1L) and ≤10 wt. eq. NaCl. Evidence for  $\Delta P$  is again suggested from the abundance of decrepitates, which in cases dominate samples (Fig. 1I, J). Rarely are CO<sub>2</sub>-rich inclusions noted which also suggest fluid unmixing accompanied vein formation.

The above observations indicate that textural equilibration of FIs is a common in gold deposit settings and, when integrated with other data, including FIAs and vein types and textures, provides more insight into the nature of processes active during ore deposit formation. Examples from other deposit settings with also be illustrated (e.g., pegmatites, porphyry, granite-related Sn) to further illustrate how widespread and potentially important these features are in ore systems.



Fig. 1. Images of fluid inclusions from deposit settings discussed. Red Lake: (A, B)  $CO_2$ -type FIA on secondary planes, (C, D) decrepitate clusters with neonates. Timmins Gap Zone: (E)  $H_2O-CO_2$  FIA with inset enlarged; (F)  $CO_2$ -rich FIA atributed to unmixing of previous FIA (G, H, I) decrepitates clusters with abundant neonates. Meguma: (J, K) abundant decrepitates populating samples with inset of decrepitate in image J, (L) typical  $H_2O-CO_2$  type FIA in the same sample as images J and K.

#### REFERENCES

- Chi G., Dubé, B., Williamson, K., & Williams-Jones, A.E. (2006) Formation of the Campbell-Red Lake gold deposit by H<sub>2</sub>O-poor, CO<sub>2</sub>-dominated fluids: Mineralium Deposita **40**, p. 726–741.
- Diamond, L.W. & Tarantola, A. (2015) Interpretation of fluid inclusions in quartz deformed by weak ductile shearing:Reconstruction of differential stress magnitude and pre-deformation fluid properties. Earth and Planetary Science Letters **417**, p. 107-119.
- Tarantola, A. Diamond, L.W. & Stünitz, H. (2010) Modification of fluid inclusions in quartz by deviatoric stress. I: experimentally induced changes in inclusion shapes and microstructures. Contributions to Mineralogy and Petrology 160, p. 825-843.
- Sterner, S.M. & Bodnar R.J. (1989) Synthetic fluid inclusions—VII. Re-equilibration of fluid inclusions in quartz during laboratory simulated metamorphic burial and uplift. Journal of Metamorphic Geology 7, p. 243–260.

# Fluid inclusion study of the Brazil Lake LCT-type pegmatite, Nova Scotia, Canada provides insight into the origin of rare-metal enrichment and occurrence of wallrock-derived CO<sub>2</sub>

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The rare-metal rich evolved pegmatites, such as those containing Li-Cs-Ta (i.e., LCT-type), represent some of the most fractionated magmas on Earth (London 2008). Whereas their chemcially evolved and magamtic nature is rarely disputed, the origin of their contained metals reamins a matter of continued debate. That primary magmatic metal concentrations occur has been aptly demonstrated in some deposits (e.g., Linnen & Cuney 2005, Linnen et al. 2012), whereas other cases provide evidence for the association of metals with zones of secondary or metasomatic origin, the most common of these being the apliltic albite zones (Linnen et al. 2012). The ca. 395 Ma Brazil Lake pegmatite (BLP) of Nova Scotia represents an example of this latter setting, as shown from previous geological, lithogeochemical and mineral chemical and isotopic studies (Kontak 2006; Kontak and Kyser 2009). The BLP, which intrudes mafic metavolcanics and interbedded black slates, consists of a primary magmatic quartz-K-feldsparspodumene±muscovite±beryl±tourmaline assemblage. The persence of quartz-spodumene intergrowth (SQUI) after petalite is noted, as it constrains the PT conditions of emplacement. Furthermore, the lack a quartz-rich core zone suggests a lack of volatile saturation. The early magmatic blocky K-feldsapr is overprinted by zones of secondary albite-muscovite±garnet±apatite with formation of abundant porosity. Textural evidence for syn-emplacement deformation is recorded by breccaited quartz megacrsyts cemented by the late-stage albite. Whole-rock geochemical data indicate a strong correlation between Ta(-Sn) enrichment and albite formation. Fluid inclusion assembalges (FIA) occur as either indeterminate or secodary types in guartz, spodumene, garnet and K-feldspar. Herein we report results of an integrated geochemical study of the guartz-hosted inclusions.

Two fluid inclusion types are present (FIg. 1) and thermometric data were collected for 500 inclusions in 66 FIAs from 10 samples. Type 1, the most abunant inclusion type, is H<sub>2</sub>O with 2.4 to 10.2 wt. % eq. NaCl and first melting data indicate they are Na-rich. The Th values range from 163° to 225°C, but for any FIA the range is <5-15°C. Lesser type 2, H<sub>2</sub>O-CO<sub>2</sub> fluid inclusions with X<sub>CO2</sub> =0.10, are also present and have 8-13 wt. % eq. NaCl based ice and clathrate melting, whereas first melting suggest Na-rich compositions. That Tm(CO<sub>2</sub>) is between -57.0° and -59.2°C suggests the presence of other gases, as confirmed with laser Raman analysis (CH<sub>4</sub> (<10mole%), N<sub>2</sub> (<35 mole%)). The Th data are between 180° to 235°C with with ranges for FIAs. Fluid inclusion extracts yielded  $\delta^{13}$ C values of -20 to -24‰ (n=9). Major and minor element chemistry of the fluids were constrained using SEM-EDS evaporate mound analysis (N=133) which indicates Na dominates (Na/∑cations ≥ 90%); minor K, Ca, Fe, S are also present. Further elemental data were acquired with LA ICP-MS analysis and the following average elemental concentrations (in ppm) are noted: Na (29300), Al (2865), Li (840), K (620), B (670), Fe (330), Cs (230), Ca (57), Rb (40), and Sr (6) with Ta and Nb below detection

These data are interpreted in the context of their chemistry and the PT diagram (Fig. 2) to suggest the follownig: 1) emplacement of an evolved LCT-type pegmatitic melt that crystallized the observed magmatic assemblage at >500°C, if not more, as indicated by SQUI after petalite and relevant experimental data (see Kontak 2006), thus P exceeded 3 bars; 2) ingress of a residual sodic-, volatile- and metal-rich melt which reacted with and metasomatized the already crystallized pegmatite. The lack of Ta and Sn in the fluid inclusions preclude rare metals being deposited from a fluid; 3) release of a Na-rich H<sub>2</sub>O fluid as part of the metasomatism; 4) convection and interaction of the H<sub>2</sub>O fluid with the metasedimentary wall rock wherein graphite was oxidzed to produce CO<sub>2</sub> with an inherited low  $\delta^{13}$ C signature implying biogenic sourced C. Note that the isochoric projections in Figure 2 suggest the latter fluid post-dated the H<sub>2</sub>O-type fluid. The presence of decrepitated fluid inclusions (Fig. 2F) in addition to deformed quartz megacrysts are consistent with syn-emplacement deformation and strain recorded in the pegmatite.

Important results of this study are: 1) thisLCT-type rare-metal system owes its metal enrichment to magmatic processes, albeit of secondary nature and not primary in the true sence; 2) the lack of a pocket

zone, common in many pegmatites, is consistent with the absence of any obvious primary fluid inclusions, or at least a lack of them; 3) isochoric proections clearly support the latter and suggest that at least in some cases the observed fluids in pegmatites post-date its crystallization; and 4) the carbonic nature of at least some LCT-type pematites is a secodary rather than primary feature of the magmatic system.



Figure 1 (left). Photomicrographs of quartz-hosted fluid inclusions, Brazil Lake. (A,B) Abundant mixed  $H_2O$  and  $H_2O-CO_2$ fluid inclusions. (C) Type 1  $H_2O$  inclusions of 20-25 µm size; (D, E) Type 2  $H_2O-CO_2$ fluid inclusions of 20-25 µm size; note the mica phase in image E. (F) Decrepitated fluid inclusions of about 100 µm length. The neonates in these inclusion types are both of type 1 and 2 types. FIgure 2 (right). P-T diagram showing the following: (1) petrogenetic grid for the Li<sub>2</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O system (see London 2008); (2) the H<sub>2</sub>O-CO<sub>2</sub>-NaCl solvus for the bulk composition X(CO<sub>2</sub>) = 0.0983, X(H<sub>2</sub>O) = 0.8843, X(NaCl) = 0.0174 with isoTh lines at 247°, 255°, 300°, 350° and 400°C (from Schmidt & Bodnar 2000), and (3) isochores for type 1 H<sub>2</sub>O inclusions (the T=200°C isochore was used for plotting) and type 2 H<sub>2</sub>O-CO<sub>2</sub> inclusions are constrained from their homogenization data and bulk compositions. The proposed fluid evolutionary path for the pegmatite is indicated by the dark arrow. Abbreviations follow: Spd = spodumene, Qtz = quartz, Pet = petalite, Ecr = eucryptite.

#### REFERENCES

- Kontak, D.J. (2006) Nature and origin of an LCT-suite pegmatite with late-stage sodium enrichment, Brazil Lake, Yarmouth County, Nova Scotia. I. Geological setting and petrology. Canadian Mineralogist 44, p. 563-598.
- Kontak, D.J. & Kyser, T.K. (2009) Nature and origin of an LCT-suite pegmatite with late-stage sodium enrichment, Brazil Lake, Yarmouth County, Nova Scotia. II. Implications of stable isotopes (δ<sup>18</sup>O, δD) for magma source, internal crystallization and nature of sodium metasomatism. Canadian Mineralogist **47**, p. 745-764.
- Linnen, R.L. & Cuney, M. (2005) Granite-related rare-element deposits and experimental constraints on Ta-Nb-W-Sn-Zr-Hf mineralization. *In* Rare-Element Geochemistry of Ore Deposits (R. Linnen & I. Samson, eds.). Geological Association of Canada, Short Course Handbook **17**, p. 45-68.
- Linnen, R.L., VanLichtervelde, M. & Cerny, P. Granitic pegmatites as sources of strategic metals. Elements **8**, p .275-280.

LONDON, D. (2008) Pegmatites. The Canadian Mineralogist, Special Publication 10, 347 p.

Schmidt, C.& Bodnar, R.J. (2000) Synthetic fluid inclusions: XVI. PVTX properties in the system H<sub>2</sub>O-NaCI-CO<sub>2</sub> at elevated temperatures, pressures, and salinities. Geochimica et Cosmochimica Acta **64**, p. 3853-3869.

#### Reassessment of the Raman CO<sub>2</sub> densimeter.

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Carbon dioxide-bearing fluids are common in many geological environments, including volcanic fumaroles and continental geothermal systems, hydrothermal vents at mid ocean ridges, in various oreforming systems, abbysal serpentinites, low to high grade metamorphic rocks, and mantle rocks sampled by upper mantle xenoliths. Additionally,  $CO_2$  is an important component in melt inclusions trapped during magmatic and high-grade metamorphic processes. Fluid and melt inclusions are the most reliable tools available to characterize the physical and chemical properties of paleo-crustal and mantle fluids, and much of our understanding of the pressure, density, temperature and composition of crustal (and upper mantle) fluids and melts comes from studies of fluid and melt inclusions. Numerous techniques are available to determine the presence and/or concentration of  $CO_2$  in fluid and melt inclusions, and the choice of which technique to use depends on several factors like size and optical limitations. As an alternative to the petrographic/microthermometric methods for identifying  $CO_2$  in FI and MI, Raman spectroscopy is sometimes used to confirm the presence of  $CO_2$  in FI and MI, even when its presence is not revealed during petrographic and/or microthermometric analyses. Carbon dioxide has a characteristic Raman spectrum that contains several well-defined and relatively intense peaks, even at relatively low  $CO_2$  densities (Fig. 1).

For the last 20 years several densimeters that use the Raman Fermi Diad splitting have been developed and applied successfully to determine the densities and concentrations of CO<sub>2</sub> in fluids trapped in different aeological settings. A review of the literature indicates that the methodologies followed to develop the various CO<sub>2</sub> densimeters are sound, yet different densimeters predict different densities for the same Fermi diad splitting. Several previous studies of the pressure and temperature (density) dependence of Raman spectral features for volatile species (CO2, CH4) have acknowledged that their results follow near parallel trends to results of earlier studies (Song et al., 2009, Wang et al., 2001; Lu et al., 2007, Lin et al., 2007). These relationships have been considered to be mostly the result of: 1) variations associated with instrumentation (hardware) (Lu et al., 2007; Wang et al., 2011), 2) variations associated with data collection, calibration, and interpretation procedures (Song et al., 2009), 3) variations associated with the experimental method and EOS used to interpret the data (Song et al., 2009; Lu et al., 2007). These possibilities led us to examine potential causes for variations in the various densimeters that have been reported in the literature by using various instrumental settings and collection parameters to analyze CO<sub>2</sub>, and to test our calibration results with those developed using other Raman instruments and analytical methods. We experimentally calibrated the relationship between the splitting of the Fermi diad of CO<sub>2</sub> and CO<sub>2</sub> density at pressures from the liquid-vapor curve (6.0 MPa) to 0.06 MPa at ambient temperature (~22°C). Twelve experiments were conducted to test the variability associated with instrumental and analytical conditions, as well as to understand the differences between the various densimeters, using three different Raman instruments, with different laser sources and gratings.

The results show that all of the Raman configurations have an effect in the splitting of the Fermi diad, and all the data sets are slightly but constantly different. We fitted a line to each data set and compare them all (Fig.1). All densimeters show a linear and parallel behaviour throughout the experimental range of pressures examined here (~0.06 to 6.0 MPa). The slopes of the lines fit to our data, as well as low density (pressure) data from other densimeters (Kawakami et al., 2003; Yamamoto & Kagi, 2008; Song et al., 2009; Fall et al., 2011; Wang et al., 2011) are remarkably similar, with a variation of about ~10% and a standard deviation of 3%. The differences observed in all densimeters, including previously published densimeters and the 12 experiments from this study, are most likely a function of variations in instrumentation, laser excitation wavelength, gratings and analytical protocols used during the experimental calibration of the splitting of the Fermi diad.



Fig. 1 (A) Density vs. splitting of the Fermi diad data sets using different Raman instruments, different laser sources and different gratings. (B) Fitted lines of all the experiments. There are small but systematic and almost parallel trends.

#### REFERENCES

Fall, A., Tattitch, B., & Bodnar, R.J. (2011) Combined microthermometric and Raman spectroscopic technique to determine the salinity of H<sub>2</sub>O-CO<sub>2</sub>-NaCl fluid inclusions based on clathrate melting. Geochimica et Cosmochimica Acta, 75, 951-964.

Kawakami Y., Yamamoto J. & Kagi H. (2003) Micro-Raman densimeter for the CO<sub>2</sub> inclusions in mantle-derived minerals. App. Spectr. 57, 1333–1339.

Lin, F., Bodnar, R.J. & Becker, S.P. (2007) Experimental determination of the Raman CH<sub>4</sub> symmetric stretching (v1) band position from 1–650 bar and 0.3–22 °C: Application to fluid inclusion studies. Geochim. Cosmochim. Acta, 71, 3746– 3756. Lu, W., Chou, I. M., Burruss, R. C., & Song, Y. (2007) A unified equation for calculating methane vapor pressures in the CH<sub>4</sub> – H<sub>2</sub>O system with measured Raman shifts. Geochim. Cosmochim. Acta, 71(16), 3969-3978.

Song, Y., Chou, I.M., Hu, W., Burruss, R. & Lu, W. (2009) CO<sub>2</sub> density-Raman shift relation derived from synthetic inclusions in fused capillaries and its application. Acta Geol. Sinica, 83, 932–938.

Wang, X., Chou, I. M., Hu, W., Burruss, R.C., Sun, Q., & Song, Y. (2011) Raman spectroscopic measurements of CO<sub>2</sub> density: Experimental calibration with high-pressure optical cell (HPOC) and fused silica capillary capsule (FSCC) with application to fluid inclusion observations. Geochimica et Cosmochimica Acta, 75 (14), 4080-4093.

Yamamoto, J. & Kagi, H. (2006) Extended micro-Raman densimeter for CO<sub>2</sub> applicable to mantleoriginated fluid inclusions. Chem. Lett. 35, 610–611.
### Synthetic fluid inclusions as mini batch reactors to monitor serpentinization reactions in the oceanic lithosphere.

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Serpentinization is an important geological process that occurs where ultramafic rocks are exposed to fluid circulation on earth and other planetary bodies. This process not only induces huge magnetic, seismic and rheological changes in the oceanic crust and mantle wedge, but also produces highly unusual mineralogy and one of the most reduced fluid environments on the planet and other planetary bodies. Despite much recent attention, aspects of serpentinization such as the order of reactions, timing and the direction in which they occur are still a matter of considerable debate in the literature. Synthetic fluid inclusions studies using the fracture – anneal technique, have been used for several decades to understand a wide variety of geologic processes, and have proven key to measure the P-V-T-X properties of fluids.

We used the synthetic fluid inclusion technique to monitor the hydration processes of ultramafic minerals, in order to further understand the serpentinization processes occurring in the oceanic crust. We trap fluids of known composition at known P-T conditions in olivine crystals to follow in-situ serpentinization reactions in a closed system at fixed water/rock ratio. Pre-fractured olivine crystals were loaded into platinum capsules along with fluids of the systems H<sub>2</sub>O-NaCl, H<sub>2</sub>O-MgCl<sub>2</sub> and H<sub>2</sub>O-NaCl-MgCl<sub>2</sub> (Na/Mg ratios of sea water 8:1) and different concentrations (1, 3.5, 6 and 10 wt%), then welded shut (Sterner & Bodnar, 1984). After trapping of fluid inclusions at the selected conditions in the samples, the inclusions were examined petrographically before the samples were placed into a furnace at ~280 °C and 1 atm. Every 5 days the samples were taken down to room temperature and observed for mineralogical and salinity changes inside the fluid inclusions. Salinity of the fluid inclusions was measured by microthermometry, and the composition of the new mineral phases were monitored by Raman spectroscopy.

Results show that the serpentinization reaction is sensitive to the salinity of the fluids. For the experiments we used a composition of  $H_2O$ -NaCl-MgCl<sub>2</sub> (Na/Mg ratios of sea water 8:1) with concentrations of 1, 3.5, 6 and 10 wt%. The synthetic fluid inclusions with the lower concentrations (1 wt% and 3.5 wt%) started reacting after 5 days, whereas the 10 wt% solution experiments took more than 120 days for the reaction to occur. Brucite and serpentine (lizardite and/or chrysotile) are the new minerals formed (Fig.1). Magnetite was also observed but only in the experiments that were monitored >3 months at the running conditions 280 °C. The salinity of the fluid inclusions increases constantly as soon as the minerals nucleate. To reproduce these observations, we conducted the same experiments at constant temperature by using a Chaixmeca stage at the same experimental conditions. Although no salinity measurements were done, the constant monitoring made evident that the reaction progresses at similar speeds.

We found that the reaction is also sensitive to the amount of Mg in the fluid. After making 4 experiments changing the chemical composition of the fluid to a  $H_2O$ -NaCl and  $H_2O$ -MgCl<sub>2</sub>, that experiments with a solution of 3.5 and 10 wt% NaCl (no Mg) reacted following the same trends to the seawater-like composition described above. In the experiments with 3.5 wt% and 10 wt%  $H_2O$ -MgCl<sub>2</sub>, no reaction was observed in the first 120 days and only after 270 days a few inclusion started to form serpentine and brucite crystals. No salinity changes were detected thus far.

To characterize the chemical composition of the newly formed phases, TOF-SIMS analyses were performed and compared with the compositions predicted by a thermodynamic model using EQ3/6 software. Magnesium number (Mg#=MgO/MgO+FeO) ratios were calculated from the data and show that there are in agreement between the thermodynamic model and our experiments. The TOF SIMS data

showed that the reaction products have a range of Mg# ratios of 88 to 94, with the olivine host having a Mg# 85, whereas the software predicts the serpentine to have a Mg# 93 to 99 if the olivine has a Mg# 85. Reaction rates were calculated using the salinity as a proxy using the initial rate method. The calculated rates of H<sub>2</sub>O consumed during serpentinization are change as a function of the salinity. At 1 wt% the rates are ~4 mol% H<sub>2</sub>O loss a day, in a 3.5 wt% ~2 mol% H<sub>2</sub>O a day are consumed, in a 6 wt% salinity ~0.5 mol% H<sub>2</sub>O, and at 10 wt% ~0.04 mol% H<sub>2</sub>O is consumed a day. Our results agree with other published data for concentrations similar to seawater concentrations, and provide a new proxy to understand the how serpentinization happens in natural systems.

This method proves to be a useful technique to closely monitor reaction product compositions and to develop reaction rates as a function of fluid composition, concentration, and temperature.



Fig. A) Reaction progress in the synthetic fluid inclusions with time. Salinity increases as reaction progresses. B) Raman mapping showing the reaction products brucite, serpentine and H<sub>2</sub>.

#### REFERENCES

Sterner S.M. & Bodnar R.J. (1984) Synthetic fluid inclusions in natural quartz. I. Compositional types synthesized and applications to experimental geochemistry. Geochimica et Cosmochimica Acta, 48, 2659-2668.

# Evidence from the fluid inclusion record of halite saturation in magmatic-hydrothermal systems

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Porphyry deposits are well-exposed examples of magmatic-hydrothermal systems associated with hydrous, intermediate composition magmas emplaced in the upper continental crust. High salinity fluids are a common characteristic of the proximal region of these systems and result from fluid phase separation of a low-salinity magmatic-derived fluid. Phase equilibria of saline aqueous systems indicates that fluids in magmatic-hydrothermal systems may also become saturated in salt at sufficiently low fluid pressures.

Fluid inclusions that homogenize by halite disappearance (e.g., fluid inclusions in which halite dissolves at temperatures higher than the bubble disappearance) are common in magmatic-hydrothermal systems associated with upper crustal plutons. These fluid inclusions can result from:

- 1. High pressure trapping of a single-phase fluid such that upon heating the vapor bubble disappears before the halite crystal (Roedder and Bodnar, 1980)
- 2. Water loss due to post-entrapment modification (Audétat and Günther, 1999)
- 3. Heterogeneous trapping of a liquid+halite mixture (Becker et al., 2008)

In this study we evaluated the distribution of fluid inclusions that homogenize by halite disappearance in porphyry systems and analyzed the thermometric data reported in the literature. We further discuss which of the hypothesis presented above are compatible with the thermometric behaviors commonly reported in porphyry systems and implications for fluid evolution in magmatic-hydrothermal systems associated with upper crustal plutons (Lecumberri-Sanchez et al. 2015).

#### REFERENCES

Audétat, A., and Günther, D., 1999, Mobility and H<sub>2</sub>O loss from fluid inclusions in natural quartz crystals: Contributions to Mineralogy and Petrology, v. 137, p. 1–14

Becker, S.P., Fall, A., and Bodnar, R.J. (2008) Synthetic fluid inclusions. XVII. PVTX properties of high salinity H2O-NaCl solutions (>30 wt % NaCl): Application to fluid inclusions that homogenize by halite disappearance from porphyry copper and other hydrothermal ore deposits: Economic Geology, v. 103, p. 539–554

Lecumberri-Sanchez, P., Steele-MacInnis, M., Weis, P., Driesner, T., Bodnar, R.J. (2015) Salt precipitation in magmatic-hydrothermal systems associated with upper crustal plutons: Geology, v.13, p. 1063-1066

Roedder, E., and Bodnar, R.J., 1980, Geologic pressure determinations from fluid inclusion studies: Annual Review of Earth and Planetary Sciences, v. 8, p. 263–301

### Fluid chemistry in a tungsten-vein deposit: Panasqueira

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Tungsten has a high heat resistance, density and hardness, which makes it widely applied in industry (e.g. steel, tungsten carbides). Tungsten deposits are typically magmatic-hydrothermal systems. Despite the economic significance of tungsten, there are no modern quantitative analytical studies of the fluids responsible for the formation of its highest-grade deposit type (tungsten vein deposits). Panasqueira (Portugal) is a tungsten vein deposit, one of the leading tungsten producers in Europe and one of the best geologically characterized tungsten vein deposits.

In this study, compositions of the mineralizing fluids at Panasqueira have been determined through combination of detailed petrography, microthermometric measurements and LA-ICPMS analyses, and geochemical modeling has been used to determine the processes that lead to tungsten mineralization. We characterized the fluids related to the various mineralizing stages in the system: the oxide stage (tin and tungsten mineralization), the sulfide stage (chalcopyrite and sphalerite mineralization) and the carbonate stage. Thus, our results provide information on the properties of fluids related with specific paragenetic stages. Furthermore we used those fluid compositions in combination with host rock mineralogy and chemistry to evaluate which are the controlling factors in the mineralizing process.

This study provides the first quantitative analytical data on fluid composition for tungsten vein deposits and evaluates the controlling mineralization processes helping to determine the mechanisms of formation of the Panasqueira tin-tungsten deposit and providing additional geochemical constraints on the local distribution of mineralization.

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## Investigating differentiation of MORB to plagiogranite through phase equilibrium experiments in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-H<sub>2</sub>O system

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The formation of oceanic crust at a mid-ocean ridge (MOR) involves magmatic and hydrothermal processes which create various type of igneous rocks and associated ore systems. A narrow horizontal gabbro-sheeted dike transition zone is usually considered the place where magmatic and hydrothermal systems overlap (Zhang et al., 2014). Notably in both drill core and ophiolites, we often observe very felsic plagiogranites sandwiched between the upper gabbros and the sheeted dikes. The genesis of plagiogranite is widely debated about whether it is controlled by extreme fractional crystallization of a mantle melt or partial melting of hydrated mafic crust. However, neither model can perfectly explain the observations such as trace elements and isotopes (Grimes et al., 2013, Wanless et al., 2010, 2011, Michael et al., 1989).

Recent work suggests an alternative differentiation mechanism whereby a crystal-melt mush within a temperature gradient evolves to silicic compositions by a process called wet thermal migration. In a 66 day piston cylinder experiment at 0.5 GPa, Huang et al. (2009) showed that andesite + 4 wt.% H<sub>2</sub>O starting material evolved to granite at the cold end of a 950-350°C thermal gradient. The diffusion-limited process of thermal migration can only affect magma compositions over >m scales if it is coupled to mm/yr rates of magma accretion (Lundstrom, 2009). Thus, we postulated that the MOR setting at the gabbro-sheeted dike contact (and a connected melt lens) might be the perfect "open system" setting to allow thermal migration to operate. To test this, we can use stable isotope ratios which are sensitive to isotope fractionation in thermal gradients (Huang et al. 2010). Notably, we have found that Fe and Si isotope ratios change systematically along a gabbro to plagiogranite transect within the Troodos ophiolite, consistent with the prediction (Huggett, 2015).

Why does the wet thermal migration of andesite form a granite at what are considered "sub-solidus" temperatures? Previous works suggest that quartz and feldspars can exist with hydrous peralkaline melt at temperatures below 400°C (Tuttle and Bowen, 1958). However, quantification of melt water content was not possible and surprisingly, no work in combined Na<sub>2</sub>O-K<sub>2</sub>O systems has occurred. Thus, there is a need to further study phase equilibria and melt composition (water and major elements) in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-



Figure 1. Na<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> tetrahedron with Petrogeny's residua shown as light gray plane. Darker plane represents the cotectic surface of quartz and feldspar. The orange arrow shows predicted melts in Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system (work in progress) while black arrow points to melt found by Lundstrom (2015). Na<sub>2</sub>O-H<sub>2</sub>O system to further understand why andesite evolves to granite in a thermal gradient. As a first step, Lundstrom (2016) did a series of low temperature (330 °C and 400 °C) experiments whereby peralkaline melt was equilibrated with feldspar components and prefractured guartz (to trap melt inclusions) at 0.5-1 kbar. XRD and xray analysis demonstrate Qtx+Albite+Kspar coexists with melt at 330-400°C. Heating stage analysis of gtz-trapped melt inclusions shows that a single phase fluid was trapped at experimental conditions indicating the melt was water undersaturated. Confocal laser Raman analysis of these inclusion indicate >40 wt.% H<sub>2</sub>O. Analysis of anhydrous melt components indicates these weight percents: SiO2, ~63; Al2O3, <2; Na2O, 30; K2O, 9. This water and alkali-rich and aluminum-poor melt is consistent with melts found in K2O-Al2O3-SiO2-H2O (Tuttle and Bowen 1958).

Given previous works and Lundstrom (2016), we suggest the more pertinent phase diagram to granite formation is the water bearing  $SiO_2-Al_2O_3-K_2O-Na_2O$  tetrahedron with a quartz–feldspar saturated surface moving down temperature with distance away from

Petrogeny's residua (Fig. 1). A key question is whether a continuum of melt compositions (in terms of alkalis and H2O) exists from the minimum melt point on Petrogeny's residua out to the Na2O-K2O-SiO2 plane. Current experiments in progress seek to obtain compositional information of melt inclusions trapped in pre-fractured quartz grains in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-H<sub>2</sub>O system at temperatures from 850 °C to 350 °C (and 1 kbar). By varying temperature and added Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> component, we seek to constrain how water content of melt increases down the quartz albite surface (the orange line in Figure 1. As a by-product of these down-temperature phase equilibrium experiments, we plan to measure the Si isotope fractionation factor between quartz and albite at different temperatures as well as investigate the Ti in quartz geothermometer. Regardless of whether this wet thermal migration process is applicable to MOR or any setting, this work will provide more detailed data about phase equilibria at temperatures relevant to metamorphism and hydrothermal activities.

It appears that water rich peralkaline melt can coexist with granitic assemblages at temperatures less than 650°C. This has important implications as small amounts of this interstitial melt can act as a carrier of mass transport and accelerator for the achievement of chemical equilibrium by its reactive nature. Addition of more components and trapping of melts via quartz provides the method by which we build a predictive database to understand the role of such melt in the upper crust. Currently we are far from application these (the volatile and major elements) behaviors to a more complex system, such as midocean ridge environment.

#### References:

Huang, F., Lundstrom, C. C., Glessner, J., Ianno, A., Boudreau, A., Li, J., ... & DeFrates, J. (2009). Chemical and isotopic fractionation of wet andesite in a temperature gradient: experiments and models suggesting a new mechanism of magma differentiation. *Geochimica et Cosmochimica Acta*, *73*(3), 729-749.

Huang, F., Chakraborty, P., Lundstrom, C. C., Holmden, C., Glessner, J. J. G., Kieffer, S. W., & Lesher, C. E. (2010). Isotope fractionation in silicate melts by thermal diffusion. *Nature*, *464*(7287), 396-400. Huggett, Nicholas L., (2015) Making oceanic plagiogranite bodies by thermal migration: evidence from the Agros transect, Troodos ophiolite, Cyprus. M.S. Thesis, Department of Geology, University of Illinois at Urbana-Champaign.

Lundstrom, C. (2009). Hypothesis for the origin of convergent margin granitoids and Earth's continental crust by thermal migration zone refining. *Geochimica et Cosmochimica Acta*, 73(19), 5709-5729.

Lundstrom, C. C. (2016). The role of thermal migration and low-temperature melt in granitoid formation: can granite form without rhyolitic melt?. *International Geology Review*, *58*(3), 371-388.

Michael, P. J., & Schilling, J. G. (1989). Chlorine in mid-ocean ridge magmas: evidence for assimilation of seawater-influenced components. *Geochimica et Cosmochimica Acta*, *53*(12), 3131-3143.

Tuttle, O. F., & Bowen, N. L. (1958). Origin of granite in the light of experimental studies in the system NaAlSi<sub>3</sub>O<sub>8</sub>–KAlSi<sub>3</sub>O<sub>8</sub>–SiO<sub>2</sub>–H<sub>2</sub>O. *Geological Society of America Memoirs*, 74, 1-146.

Wanless, V. D., Perfit, M. R., Ridley, W. I., & Klein, E. (2010). Dacite petrogenesis on mid-ocean ridges: evidence for oceanic crustal melting and assimilation. *Journal of Petrology*, *51*(12), 2377-2410. Wanless, V. D., Perfit, M. R., Ridley, W. I., Wallace, P. J., Grimes, C. B., & Klein, E. M. (2011). Volatile abundances and oxygen isotopes in basaltic to dacitic lavas on mid-ocean ridges: the role of assimilation at spreading centers. *Chemical Geology*, *287*(1), 54-65.

Zhang, C., Koepke, J., Kirchner, C., Götze, N., & Behrens, H. (2014). Rapid hydrothermal cooling above the axial melt lens at fast-spreading mid-ocean ridge. *Scientific reports*, *4*.

### Chemical and isotopic comparison of Illinois Basin brines and fluid inclusions in the Illinois-Kentucky Fluorspar District: Implications for the origin, paleohydrology, and preservation of Permian ore fluids

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Topographically driven fluid flow related to Permian uplift of the Ouachita fold belt is believed to have caused brine to migrate >1200 km from the Arkoma-Black Warrior basin, northward through the Reelfoot rift, to the Upper Mississippi Valley (UMV) Pb-Zn district at the northern margin of the Illinois basin (Rowan and Goldhaber, 1995; Rowan and Marsily, 2001). Basal Cambrian-Ordovician siliciclastic and Mississippian karst aquifers are inferred to be the primary fluid conduits for brine migration. The IL-KY Fluorspar district formed along normal faults in the Mississippian aquifer near Hicks dome at the northern end of the Reelfoot rift from hot (~130°C), saline (~ 20 wt. % NaCl) residual brines produced by the evaporation of seawater (Viets et al., 1994, Pelch et al., 2015). The similar age of the IL-KY Fluorspar district (~272 ±14 Ma) and mafic alkalic dikes (272 ±1 Ma) at Hicks dome (Chesley et al., 1994) led to speculation that concealed intrusions supplied heat and HF laden magmatic vapor to migrating brines (Plumlee et al., 1995). Importantly, there is no geologic evidence for Mesozoic or Cenozoic evaporites in the region and, therefore, no later source of brine to recharge the Illinois basin. Thus, we evaluate the possibility that modern brines in the Illinois basin are, in fact, remnants of Permian brines that formed the IL-KY Fluorspar and UMV Pb-Zn districts.

To evaluate this hypothesis and to look for evidence of magmatic fluid input, we compiled published elemental and H-O isotopic data on modern brines in Cambrian through Pennsylvanian units (N=503; Clayton et al., 1966; Siegel and Mandel, 1984; Stueber and Pushkar, 1987; Walter et al., 1990; Stueber et al., 1993; Demir and Seyler, 1999; Chen et al., 2001; Panna et al., 2013; Labotka et al., 2015) and bulk extraction and single fluid inclusion data from minerals in the IL-KY Fluorspar district (N=948; e.g. Hall and Friedman, 1963; Cunningham and Heyl,1980; Richardson and Pinckney, 1984; Richardson et al., 1988; Spry et al., 1990; Spry and Fuhrmann, 1994; Kesler et al., 1995; Viets et al., 1996; Pelch et al., 2015). To fill data gaps we collected additional T<sub>h</sub>, salinity, elemental, and isotopic data (N=31). Our data and that collected by different workers using different analytical methods were found to yield comparable results. To utilize both concentration and element ratio data, all data were normalized to molar element ratios. The following parameters were compared on a series of X-Y plots: T<sub>h</sub>, NaCl eq. wt. %, Cl/Br, Na/Br, Na/Cl, Na/K, Na/Mg, Na/Ca, Na/Sr, and Na/Ba, Na deficit, and Ca excess.

The Na/Cl, Na/Br, Cl/Br, Na/K, and Na/Ca ratios show that Permian fluid inclusions in the IL-KY Fluorspar district and modern brines in Cambrian-Ordovician siliciclastic units have strikingly similar compositions that are typical of brines formed by evaporation of seawater well beyond halite saturation. However, the Na/Mg and Na/Sr ratios of fluid inclusions are higher than those of brine in the Cambrian-Ordovician units. Similarly, Pelch et al. (2015) found that Na/Mg ratios of fluid inclusions in the IL-KY Fluorspar district are higher than those in other midcontinent MVT districts. The high Na/Mg and Na/Sr ratios may be due to magmatic fluid inputs or reactions with country rocks in the Fluorspar district.

Unlike the Cambrian-Ordovician units, the Silurian-Pennsylvanian units contain halite dissolution brines, which may have been derived from Mississippian and Silurian evaporites in the region, as suggested by previous workers.

The H and O isotopic and salinity variations of fluid inclusions provide evidence for infiltration of meteoric water and mixing with evaporative brine in Permian time during precipitation of paragenetically late calcite, barite, and witherite (Richardson et al., 1988). Mixing between Pleistocene glacial melt water and both evaporative brine in Cambrian-Ordovician units and halite dissolution brine in Silurian-Pennsylvanian units is evident at the north end of the basin (Siegel and Mandle, 1984).

The evidence indicates that remnants of the fluid that formed the Permian IL-KY Fluorspar district are still present in Cambrian-Ordovician units of the Illinois basin. This interpretation supports previous models for northward fluid flow in the region and demonstrates the importance of density stratification in the preservation of brines in sedimentary basins. There is only limited and/or inconclusive evidence for magmatic fluid inputs.

REFERENCES

- Chen, Z., Riciputi, L.R., Mora, C.I., Fishman, N.S. (2001) Regional fluid migration in the Illinois basin: Evidence from in situ oxygen isotope analysis of authigenic K-feldspar and quartz from the Mount Simon Sandstone. Geology. 29. 1067-1070.
- Chesley, J.T., Halliday, A.N., Kyser, T.K., Spry, P.G. (1994) Direct dating of Mississippi Valley-type mineralization: Use of Sm-Nd in fluorite. Economic Geology. 89. 1192-1199.
- Clayton, R.N., Friedman, I., Graf, D.L., Mayeda, T.K., Meents, W.F., Shimp, N.F. (1966) The Origin of Saline Formation Waters. Journal of Geophysical Research. 71. 3869-3882.
- Cunningham, C.G. and Heyl, A.V. (1980) Fluid inclusion homogenization temperatures throughout the sequence of mineral deposition in the Cave-In-Rock area. Economic Geology. 75. 1226-1231.
- Demir, I. and Seyler, B. (1999) Chemical Composition and Geologic History of Saline Waters in Aux Vases and Cypress Formations, Illinois Basin. Aquatic Geochemistry. 5. 281-311.
- Hall, W.E. and Friedman, I. (1963) Composition of fluid inclusions, Cave-In-Rock fluorite district, Illinois, and Upper Mississippi Valley zinc-lead district. Economic Geology. 58. 886-911.
- Kesler, S.E., Appold, M.S., Martini, A.M., Walter, L.M., Huston, T.J., Kyle, J.R. (1995) Na-Cl-Br systematics of mineralizing brines in Mississippi Valley-type deposits. Geology. 23. 641-644.
- Labotka, D.M., Panno, S.V., Locke, R.A., Freiburg, J.T. (2015) Isotopic and geochemical characterization of fossil brines of the Cambrian Mt. Simon Sandstone and Ironton-Galesville Formation from the Illinois Basin, USA. Geochimica et Cosmochimica Acta. 165. 342-360.
- Panno, S.V., Hackley, K.C., Locke, R.A., Krapac, I.G., Wimmer, B., Iranmanesh, A., Kelly, W.R. (2013) Formation waters from Cambrian-agte strata, Illinois Basin, USA: Constraints on their origin and evolution. Geochimica et Cosmochimica Acta. 122. 184-197.
- Pelch, M.A., Appold, M.S., Emsbo, P., Bodnar, R.J. (2015) Constraints from Fluid Inclusion Compositions on the Origin of MVT Mineralization in the Illinois-Kentucky District. Economic Geology. 110. 787-808.
- Plumlee, G.S., Goldhaber, M.B., Rowan, E.L. (1995) The potential role of magmatic gases in the genesis of IL-KY fluorspar deposits: Implications from chemical modeling. Economic Geology. 90. 999-1011.
- Richardson, C.K., Pinckney, D.M. (1984) The Chemical and Thermal Evolution of the Fluids in the Cave-In-Rock District: Mineralogy, Paragenesis, and Fluid Inclusions. Economic Geology. 79. 1833-1856.
- Richardson, C.K., Rye, R.O., Wasserman, M.D. (1988) The Chemical and Thermal Evolution of the Fluids in the Cave-In-Rock Fluorspar District, Illinois: Stable Isotope Systematics at the Deardorff Mine. Economic Geology. 83. 765-783.
- Rowan, E.L. and Goldhaber, M.B. (1995) Duration of mineralization and fluid-flow history of the Upper Mississippi Valley Zinc-Lead district. Geology. 23. 609-612.
- Rowan, E.L., and de Marsily, G. (2001) Infiltration of Late Paleozoic evaporative brines in the Reelfoot rift: a possible salt source of Illinois basin formation waters and MVT mineralizing fluids. Petroleum Geology. 7. 269-279.
- Siegel, D.I. and Mandle, R.J. (1984) Isotopic Evidence for Glacial Meltwater Recharge to the Cambrian-Ordovician Aquifer, North-Central United States. Quaternary Research. 22. 328-335.
- Spry, P.G. and Fuhrmann, G.D. (1994) Additional Fluid Inclusion Data for the Illinois-Kentucky Fluorspar District: Evidence for the Lack of a Regional Thermal Gradient. Economic Geology. 89. 288-306.
- Spry, P.G., Koellner, M.S., Richardson, C.K., Jones, H.D. (1990) Thermochemical changes in the ore fluid during deposition at the Denton Mine, Cave-In-Rock District. Economic Geology. 85. 172-181.
- Stueber, A.M. and Pushkar, P. (1987) A strontium isotopic study of formation waters from the Illinois basin, U.S.A. Applied Geochemistry. 2. 477-494.
- Stueber, A.M., Walter, L.M., Huston, T.J., Pushkar, P. (1993) Formation waters from Mississippian-Pennsylvanian reservoirs, Illinois basin, USA: Chemical and isotopic constraints on evolution and migration. Geochimica et Cosmochimica Acta. 57. 763-784.
- Viets, J.G., Hofstra, A.H., Emsbo, P. (1996) Solute compositions of fluid inclusions in sphalerite from North American and European Mississippi Valley-Type ore deposits: Ore fluids derived from evaporated seawater. Society of Economic Geologists. 4. 465-482.
- Walter, L.M., Stueber, A.M., Huston, T.J. (1990) Br-Cl-Na systematics in Illinois basin fluids: Constraints on fluid origin and evolution. Geology. 18. 315-318.

### New fluid inclusion evidence of multi-phase hydrocarbon migration in fracture systems of Triassic–Jurassic strata of SW Hungary

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Despite thousands of wells drilled over the past 75 years in Hungary, no oil or gas fields have been discovered in the Mecsek Mountains region of western Hungary. This study is the first to apply modern fluid inclusion techniques to identify and delineate hydrocarbon migration pathways in this region.

Fracture and void-filling calcite, dolomite and quartz cements contain hydrocarbon-bearing fluid inclusion assemblages at four localities in the Mecsek Mountains, Southwest Hungary (Pécsvárad, Pécs-Vasas, Kantavár, Árpádtető,) in strata of Triassic to Early Jurassic age. Secondary hydrocarbon-bearing fluid inclusions (HCFIs) found in calcite veins in the Early Jurassic Hosszúhetény Calcareous Marl Formation near Pécsvárad are colorless in plane polarized light and display yellowish blue, light blue and vivid blue fluorescence under UV-light. These inclusions homogenize to the liquid phase at temperatures between 30 °C and 100 °C (Lukoczki et al. 2012). Primary, green fluorescent HCFIs in quartz crystals were found in the Pécs-Vasas coal pit at the contact of magmatic dykes and silty sandstones (Mecsek Coal Formation, Early Jurassic). These contain gas-dominant two-phase fluid inclusions (gas+liquid), which homogenize to the gas phase between 93 °C and 97 °C suggesting entrapment from a gas phase (Jáger, V., pers. comm.). Blue fluorescent HCFIs were found in calcite veins in a quarry at Kantavár (Kantavár Formation, Late Triassic). This abstract focuses on the HCFI occurrences at Árpádtető.

At Árpádtető, HCFIs are present in planar-s dolomite crystals in medium crystalline host dolomite rock, as well as in fracture-filling calcite, void-filling saddle dolomite, and in quartz cements. The fracture-filling, medium to coarse crystalline blocky calcite appears as thin (<1cm) veins cross-cutting the host dolomite rock, but not affecting the other cement phases. The medium to coarsely crystalline saddle dolomite occurs as void lining cement, where the medium to extremely coarsely crystalline subhedral quartz, where present, is the final cement phase. Based on textural relationships, a calcite  $\rightarrow$  dolomite  $\rightarrow$  quartz cement paragenesis can be established.

The dolomite rock contains blue fluorescent HFCIs in trails that cross-cut several crystals, implying a secondary origin. These fluid inclusions are very small (<5  $\mu$ m) and not suitable for further analysis. In the fracture-filling calcite fluid inclusions are small (<10  $\mu$ m) and contain two phases (liquid<sub>aq/hc</sub>+vapor/gas; aq=aqueous, hc=hydrocarbon). Sparse, blue-fluorescent HCFIs are scattered in the calcites, which makes the determination of their primary or secondary origin difficult. Also, their small sizes impede their detailed investigation. The void-filling saddle dolomites contain small (<10  $\mu$ m) HCFIs arranged mostly along growth zones, suggesting a primary origin. Both the aqueous and the HCFIs contain two phases (liquid<sub>aq/hc</sub>+vapor/gas) and the hydrocarbon-bearing liquid displays blue fluorescence in UV-light. Again, due to their small sizes further investigations of these fluid inclusions could not be performed.

Three fluid inclusion generations were distinguished in the void-filling quartz crystals: one aqueous and two with hydrocarbon-bearing fluids. Phase volume ratios were estimated visually.

- Aqueous fluid inclusion generation (Aq-FIG): Primary, two-phase (liquid+vapor) aqueous fluid inclusions (5–20 μm) occur with constant volume ratios, the liquid phase being the dominant. The shape of the fluid inclusion vacuole is usually angular.
- Hydrocarbon fluid inclusion generation 1 (HC-FIG-1): Secondary one-, two- and three-phase HCFIs (liquid<sub>aq/hc</sub>, liquid<sub>aq</sub>+liquid<sub>hc</sub>, liquid<sub>aq/hc</sub>+gas and liquid<sub>aq</sub>+liquid<sub>hc</sub>+gas) (5–30 μm) occur with varying volume ratios. The fluid inclusion vacuoles have irregular shapes, in many cases with the presence of necks, suggesting necking-down. The hydrocarbon-bearing liquid is colorless in plane polarized light and displays blue fluorescence under UV-light.
- Hydrocarbon fluid inclusion generation 2 (HC-FIG-2): Large (50–200 μm), variously shaped, three- or four-phase secondary HCFIs (liquid<sub>hc</sub>+solid+gas, liquid<sub>aq</sub>+liquid<sub>hc</sub>+solid+gas) have yellowish brown color in plane polarized light and display blue fluorescence under UV-light. The solid phase occurs seemingly attached to the inclusion walls, has brown color, and displays no fluorescence under UV-

light. The liquid<sub>hc</sub>–solid–gas volume ratios are constant in the three-phase HCFIs. A rim of aqueous liquid is discernible under UV-light in some of the HCFIs. Co-genetic two-phase (liquid<sub>aq</sub>+vapor) aqueous fluid inclusions could not be distinguished.

 $T_h$  measurements were performed on fluid inclusion assemblages (FIA) only from Aq-FIG and HC-FIG-2. The two-phase (liquid+vapor) primary aqueous fluid inclusions of FIA-1 from Aq-FIG homogenized to the liquid phase between 129 °C and 156 °C (n=11), and the vapor phase did not reappear upon cooling. Threephase HCFIs with constant liquid-solid-gas volume ratios of FIA-1 from HC-FIG-2 homogenized to the liquid phase between 76 °C and114 °C (n=76), and the solid phase did not show any phase changes during heating up to 200 °C.

These data are interpreted as follows: *T*<sub>h</sub> data from Aq-FIG represents the minimum temperature of formation of the quartz cement. HC-FIG-1, the colorless secondary fluid inclusion generation with variable phase ratios, suggest entrapment of a heterogeneous fluid containing hydrocarbon and aqueous liquids. HC-FIG-2, with constant liquid–solid–vapor volume ratio, suggests the presence of a homogeneous hydrocarbon-bearing fluid during entrapment, *i.e.*, the aqueous phase present in the inclusions may have been wall-wetting water or H<sub>2</sub>O dissolved in the HC fluid and exsolved upon cooling. The solid phase likely is a hydrocarbon daughter phase that may have formed from the hydrocarbon liquid. Lack of phase change upon heating may be explained by irreversible alterations, such as hydrogen diffusion (Goldstein 2003). The blue fluorescence of both secondary fluid inclusion generations likely is caused by mature hydrocarbon content, although other factors can also be responsible for blue fluorescence of hydrocarbon fluids, *i.e.*, source rock that expelled hydrocarbons with low concentrations of fluorescence quenchers, or mixing with dry gas (Oxtoby 2002).

Primary HCFIs at Árpádtető occur in saddle dolomite cement, which formed at elevated temperature (Lukoczki & Haas 2013) suggesting that hydrocarbon migration occurred during deep burial and/or is related to hydrothermal events, likely during the Early Cretaceous when the Middle Triassic carbonates were deeply buried and magmatic events occurred in the Mecsek Mountains (Vető-Ákos 1978).

Differences between the hydrocarbons entrapped in fluid inclusions at Árpádtető (colorless and yellowish brown HCFI generations) and at other localities (Pécsvárad, Pécs-Vasas, Kantavár) suggest multiple stages of hydrocarbon migration and/or different source rocks. Five Mesozoic formations can be considered as potential source rocks in the Mecsek Mountains (Badics & Vető 2012; Lukoczki et al. 2012). However, it remains an open question which stratigraphic units served as the source rock(s) for the hydrocarbons entrapped in the studied fluid inclusions. Chemical alteration of the hydrocarbons due to thermal or biogenic processes during migration or during/after entrapment also could have led to the differences observed at each occurrence.

This study leads to two important conclusions and a question: i) oil and/or gas have migrated through the Triassic–Early Jurassic strata of the Mecsek region multiple times, most likely during and after the Early Cretaceous; ii) considering the lack of success in hydrocarbon exploration in the Mecsek Mountains and surrounding region in the past, commercially significant amounts of hydrocarbons may not have been generated; and iii) where did the hydrocarbons that migrated within and through the region eventually go?

#### REFERENCES

- Badics, B. & Vető, I. (2012) Source rocks and petroleum systems in the Hungarian part of the Pannonian Basin: The potential for shale gas and shale oil plays. Mar. and Pet. Geol. 31, 53–69.
- Goldstein, R. H. (2003) Petrographic analysis of fluid inclusions. In: Samson, I., Anderson, A., Marshall, D. (eds): Fluid inclusions: Analysis and interpretation. Mineral. Assoc. Can., Short Course 32, 9–53.
- Lukoczki G., Schubert F., Hámor-Vidó M. (2012) Traces of hydrocarbon migration near Pécsvárad (Mecsek Mts.) Földtani Közlöny 142/3, 229–241.
- Lukoczki G., Haas J. (2013) Diagenetic history of Middle Triassic shallow marine carbonate rocks of South-Transdanubia. Proceedings of the 4th Petrographical-Geochemical Congress, Orfű, Hungary, September 12–14, 2013, 21–25.
- Oxtoby, N. H. (2002) Comments on: Assessing the maturity of oil trapped in fluid inclusions using molecular geochemistry data and visually-determined fluorescence colours. Applied Geochemistry 17/10, 1371–1374.

Vető-Ákos, É. (1978) Fluid-gas inclusion test for reconstructing the palaeotemperature of the Mesozoic near Pécs, S Hungary. M. Áll. Földtani Intézet Évi Jelentése, 309–318.

# Fluid inclusions that homogenize by halite disappearance in porphyry copper deposits: Heterogeneous entrapment along the liquid-vapor-halite curve

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Halite-bearing fluid inclusions (FIs) commonly contain an aqueous liquid, one or more solid phases, and a vapor bubble at room temperature. During heating from room temperature, the liquid-vapor homogenization (ThI-v) of a halite-bearing FI may occur at temperature higher than, lower than, or equal to the halite dissolution temperature (Tm<sub>halite</sub>). Microthermometric data from FIs that homogenize by halite disappearance indicate that inclusions may have (1) trapped a high salinity, single-phase liquid at high pressure (Roedder and Bodnar, 1980); (2) re-equilibrated, i.e., loss of H<sub>2</sub>O from the inclusions (Audétat and Günther, 1999); or (3) heterogeneously trapped solid halite together with liquid under halite-saturated conditions (Becker et al., 2008). Natural halite-bearing FIs that homogenize by halite dissolution are nearly ubiquitous in porphyry copper deposits, and also occur in many other ore forming environments. For most of the porphyry copper deposits, the formation pressure estimates are much lower than the pressures determined from the FIs that show  $Tm_{halite} > ThI-v$  (Lecumberri-Sanchez et al., 2015). Additionally, published studies reported the coexistence of vapor-rich FIs with FIs that homogenize by halite dissolution, and that fluid inclusion assemblages (FIAs) with  $Tm_{halite} > ThI-v$  show no evidence of post-entrapment modification. These results exclude scenarios (1) and (2) as major contributors to the formation of FIs that homogenize by halite dissolution.



Fig 1A Image of synthetic fluid inclusions trapped at 250 bars and 450-650°C; 1B Plot of the liquid –vapor homogenization (ThI-v) and halte disapperance (Tm<sub>halite</sub>) temperature of synthetic, halite bearing fluid inclusions.

In this study, fluid inclusions were synthesized in quartz in the presence of known brine compositions (50 wt% with KCI/NaCI=1:9) at 250 bars, and at the temperature of 450-650°C. Then, the ThI-v and Tmhalite were determined on the Linkam TS1400XY stage. At room temperature, halite-bearing FIs formed by healing fractures were concentrated along the edge of each chip where the fracturing was most intense. Halite-bearing and vapor-rich FIs coexist in the same FIAs (Fig 1A), and few vapor FI contain a halite solid phase. Microthermometric data were obtained from 159 FIs in 5 samples. As shown in Fig 1B, 39 inclusions homogenize by halite dissolution. These FIs should represent heterogeneous trapping of liquid and halite.

An additional 53 inclusions have simultaneous ThI-v and Tmhalite, which indicates that FIs only trapped an NaCI-saturated liquid. The rest of the inclusions homogenize by vapor bubble disappearance. The data suggest that FIs either trapped liquid + vapor ± halite or experienced leakage or necking down. Petrographic and microthermometric analyses are in good agreement with previous published results of natural inclusions from porphyry copper deposits. The widespread occurrence of inclusions that homogenize by halite dissolution in porphyry copper deposits could be a direct consequence of halite saturation and heterogeneous entrapment along the liquid-vapor-halite curve.

#### REFERENCES

Audétat, A. and Günther, D. (1999) Mobility and H2O loss from fluid inclusions in natural quartz crystals. Contributions to Mineralogy and Petrology. 137. 1-14.

Becker, S.P., Fall, A. and Bodnar, R.J. (2008) Synthetic fluid inclusions. X VII. PVTX properties of high salinity H2O-NaCl solutions (>30 wt% NaCl): Application to fluid inclusions that homogenize by halite disappearance from porphyry copper and other hydrothermal ore deposits. Economic Geology. 103. 539-554.

Lecumberri-Sanchez, P., Steele-MacInnis, M., Weis, P., Driesner, T. and Bodnar, R.J. (2015) Salt precipitation in magmatic-hydrothermal systems associated with upper crustal plutons. Geology. 43. 1063-1066.

Roedder, E. and Bodnar, R.J. (1980) Geologic pressure determinations from fluid inclusion studies. Annual Review of Earth and Planetary Sciences. 8. 263-301.

### Fluid inclusions in stibnite from the Yellow Pine deposit, Idaho

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The historic Yellow Pine Au-Sb-W mining district in east central Idaho is located in the Atlanta lobe of the Cretaceous Idaho batholith adjacent to the Eocene Thunder Mountain Caldera. Mineralization is localized along dilatant second order faults and damage zones related to the regional NE-trending Meadow Creek fault (Stewart et al., 2015). In the Yellow Pine and Hangar flats deposits, ore is hosted in Cretaceous quartz monzonite, granite, alaskite and pegmatite dikes. In the West End deposit, ore occurs in roof pendants comprised of metamorphosed Lower Paleozoic sedimentary rocks. In the West End deposit, veinlets and alteration halos contain adularia that produced an age of ~51 Ma (51.7 Ma  $\pm$  0.3 Ma, 51.0  $\pm$  0.4 Ma and 50.8  $\pm$  0.3 Ma; Gillerman et al., 2014). In drill core from the Yellow Pine deposit, 4 vein types are common: (1) preore quartz veins with brassy, medium- to fine-grained pyrite, (2) ore stage veinlets filled with dark, fine-grained pyrite +/- quartz, (3) late ore stage, coarse-grained stibnite-quartz veins, and (4) post ore, pink dolomite or calcite veinlets. To advance understanding of ore formation in this hydrothermal system, the character of fluid inclusions associated with each vein type is being studied. Herein we present results on fluid inclusions in the stibnite-quartz veins (Fig. 1).

Polished thick sections of the stibnite-quartz veins were examined using infrared microscopy (Campbell et al., 1984). Stibnite laths generally form massive aggregates that are intergrown with local quartz crystals. The stibnite is commonly highly fractured, in which case it generally lacks visible inclusions. In unfractured stibnite crystals, four inclusion populations have been observed at room temperature: type 1a elongate liquid-rich inclusions along growth planes (~7-10% vapor); type 1b stubby liquid-rich inclusions, which may be the cross-section view of type 1a; type 2 gas-rich inclusions that occur in cross-cutting trails; type 3 single-phase (empty?) inclusions that occur along growth planes; and small type 4 liquid-rich inclusions (3% vapour) that occur in in cross-cutting trails (Fig. 1).

Heating runs on the fluid inclusions assemblages (FIAs) proved difficult because individual inclusions would often decrepitate, generating cracks that opened neighboring inclusions. On cooling the liquid-rich FIAs, no clathrate was observed. Microthermometry of the type 1a and 1b inclusions in the stibnite yielded  $Tm_{ice} = -2.3$  to  $-7.3^{\circ}C$  and Th = 160 to  $189^{\circ}C$ . For type 2 inclusions,  $Tm_{ice} = -3.9$  to  $-6.5^{\circ}C$  and inclusion decrepitation occurred between 144 and  $195^{\circ}C$ . For type 4 inclusions,  $Tm_{ice}=0^{\circ}C$  and  $Th=105^{\circ}C$ . In the type 3 single phase inclusions, no phase changes were observed during cooling to  $-196^{\circ}C$ , although they may simply be too dark to see through. Secondary inclusion trails in quartz phenocrysts in the altered host cut by the stibnite veins contain three phase aqueous carbonic inclusions and laser Raman spectra indicate the presence of  $CO_2$  and  $CH_4$ . Although the relative timing of the secondary inclusions in the quartz and the type 3 inclusions in stibnite is uncertain, the single phase inclusions may contain  $CO_2$  or  $CH_4$ , or perhaps they are just water vapor. Mass spectrometric analysis of inclusions in the stibnite-quartz veins will be undertaken to determine their gas compositions.

Based on these data, the stibnite at Yellow Pine was deposited from moderately saline (4.2-10.9 wt. %) fluids at temperatures (160-189°C) and pressures (11-6 bars) typical of the epizonal environment. Similar results have been obtained on liquid-rich inclusions in stibnite from antimony deposits in Germany (Th=115-170°C Tm<sub>ice</sub> = 0 to -3°C, Lüders, 1996); and in France (Th=142-240°C and Tm<sub>ice</sub> = -0.5 to -4 °C, Baily et al., 2000). The temperature of homogenization for the stibnite is 10 to 30°C lower (see Bennett et al., this volume) than that for the inclusions measured in associated quartz, suggesting that decompression and cooling maybe the cause of stibnite precipitation.



Figure 1: Photomicrographs of fluid inclusions in stibnite from the Yellow Pine deposits A) type 1a elongate liquid-rich primary inclusion B) type 1b stubby liquid-rich primary inclusions C) type 2 gas-rich secondary inclusions.

#### REFERENCES

Bailly, L., Bouchot, V., Bény, C., and Milési, J. P., 2000, Fluid inclusion study of stibnite using infrared microscopy: An example from the Brouzils antimony deposit (Vendee, Armorican massif, France): Economic Geology, v.95, p.221-226.

Bennett, M., Marsh, E., and Hofstra, A., 2016, Cathodoluminescence and Fluid Inclusion Investigations in Quartz: Preliminary Results from the Yellow Pine Au-Sb deposit, Idaho: Pan-American Current Research on Fluid Inclusions (PACROFI-XIII) University of Missouri—Columbia, May 24-26, 2016, Abstract Volume

Campbell, A.R., Hackbarth, C.J., Plumlee, G. S., and Petersen, U., 1984, Internal features of ore minerals seen with the infrared microscope: Economic Geology, v.79, p.387-1392

Gillerman, V.S., Schmitz, M.D., Benowitz, J., layer, P.W, 2014, Geochronology of intrusive rocks and hydrothermal alteration at the structurally controlled Stibnite Au-Sb-W deposit, Idaho: GSA Annual Meeting, Abstracts with programs, v. 46, No. 6 p. 165.

Lüders, V., 1996, Contribution of infrared microscopy to fluid inclusion studies in some opaque minerals (wolframite, stibnite, bournonite): Metallogenic implications: Economic Geology, v. 91, p. 1462–1468.

Stewart, D.E., Stewart, E.D., Lewis. R.S., and Weppner, K.N., 2015, Geologic map of the Stibnite quadrangle, Valley County, Idaho: Draft Plate 1, Idaho Geological Survey, University of Idaho, Moscow, Idaho.

### Melt inclusions of native-silver and native-bismuth at Cobalt, Ontario: An example of native-metal enrichments using experimental and in-situ melting studies.

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Early work on metal-sulphide or native metal melts in naturally occuring samples (*cf.* Hofmann, 1994; Tomkins and Mavrogenes, 2002) pioneered some new thinking on models on metal transport and enrichment in a variety of ore deposit models. Veinlets and trails of melt inclusions of both native bismuth (Fig. 1) and silver crosscutting silicate and carbonate vein fill and alteration minerals in the five-element veins at Cobalt, Canada. The low melting temperature of bismuth (271 °C) is consistent with the current estimates of vein formation at Cobalt and melt textures are displayed with native bismuth (Bi) inclusions and trails. Native silver displays identical textures and these are also interpreted to have formed from a melt. However, native silver melts above 950 °C, which is in direct conflict with current estimates of silver deposition within the Cobalt camp. In light of the similarities in textures, existing temperature evidence, the lack of experimental studies in the Co-As-Ag ternary, and recent advances in the study of melt inclusions in sulfide deposits, the native silver textures were also interpreted to have formed at temperatures as low at 350 °C (Marshall, 2008).

The silver-bearing five-element veins at Cobalt, Ontario have produced almost a half a billion ounces of silver. The silver in these veins contains minimal amounts of a few weight percent of dissolved mercury, antimony, and bismuth. Fluid inclusion evidence is consistent with high salinity fluids at Cobalt. Experimental studies using silver compositions with high CI contents, and minor amounts of Hg, Sb, and Bi utilize "gravity-dribble" experiments. These experiments place known mixtures of metals at the top of a graphite capsule, overlying a column of graphite spheres. The capsule is then placed within a piston-cylinder apparatus with a calibrated vertical temperature-gradient ranging from 550 °C at the top of the capsule to 300 °C at the bottom of the capsule. If the metal-salt mixture at the top of the capsule melts it dribbles down through the network of graphite spheres until either it cools sufficiently within the thermal gradient to partially solidify or it ponds at the bottom of the capsule. These experiments show that the silver (+Bi +Hg +Sb +Cl) melts remain liquid at temperatures down to 375 °C. The experiments are consistent with increased Sb and Hg concentrations in silver solidifying at higher temperatures, with slightly higher concentrations of Bi persisting in the melts to lower temperatures.

Veinlets of native bismuth and associated trails of metallic inclusions of native bismuth (Fig 1) have been studied using a standard fluid inclusions heating-freezing stage coupled to a Laser Raman microprobe to perform in-situ melt experiments of the bismuth solid inclusions from the silver deposits at Cobalt Ontario. The bismuth veinlets and solid inclusions exposed at surface have been analysed with an SEM equipped with EDS detector and are virtually pure bismuth. Bismuth exposed at the surface of a doubly polished plate shows some laser damage from Raman analysis and this develops a corresponding Raman peak at approximately 312 cm-1. This peak is attributed to bismuth-oxide (Trentleman, 2009) and is not seen and does not develop on a solid inclusion of native bismuth entirely contained within the host mineral. A single bismuth solid inclusion hosted within calcite was heated and the Raman spectrum recorded. Although thermoluminescence and fluorescence in the host calcite does present some analytical challenges, the 95



Fig. 1. Composite Raman spectra of sub-surface bismuth melt inclusions hosted in calcite over a range of temperatures. At room temperature three peaks for calcite at 180, 308, and 707 cm<sup>-1</sup> and the two peaks for bismuth metal at 95 and 68 cm<sup>-1</sup> are present. However, the bismuth peaks disappear upon melting at 235 °C. Inset: a veinlet of native bismuth terminating in a trail of native bismuth solid inclusions hosted in calcite. The bismuth exposed at surface (red arrows) is polished and reflective while the inclusions contained in the host (black arrows) are dark and non-reflective.

and 68 cm-1 Raman bands diminish and disappear at 235 °C indicating that the bismuth was molten by this temperature. This is well below the melting point of pure bismuth. Silver is Raman inactive, however trace amounts of other unidentified compounds within solid silver inclusions display Raman peaks. These inclusions heated can be while collecting Raman spectra at various temperatures. When these peaks from the unknown compounds within the inclusions disappear and do not reappear on cooling to room temperature, it is these interpreted that solids have moved out of the beam path because the silver has melted. These experiments suggest that silver inside these solidsilver inclusions melts at approximately 300 °C.

Evidence from dribble experiments and Raman data are consistent with the observed temperatures of formation for the silver veins at Cobalt, Ontario and consistent with silver and bismuth mobilization and concentration as molten metals.

#### REFERENCES

Hofmann, B.A. 1994. Formation of a sulfide melt during Alpine metamorphism of the Langenbach polymetallic sulfide mineralization, Binntal, Switzerland. Mineralium Deposita, 29, 439-442.

Marshall, D., 2008. Melt inclusions of native-silver and native-bismuth: A mechanism for native-metal enrichments in five-element deposits. Geoscience Canada, 35, 137-145.

Tomkins, A.G., and Mavrogenes, J.A. 2002. Mobilization of gold as a polymetallic melt during pelite anatexis at the Challenger deposit, South Australia: A metamorphosed Archean gold deposit: Economic Geology, 97, 1249–1271.

Trentelman, K. 2009. A note on the characterization of bismuth black by Raman microspectroscopy. Journal of Raman Spectroscopy, 40, 585-589.

### Integration of fluid inclusion studies with in situ micro-analysis (SIMS, LA ICP-MS) to address the nature of fluids in diagenetic settings

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Understanding fluid and mineralization processes using the classic approach of bulk analysis on a large sample set has become all but obsolete in this age of in situ analytical methods. Instead of the traditional broad-brush methods, a detailed in situ micro-analytical study on a small representative sample set can be used to characterize an entire basin or deposit. For example, secondary ion mass-spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometer (LA ICP-MS) can measure and detect variations in isotopic (e.g.,  $\delta^{18}$ O,  $\delta^{34}$ S) and geochemical composition (e.g., REE), respectively, of adjacent phases or within a single phase at the micron-scale. This scale allows for highly detailed insight into the processes responsible for the phase(s) in question. Integration of fluid inclusion and evaporate mound analyses into a study provides direct information about the precipitating fluid that can then be used to augment data from the other analytical methods.

The multi-analytical in situ approach presented here demonstrates the power of integrating multiple in situ techniques. The combined data set provides a detailed understanding of the geological history of an area, with respect to fluid behavior. In addition to great refinement and detail, this approach enables the use of information from one technique to supplement missing or ambiguous information (e.g., metastable fluid inclusions and thus no salinity) obtained using another technique. Ambiguities are commonly encountered in interpretations, and without key information, the ambiguities may be unresolvable. Each technique; this can then be carried forward to resolve ambiguities elsewhere, causing a domino effect. For example, the temperature and salinity provided by fluid inclusions can be used to refine isotopic interpretations, which can lead to timing constraints, which can lead to fluid mobilizing events. Other issues, such as limitations of individual techniques, can be overcome. For example, fluid inclusions can identify if precipitation was the result of fluid cooling or fluid mixing, by recording homogenization temperatures and fluid salinities, but if fluid inclusions are necked and/or metastable at low temperatures, or if different fluids have similar characteristics, other techniques, such as evaporate mound analysis, are required to determine fluid behavior.

Examples from Victoria Island (Northwest Territories, Canada) are used to demonstrate the efficiency of this protocol in determining diagenetic histories. Mathieu et al. (2013) used evaporate mound analyses to supplement a fluid inclusion study because of issues with metastability. The combined methods pointed to fluid mixing and possible sources for the fluids but scope for further interpretation was limited. Stable isotope (O and S) and REE geochemistry was then incorporated (Mathieu et al., 2015) to characterize the diagenetic history of two areas more completely. This approach allowed for identification of fluid sources, fluid pathways and rock interactions, water-rock ratios, timing, and precipitation mechanism for diagenetic cements.

#### REFERENCES

Mathieu, J., Kontak, D.J., and Turner, E.C. (2013) A fluid inclusion study of diagenetic fluids in Proterozoic and Paleozoic carbonate rocks, Victoria Island, NWT. Geolfuids, v. 13(4), p. 559-578.
Mathieu, J., Kontak, D.J., Turner, E.C., Fayek, M., and Layne, G (2015) Geochemistry of Phanerozoic diagenesis on Victoria Island, NWT, Canada. Chemical Geology, v. 415, p. 47-69.

## Characterization of copper mineralization at the Storm copper showing, Cornwallis District, Arctic Canada

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The Cornwallis District in the Canadian arctic hosts, in addition to the world-class Polaris Zn-Pb deposit (20 Mt at 13.4 %Zn and 3.6 %Pb; operational 1982-2002), numerous other Zn-Pb showings; copper showings, conversely, are much fewer. The Storm Cu showing on Somerset Island is a promising sediment-hosted showing with potential of being a deposit. Copper mineralization at Storm is associated with gangue minerals (dolomite and calcite) that provide information that lends to the better understanding of the diagenetic and mineralization history of this area. The mineral paragenesis is summarized in Figure 1 along with representative photos of the ore and cements, including fluid inclusions, in Figure 2. In situ multi-analytical techniques on fluid inclusions (i.e., microthermometry, SEM-EDS analysis of evaporate mounds) and cement phases and sulfide mineralization (SIMS for  $\delta^{18}$ Ov-SMOW and  $\delta^{34}$ Sv-CDT; LA ICP-MS for trace and REE) were combined to fully characterize the mineralizing fluids and their histories.

Copper mineralization is hosted by Paleozoic Allen Bay Formation dolostone and can be divided into four assemblages: (A1) early copper, (A2) main copper 2, (A3) replacement copper, and (A4) secondary

	A1	A2	A3	A4
Dstn -	-8			
Dolomite	D1	D2		
Calcite			<u></u> C1	<u>C2</u>
Quartz				-
Pyrite	Py1	Py2		
Chalcopyrite	Cpy1	Сру2	Сру3	
Bornite	_			
Digenite				
Covellite				
Native copper				—
Hematite				
Cuprite				
Atacamite				

**Figure 1.** Paragenesis of Storm Cu mineralization that shows the relative timing of mineral precipitation.

copper alteration; whereas the A1 and A2 are hypogene in origin, A3 and A4 are possibly supergene. A1 minerals record the incursion of (at least) two reduced (i.e., cements lack shale-normalized Ce anomalies) and moderately saline (17 wt. % equiv. NaCl) fluids that equilibrated with surrounding rocks at depth ( $T_h = 110^{\circ}C$ ,  $\delta^{18}O_{H2O}$  = +10‰) and mixed on site (variable fluid cation concentration). Sulfur ( $\delta^{34}S_{Cpv}$  = 0‰) was probably sourced from the Proterozoic igneous/gneissic basement rocks based on +Eu anomalies for shalenormalized REE patterns of cements and Krich-mound chemistry, whereas copper was sourced from sedimentary units. A2 minerals record the presence of (at least) two reduced (cements lack shale-normalized Ce anomalies), moderately saline (qualitatively assumed) fluids that equilibrated with surrounding rocks at depth ( $T_h = 110^{\circ}C$ ,  $\delta^{18}O_{H2O}$  = +10‰) and mixed on site (variable fluid cation concentration). Sulfur ( $\delta^{34}S_{Cpy}$  = 20‰) was probably sourced from seawater

sulfate, whereas Cu was sourced from sedimentary units. A3 minerals record single (uniform fluid composition) oxidized (cements have a negative shale-normalized Ce anomaly), low-salinity (0.3 wt. % equiv. NaCl) meteoric ( $\delta^{18}O_{H2O} = <-0\%$ ) fluid that upgraded copper through supergene processes. A4 minerals record passage of a single oxidized (cements have a negative shale-normalized-Ce anomaly), low-salinity (qualitatively assumed) meteoric ( $\delta^{18}O_{H2O} = <-10\%$ ) fluid that leached copper and other metals from pre-existing copper phases, precipitating secondary copper minerals. Late-stage alteration in an arid environment precipitated atacamite.

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**Figure 2.** Reflected- and transmitted-light photomicrographs of copper phases and FIAs in their associated carbonate cement in (A and B) Assemblage 1 (A1) chalcopyrite (Cpy) and Dolomite1 (D1), (C and D) A2 Cpy2 and D2, (E and F) A3 Cpy3 and Caclite 1, and (G and H) A4 cuprite (Cp) altered to atacamite (At) and dendritic native copper (Cu).

The above data indicate the for this sediment-hosted mineralization the main stage Cu event represents hypogene enrichment rather than the product of supergene processes. The changing pathways recorded by the fluids of the different assemblages may reflect changing tectonic influence during the Ellesmerian Orogeny at ca. 400-350 Ma, with the latest oxidized meteoric alteration taking place after the orogeny, and probably quite recently (high-latitude meteoric fluid).

Despite analytical and interpretive challenges, which commonly complicate this type of study, the multianalytical approach provided the necessary information from one technique that was needed to interpret the data from another technique. The detailed fluid and mineralization history achieved through the combination of techniques is beyond that which can be obtained through traditional studies.

## Chemistry of ore fluids during sphalerite growth: OH Vein, Creede Mining District, San Juan Mountains, Colorado

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Detailed fluid inclusion studies were conducted on 4 samples of coarse-grained sphalerite from the OH vein, Creede, Colorado (Fig. 1). The sample sites (PMB-AI, PMB-BS, PBB-83 and PBB-89) are from different mine levels in the OH vein (~250, ~350, ~400, and ~450m, respectively) and exhibit 3 to 5 color bands or growth zones that contain fluid inclusions with a wide range of  $T_h$  and salinity. The most distinctive marker is the outer-orange-brown-band that is preceded by an inner-yellow-white-band and succeeded by an outer-yellow-white-band. In sample PMB-BS, the outer-yellow-white-band is succeeded by outer-orange-brown-band2 and outer-yellow-white-band2. In each band, there are large, primary, liquid-rich inclusions with ~20 volume % vapour (Fig. 1b) as well as smaller, secondary, inclusions with similar phase ratios (Fig. 1c).

Roedder (1977) reached three important conclusions pertinent to sphalerite growth in the OH vein: (1) the color band variations in sphalerite are paralleled by changes in temperature and salinity of fluid inclusions, (2) salinity and temperature do not simply decrease with time, and (3) the temperature and salinity of fluid inclusions typically change abruptly at each zone boundary, but remain constant during the growth of each band. The  $T_h$ , salinity, H and O isotope variations led Hayba (1997) to conclude that mixing at the interface between moderately saline hydrothermal fluids derived from moat sediments in the adjacent Creede caldera with overlying dilute meteoric ground water was the dominant ore-forming process in the OH vein.

To enhance understanding of the chemical composition and source(s) of salt and volatiles in ore fluids during sphalerite growth in the OH vein, several modern analytical techniques were applied to primary and secondary fluid inclusion assemblages (FIA) in each color band in each sample. The large size of the sphalerite crystals, growth bands, and fluid inclusions (Fig. 1) made it possible to conduct laser raman spectroscopy (LRS), high-resolution sector mass spectrometry (HRSMS), microthermometry, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and ion chromatography (IC) on several FIA. As needed, background subtractions were made to account for contributions from the host sphalerite and the chemical composition of the host sphalerite was determined by LA-ICP-MS. The measured FIA compositions were compared to fluid compositions calculated from equilibrium chemical models (Plumlee, 1994).

In each FIA, LRS analyses of the vapour phase for CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> were below detection. HRSMS analyses of noble gases (He, Ne, Ar) in extracts from 4 primary FIA were at or near blank levels, which precluded isotopic analysis. The low abundance of active and noble gases in the extracts suggests that ore fluids were degassed prior to trapping, as proposed by Plumlee (1994) and Hayba (1997).

Salinities (6-16 wt. %) were calculated from Tm<sub>ice</sub> using the H<sub>2</sub>O-NaCl system because IC data show that Na and Cl are the predominant ions; dark bands have the highest salinities. The salinity of each FIA was used to calculate ppm Na and Cl, which served as the internal standards for LA-ICP-MS and IC.

Elements detected by LA-ICP-MS in the sphalerite host above and/or below the analyzed fluid inclusions that yielded consistent data ( $\leq$  1 order of magnitude) across multiple growth bands include in decreasing order of abundance: Zn, S, Fe, Cd, Mn, and In, with higher Fe in the dark bands. In contrast, the abundance of Cu, Ag, and Ga varies by more than 2 orders of magnitude. Ga-zoning is unusual in that it is independent of the Fe-zoning in sphalerite.

Elements detected by LA-ICP-MS in primary and secondary FIA with positive inter-element correlations include in decreasing order of abundance: Na, Ca, K, Mn, Sr, Li, Ba, Rb, Mg, Cs, W, Bi and Ce. The inner-yellow-white-band is distinct in that it contains more Cs. At the lower concentration side of the distribution, Cu and Ag have a positive correlation with these elements. Uncorrelated elements include Al, As, Ga, Sb, Tl, and Pb. Accidental trapping of minerals is evidenced by single inclusions with high In, Au, or Mo-W-Bi, several inclusions in the outer-yellow-white-band with high Mg ± Al, and

numerous inclusions in each band with high Cu, Pb, Ag, or Ga. The weak correlation of Mg with Al is probably due to accidental trapping of a Mg-Al silicate such as chlorite. Given that galena and chalcopyrite are intergrown with sphalerite and native silver is present in the system (Barton et al. 1977), the variability of Cu, Pb, and Ag at high concentrations is probably due to accidental trapping of these minerals. Although Ga may substitute into the sphalerite lattice (Cooke et al. 2009), its association with high Al, Cu, and Ag in fluid inclusions suggests that the highest values are due to mineral inclusions or, perhaps, to erroneous background subtractions due to fine scale Ga-zoning in sphalerite.

lons detected by IC in primary and secondary FIA extracts with positive inter-ion correlations include in decreasing order of abundance: Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and Br<sup>-</sup>. Uncorrelated ions include Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, F<sup>-</sup>, and acetate. S<sub>2</sub>O<sub>3</sub><sup>2-</sup> is produced by the oxidation of reduced S species during analysis. Li<sup>+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, and PO<sub>4</sub><sup>3-</sup> were detected in a few extracts. Accidental trapping of anhydrite in fluid inclusions is evident in some FIA extracts with high Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>.

In comparison to the model fluid compositions, the FIA have similar abundance of CI, Na, Ca, K, Pb, and Ba but higher AI, Cu, and Ag. However, the lowest measured S<sub>red</sub>, F, Cu, and Ag concentrations in the FIA are similar to those in the model fluids. This relationship supports our interpretation that accidental trapping of mineral inclusions in fluid inclusions was relatively common, as noted recently by Pelch et al. (2015). Consequently, only the minimum concentrations of the affected elements in an FIA may be representative of their abundance in ore fluids.

The Na/CI and CI/Br ratios of the fluid inclusion extracts cluster near the bottom of the field for diverse magmatic hydrothermal deposits (Hofstra and Emsbo, 2005), which suggests that the salt in ore fluids derived from the Creede caldera during sphalerite growth was exsolved from underlying intrusions. The multielement correlations in FIA across the sphalerite crystal stratigraphy suggests that there were 2 input fluids that were diluted to varying degree by local meteoric water. The input fluid in FIA from the inner-yellow-white-band is enriched in Cs compared to the input fluid in FIA from the other bands. Cooling and dilution of the input fluids led to sphalerite precipitation (Plumlee, 1994; Hayba, 1997) and can account for the variations in  $T_h$  and salinity documented by Roedder (1977).



Figure 1. A. Coarse-grained sphalerite crystal (PBB-83) with schematic showing three growth bands (i.e. inneryellow-white-band (IYWB), outer-orange-brown-band (OOBB), and outer-yellow-white-band (OYWB)). B. Primary FIA in the IYWB. C. Secondary FIA in the OOBB.

#### REFERENCES

- Barton P.B. Jr., Bethke P.M., and Roedder, E. (1977) Environment of ore deposition in the Creede mining district, San Juan Mountains, Colorado: Part III. Economic Geology. 72. 1-24.
- Cook N.J., Ciobanu C.L., Pring A., Skinner W., Shimizu M., Danyushevsky L., Saini-Eidukat B., Melcher F. (2009) Trace and minor elements in sphalerite: A LA-ICPMS study. Geochimica et Cosmochimica Acta. 73. 4761-4791.
- Hayba D.O. (1997) Environment of Ore Deposition in the Creede Mining District, San Juan Mountains, Colorado: Part V. Epithermal Mineralization from Fluid Mixing in the OH Vein. Economic Geology. 92. 29-44.
- Hofstra A.H. and Emsbo P. (2005) Source of salt in hydrothermal fluids based on Na–Cl–Br of fluid inclusions. Geochimica et Cosmochimica Acta, 69 (Suppl), 881.
- Pelch, M. A., Appold, M. S., Emsbo, P., and Bodnar, R. J. (2015) Constraints from fluid inclusion compositions on the origin of Mississippi Valley-Type mineralization in the Illinois-Kentucky District. Economic Geology. 110. 787-808.
- Plumlee G.S. (1994) Fluid Chemistry Evolution and Mineral Deposition in the Main-Stage Creede Epithermal System. Economic Geology. 89. 1860-1882.
- Roedder E. (1977) Changes in ore fluid with time, from fluid inclusion studies at Creede, Colorado: In: IAGOD Symposium, 4<sup>th</sup>, Varna, Bulgaria, 1974, Proceedings, 2. 179-185.

## Diagenetic history of Mississippian carbonate rocks in the Nemaha Ridge area, north-central Oklahoma, USA

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Mississippian rocks in north-central Oklahoma were deposited on a ramp/shelf system that trended along an approximate northeast-southwest strike and that deepened to the southeast and southwest into the Arkoma and Anadarko basins. This system is bounded by the Ozark uplift on the east and by the Anadarko Basin to the west. Structure in this area is dominated by faulting associated with the Transcontinental Arch (Nemaha Uplift). Shallower water (shelf) depositional settings dominate in the northern part of the study area and deepen toward the south into the basins (Fig. 1) (LeBlanc, 2014).

Subsurface cores of Mississippian carbonate rocks on and near the Nemaha Ridge were studied. Sedimentary rocks on the carbonate ramp are dominated by cyclic, partially dolomitized, argillaceous mudstones interbedded with fine grain wackestones to grainstones (LeBlanc, 2014). Fracture and vug porosity are filled by calcite and less commonly, by quartz cements. Fracture- and vug-filling calcite and quartz cements display a coarse, blocky habit. The calcite cements typically are uniform bright orange to faintly zoned under cathodoluminescence (CL) excitation. Quartz cements display no CL response.

The  $\delta^{18}O_{(VPDB)}$  and  $\delta^{13}C_{(VPDB)}$  values of calcite micrite and cemented skeletal debris (n=41) average -3.5% and +1.0%, respectively (Fig. 2). The  $\delta^{18}O$  and  $\delta^{13}C$  values for dolomite replacing limestone (n=4) average -0.4% and +2.5%, respectively. Those for fracture-filling calcite cements range from -1.1 to -7.6% and +2.3 to -4.9%, respectively. Carbon and oxygen isotope values for limestones and replacive dolomite are consistent with precipitation from Mississippian seawater and mixed seawater-meteoric water. Stable isotope values for fracture-filling calcite cements are consistent with precipitation from Seawater and evolved basinal waters. Strontium isotope data for calcite micrite, replacement dolomite, and fracture-filling calcite range from  ${}^{87}$ Sr/ ${}^{86}$ Sr values of 0.7077 to 0.7112. The lower values are consistent with Mississippian seawater through most of the study area. More radiogenic  ${}^{87}$ Sr/ ${}^{86}$ Sr values for fracture-filling calcite cements in the northeast part of the study area indicate interaction with continental basement or siliciclastic rocks derived from continental basement.

Two-phase (liquid plus vapor) aqueous and petroleum inclusions were observed in fracture-filling calcite and quartz cements. The two-phase aqueous inclusions have homogenization temperatures ranging from 48° to 156°C and have salinities ranging from 0 to 25 equivalent weight % NaCl, reflecting the presence of dilute and saline fluid end-members (Fig. 3). Calculated equilibrium  $\delta^{18}O_{water}$  values (VSMOW) for fluids that precipitated fracture-filling calcite cements are variable, ranging from -0.3 to +14.5‰, and do not reflect a single end-member water.

Early diagenesis was dominated by seawater cementation with likely modification by meteoric water during sea level low-stands. Fracture-filling calcite and quartz represent a later stage of diagenesis associated with petroleum generation and migration. Overlapping calculated  $\delta^{18}O_{water}$  values for carbonate cement and host limestone in most areas of north-central Oklahoma suggest cement-depositing fluids approached isotopic equilibrium with the host carbonate rocks. Alternatively, the overlapping values could represent mixing between resident and non-resident fluids, dominated by resident fluids in equilibrium with the host limestone.

#### REFERENCES

Harris, S. A. (1987) Hydrocarbon accumulation in "Meramec-Osage" (Mississippian) rocks, Sooner Trend, Northwest-Central Oklahoma. In B. Rascoe, Jr., and N. J. Hyne, eds. Petroleum geology of the mid-continent. Tulsa Geological Society Special Publication 3. 74-81.

LeBlanc, S. L. (2014) High resolution sequence stratigraphy and reservoir characterization of the "Mississippian limestone" in north-central Oklahoma. M.S. thesis. Oklahoma State University. 449 p.



Figure 1. Map of Oklahoma showing the study area (tan rectangle), core localities, the Mississippian isopach, and major regional structural features.



Figure 2. The  $\delta^{18}O$  and  $\delta^{13}C$  values (per mil VPDB) for carbonate samples in the study area.



Figure 3. Fluid inclusion assemblages measured in fracture-filling calcite and quartz cements plotted as  $T_h$  values vs. salinity.

### The CO<sub>2</sub> content of primitive bubble-bearing island-arc melt inclusions: a comparative study of Raman-spectroscopy of melt inclusion bubbles, mass-balance calculations and experimental homogenization of melt inclusions

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In the interest of constraining the volatile budgets of the Earth's interior, melt inclusions are a valuable tool because they provide a geologically persistent record of melt volatile contents before they degas to the atmosphere during volcanic eruptions. However, melt inclusions require special care because of the possibility for volatile elements to diffuse from the glass into a separate fluid phase (bubble; e.g.  $CO_2$ ) or out of the olivine host (e.g.  $H_2O$ ). For example, Mironov et al. (2015) recently demonstrated that it is possible to completely homogenize naturally dehydrated melt inclusions under high  $H_2O$  pressure and controlled  $fO_2$  and redissolve all the  $CO_2$  lost to vapor bubbles into the melt (glass). We used these experimental data and obtained  $CO_2$  content in melt inclusions to test an alternative approach based on Raman spectroscopy of vapour bubbles and mass-balance calculations (following the methods described by Moore et al., 2015) to quantify bulk  $CO_2$  contents of primitive arc melt inclusions from the same samples studied by Mironov et al. (2015).

The inclusions analysed come from two populations of olivine phenocrysts from the Klyuschevskoy volcano: 1) naturally quenched H<sub>2</sub>O-rich inclusions from tephra samples, and 2) naturally-dehydrated H<sub>2</sub>Opoor inclusions from lava samples, experimentally reheated and partially homogenized (melt+vapor bubbles) at 1 atm. We were able to quantify the density of CO<sub>2</sub> in 37/77 the natural inclusions and 11/20 of the reheated samples using Raman spectra. In general, the reheated inclusions tend to have larger bubbles (~3-10 vol%) than the natural inclusions (~1-5 vol%) and contain a lower density fluid (reheated: up to ~0.17  $g/cc CO_2$ ; natural: up to ~0.21  $g/cc CO_2$ ). Additionally, a carbonate peak is present in some of the Raman spectra of the natural inclusions, indicating that carbonate minerals are present on the surface of the bubble. Also, a secondary set of CO<sub>2</sub> peaks in the Raman spectra of the reheated inclusions suggests that CO<sub>2</sub> may be present as a liquid near the surface of the vapor bubble, so that the total density of the fluid in some of the reheated inclusions is significantly higher than the range given above. Although we have not analyzed the CO<sub>2</sub> content of the glass, it is possible to calculate minimum concentrations of CO<sub>2</sub> in the inclusions using mass balance calculations that ignore CO<sub>2</sub> in the glass. The amount of CO<sub>2</sub> stored in the bubbles corresponds to about 1400-2400 ppm for the natural inclusions and about 2300-4000 ppm for the reheated inclusions (interguartile range). Our minimum CO<sub>2</sub> contents for the reheated inclusions are in agreement with the results obtained by the rehydration method. Because we observed more CO<sub>2</sub> in the bubbles of reheated samples it is apparent that during dry reheating conditions, most of the CO<sub>2</sub> in the glass – and possibly some of the "CO2" in carbonates - has likely diffused into the bubble. This suggests that the rehydration technique of Mironov et al. (2015) is an effective way to rehomogenize melt inclusions, and that dry reheating will remove CO<sub>2</sub> from the glass and carbonates and sequester them in fluid bubbles.

Finally, in order to compare CO<sub>2</sub> contents obtained using both independent approaches, we calculated bulk (glass + bubble) CO<sub>2</sub> concentrations using a range of analyses of melt inclusion glass from the naturally-quenched tephra samples (880-1200 ppm; Mironov et al., 2015), and the reheated lava samples (80-270 ppm; Mironov & Portnyagin, 2011). For both cases, we used the upper quartile value obtained from Raman analysis of bubbles to account for the effect of degassing. Restored CO2 concentrations are about 3280-3600 ppm for naturally-quenched melt inclusions and 4080-4270 ppm for reheated melt inclusions, which are in agreement with the range of 3600-4000 ppm for completely homogenized melt inclusions reported by Mironov et al. (2015) using the experimental rehydration method.

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Figure 1: Results of Raman spectroscopic analyses of bubble-bearing melt inclusions from Klyuchevskoy Volcano. Circles and triangles represent naturally-quenched and reheated (dry + 1 atm) inclusions respectively. Contours represent the minimum  $CO_2$  concentration for bubble-bearing inclusions as a function of bubble volume fraction and vapor density. The shaded region indicates uppermost  $CO_2$  concentrations of rehydrated melt inclusion glasses (i.e.  $CO_2$  content of completely homogenized melt inclusions) analyzed by Mironov et al. (2015). Uncertainties for vapor density and bubble volume fraction ( $2\sigma$ ) are approximately ±0.02 g/cm<sup>3</sup> and ±0.02 (or 2 volume %) respectively.

#### REFERENCES

- Mironov, N.L., Portnyagin, M.V. (2011) H2O and CO2 in parental magmas of Klyuchevskoy volcano inferred from study of melt and fluid inclusions in olivine. Russ. Geol. Geophys v 52. p 1353-1367.
- Mironov, N., Portnyagin, M., Botcharnikov, R., Gurenko, A., Hoernle, K., Holtz, F. (2015) Quantification of the CO2 budget and H2O-CO2 systematics in subduction-zone magmas through the experimental hydration of melt inclusions in olivine at high H2O pressure. Earth Planetary Science Letters. v 425. p 1-11.
- Moore, L.R., Gazel, E., Tuohy, R., Lloyd, A.S., Esposito, R., Steele-Macinnis, M., Hauri, E.R., Wallace, P.J., Plank, T., Bodnar, R.J., (2015) Bubbles matter: An assessment of the contribution of vapor bubbles to melt inclusion volatile budgets. American Mineralogist. v 100. p 806-823.

# Characterization of mineralized fluids from Chancón mining district; applications in energy-related technologies

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Critical and strategic minerals do change with time. To develop new technologies, some elements are needed to produce, transmit, store and conserve energy. In recent years a wide variety of rare metals, including indium, selenium and tellurium, have found important applications in energy-related technologies such as advanced photovoltaic solar cells (Jaffe et al., 2011). These metals are produced commercially as a by-product in the refining of porphyry copper and similar ores, and from indium-selenium- and tellurium-rich epithermal deposits. The Chancón mining district shows characteristics and mineralization that can be produced as by-product from the gold mineralization (e.g. tellurium or selenium) to the base metal mineralization zinc (e.g. Indium). The proposed study will involve analyses in In, Se, and Te of well-characterized fluid inclusions from barren and mineralized veins to identify differences in fluid chemistry, including metal contents, that may help to better understand metal transport and deposition in these Andean systems.

The vein La Leona is located 69 km southwest from Santiago within the East of Coastal Range of Central Chile (34°07'S, 70°38'W). This deposit is an Au-Ag epithermal with base metal mineralization (e.g. sphalerite and galena) (Munzenmayer, 2002). Two paleogeographic periods characterize the mining district of Chancón. First event developed during Upper Cretaceous is marked as being a period of transition extension to compression and begins Chilean-type subduction (Charrier et al., 2007). In this period was deposited the main unit that form the mining district and its formed by dacitic and andesitic rocks (Munzenmayer, 2002). Subsequently, were emplaced monzodioritic intrusive bodies, product of the resumption of alkaline magmatism (Charrier et al., 2007; Munzenmayer, 2002). Second event developed during Paleogene is characterized by the emplacement of a dacitic intrusive and then a folding stage. Later tectonism generated fault and fractures that allowed the participation of magmatic fluids and meteoric water in the mineralizing event (Munzenmayer, 2002). Previous work by Anderson (1953) and Schwartz et al., (2002) indicate that in many cases some of base metal, are mineralized as sphalerite and galena, have significant concentration of Indium with potential to be exploited. This study provides the opportunity to better understanding of the Andean epithermal system and evaluates if these and other common features in epithermal deposits may used to detect, if exist, extractive potential for critical elements.

In the Vein La Leona, exist a mineral zonation from the surface to the base. The shallow part has minerals such as quartz, calcite, and pyrite, with gold and silver mineralization. While in the the deepest levels sampled shows minerals such as feldspar, chloride, epidote, chalcopyrite, sphalerite and galena. Petrographic evidence shows the evidence of primary and secondary Fluid Inclusion Assemblages (FIA's) hosted in quartz and were classified as containing (1) only liquid-rich inclusions with consistent liquid-to-vapor ratios, (2) secondary assemblages consisting of only vapor-rich inclusions (Fig. 1B), (3) liquid-rich inclusions with consistent liquid-to-vapor ratios hosted in sphalerite (Fig. 1A). Common quartz's textures are zonal, crustiform and jigsaw. The final product of this study will be a three dimensional model that relates host mineral charasteristics to fluid inclusion characteristics and ore grade and metal ratios to better understand the Andean epithermal system.

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Figure 1: Photomicrograph showing quartz under plain transmitted light. Primary FIA hosted in sphalerite (A). Secondary FIA consisting of only vapor-rich inclusions, indicative of "flashing" or intense boiling of the hydrothermal fluid.

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#### REFERENCES

- Anderson, J. (1953). Observations on the geochemistry of indium: Geochimica et Cosmochimica Acta, Vol 4 p. 225-240.
- Charrier, R., Pinto, L. and Rodríguez, M.P. (2007). Tectonostratigraphic evolution of the Andean Orogen in Chile. Geological Society Special Publication: The Geology of Chile: Londres, p. 21-114.
- Jaffe, R., Price, J.G., Ceder, G., Eggert, R., Graedel, T., Gschneidner, K.J., Hitzman, M., Houle, F., Hurd, A., Kelley, R., King, A., Milliron, D., Skinner, B. and Slakey, F. (2011). Energy critical elements: securing materials for emerging technologies. 28 p

Munzenmayer, M. (2002). Procesos de mineralización y alteración del distrito minero Chancón, VI Región, Chile. Memoria para optar al título de geólogo. Universidad de Concepción. Chile. 148 p.

Schwarz, U., Herzig, P., (2002). Indium. Geology, Mineralogy, and Economics: Springer Science and Business Media, 264p.

# Properties of fluids attending recrystallization of quartzite in the contact aureole of the Eureka Valley-Joshua Flat-Beer Creek Pluton, California

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The contact aureole of the Eureka Valley-Joshua Flat-Beer Creek (EJB) pluton in the White-Inyo Range in eastern California has undergone metamorphism, intense deformation and variable recrystallization during emplacement of the pluton. Quartzites, marbles, calc-silicates and schists dominate the aureole. The sedimentary formations were intensely attenuated and reoriented in a ductile manner to concordancy with the pluton's contacts during magma emplacement. Crystallographic preferred orientations and microstructures in quartzites have an unusual distribution in that within 250 m from the pluton, they exhibit mostly "low-temperature" deformation, including relic sedimentary grain shapes and only small amount of grain-boundary migration (Morgan et al., 2016). Further from the pluton, they generally exhibit complete recrystallization with extensively migrated grain boundaries. Oxygen isotope ratios in the inner aureole are only slightly shifted from their original values, but are more shifted in the outer aureole. The lack of extensive grain-boundary migration in the inner aureole is attributed to reduction of  $fH_2O$  due to reaction of quartz with calcite cement that produced wollastonite and CO<sub>2</sub>.

Fluid inclusions in the aureole were analyzed by microthermometry, Raman spectroscopy, and laser-ICP-MS to elucidate properties of fluids that attended contact metamorphism. Three types of inclusions occur in the quartzites: Type I are wholly aqueous, Type II are aqueous with vapor bubbles dominated by CH<sub>4</sub> with some N<sub>2</sub>, and Type III are aqueous with CO<sub>2</sub> bubbles. Types I inclusions occur along grain margins in both unrecrystallized and recrystallized quartzites and type II inclusions occur along grain boundaries of poorly recrystallized quartzite only. Both types have homogenization temperature (uncorrected for pressure) mostly between 150 and 250°C. In type II inclusions, the prevalence of CH<sub>4</sub> with minor N<sub>2</sub> in the carbonic component and presence of H<sub>2</sub>S in the aqueous phase indicate low *f*O<sub>2</sub> conditions in parts of the inner aureole. Type III inclusions are H<sub>2</sub>O-dominated but also contain CO<sub>2</sub>, which probably comes from reaction of H<sub>2</sub>O with graphite at elevated *f*O<sub>2</sub>. These inclusions only occur in interiors of recrystallized quartz grains. On average, they have the highest homogenization temperatures, in the range 250 to 550°C.

The aqueous phases of all three types of inclusions have freezing-point depressions and eutectic temperatures (-40 to  $-20^{\circ}$ C) that correspond to variable CaCl<sub>2</sub> and NaCl that dominate the solutes. KCl and FeCl<sub>2</sub> also occur in significant concentrations. The exceptions are -70 to  $-55^{\circ}$ C eutectic temperatures of the aqueous phase in type II inclusions, which are attributed to the presence of H<sub>2</sub>S.

The similar solute concentrations and homogenization temperatures of types I and II inclusions suggest that the trapped fluids are local pore fluids that equilibrated at high rock/water ratios with the metasedimentary rocks at the ambient greenschist-facies regional conditions. They were probably trapped during grain-boundary migration due to deformation. However, only the aqueous portion of the fluid was trapped because CO<sub>2</sub> that must have been present from production of wollastonite is not observed. Type III inclusions, which occur inside grains, probably represent bulk fluid composition that attended extensive grain-boundary migration in the outer aureole. However, their similar eutectic and freezing point depression temperatures to type I inclusions suggest that they also originated as pore fluids that were present in the metamorphic rocks before emplacement of the pluton. All inclusions reequilibrated to some extent after contact metamorphism and during uplift of the White-Inyo Range.

#### REFERENCE

Morgan, S.S., Nabelek, P.I., Student, J., Sadorski, J.F. (2016) Fluid-controlled grain boundary migration and switch in slip systems in a high strain, high temperature contact aureole, California, USA. Tectonophysics. In press

# Hydrocarbon Fluid Inclusions: Fluorescence Spectral Signatures - An indicator of API Gravity

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Fluid inclusions (FI) trapped and sealed in the cavities of framework/matrix mineral particles, are true- micro-samples of fluids that circulated during diagenetic mineral growth and/or subsequent lithification. FI technology is greatly diverse in its application in oil exploration and invaluable in the reconstruction of fluid flow histories in reservoir rocks, indirectly yielding valuable data on the temperature, salinity, and composition of circulating fluids through the basin fill in the geological past. Or else, FIs are micro- samples of circulating reservoir fluids through various lithological/ geological horizons. Neo-formed mineral particles in source/reservoir lithotypes host/trap micro samples of crude oil. Healed secondary micro fractures crosscutting mineral phases as well as cements trap large quantities of oil inclusions.

We researched the Hydrocarbon Fluid Inclusions (HCFI) trapped in neoformed single mineral particles or in diagenetic overgrowths on detrital grains derived from cuttings in a dry well (RV-1)in the producing Bombay High offshore basin of India. With an appropriate instrumentation, we captured and recorded the Fluorescence Emission Spectra of HCFIs in several grain samples. Also estimated was API gravity values of micro-samples of trapped oil in the same grains.

Estimation of API gravity is one of the several tests during pre- commercialisation of crude oil of any oil field. We report here a quick and reliable test to read off the API gravity of crude oil. For this we designed a X-Y plot or scatter-gram of API values vs. fluorescence emission spectral ratios of HCFIs and fitted a predicted straight line to this scattergram. The latter works as a handy predictive tool of API values of new crude oil samples, even if samples are in the micro-size.

Data on the fluorescence emission (FE) came from '13 live' oil samples with known API gravities using a laser excitation at 405nm. The calculated spectral emission ratios at F620/F560 and their corresponding API gravity values go to making the scattergram. An empirical relationship or a formula, defining the fitted straight line was also derived from the graph, which predicts the API gravity of oils of known Fluorescence emission ratio at F560/F620.

Further, FEs of HCFIs for 11 oil samples have been estimated (under conditions identical to the earlier run of 'live' samples) and the emission ratios at F620/F560 were calculated. These ratios of 11 samples were used to read off the corresponding API values from the above scattergram. This enabled testing of our empirical tool which gave elegant results and proved ease and reliability of estimating the API gravities of minutely sized HCFIs or micro-samples of oil - a significant leap forward in the petroleum exploration and industry.

#### REFERENCES

- 1. Roedder E (1984), Fluid inclusions. Mineralogical Society of America, *Reviews in Mineralogy and Geochemistry*, **12**, 1-644.
- 2. Goldstein RH (2001) Fluid inclusions in sedimentary and diagenetic systems, *Lithos*, **55**, 159-193.

## Variability of major-element chemistry of magmatic-hydrothermal fluids

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Experimental mineral solubility and derived thermodynamic data provide us with estimates of likely major-element concentrations and element ratios in hydrothermal fluids exsolved from felsic magmas that can be compared with LA-ICP-MS and other sources of fluid inclusion multi-element data.

Broadly uniform cation ratios have been determined for fluids in and associated with intrusion-centred magmatic-hydrothermal ores and occurrences of various metals (Audétat et al., 2008), and for intermediate density fluids in deeper levels of porphyry Cu±Au±Mo ore related hydrothermal systems that are interpreted to be ore fluids prior to phase separation (Landtwing et al., 2010; Rusk et al., 2004; Stevanova et al., 2014). Fluids in all of these settings have Na > K ~ Fe > Ca. Potassium/(K+Na) ratios on a mass basis of between 0.3 and 1 are consistent with the experimental results of Orville (1963) on Na and K partitioning between chloride-bearing waters and albite and K-feldspar at magmatic temperatures. Iron concentrations are likewise broadly consistent with the determination of equilibrium between magnetite, rhyolite melt and chloride solutions of Simon et al (2004). Calcium is infrequently reported in low-salinity inclusions, because of high limits of detection, and in contrast to Fe and K may be generally higher than Ca/(Ca+Na) ratios determined for equilibrium between plagioclase and water by Shmulovich and Graham (2008).

We have analysed fluid inclusions that can be interpreted as trapped magmatic-hydrothermal fluids within felsic intrusions in a number of tectonic settings that differ from those summarised above. All sites are potentially related to gold-only ores. Stable isotope data of vein quartz and host rock implies no or minimal input of externally derived waters into each hydrothermal system. The analyses include fluids from:

(a) Gold-bearing quartz - K-feldspar veins with sericitic alteration haloes at the Fort Knox Intrusion Related Gold Deposit (IRGD) in the Tintina Gold Province of Alaska.

(b) In unmineralised granodiorite in felsic stocks of the same intrusive suite as hosts the Fort Knox IRGD.

(c) In quartz-veins without alteration haloes, in quartz in pegmatitic segregations associated with aplite dykes in evolved granodiorite to granite mid- to upper-crustal plutons that are the same age as orogenic gold ores in adjacent greenstone belts in the Archean Wyoming and Yilgarn Cratons,

(d) In quartz-veins without alteration haloes, in quartz in pegmatitic segregations associated with aplite dykes in an evolved granodiorite to granite mid- to upper-crustal pluton along strike of the Carlin Trend gold deposits in Nevada and probably genetically related to the geophysically imaged intrusions below the deposits.

At all sites, the dominant inclusions are relatively low-salinity (2 – 9 wt% NaCl equivalent) with visible or detectable CO<sub>2</sub> content at all sites and in most inclusion assemblages. Conditions of inclusion entrapment are not in all cases well defined. Inclusion homogenisation is by vapour-phase disappearance at temperatures of 250 – 350 °C, consistent with the extent of the two-phase field for fluids of these compositions. For the veins with sericitic alteration haloes at the Fort Knox IRGD, entrapment temperatures of around 450 °C are implied based on vein and alteration mineralogy and estimated depths of intrusion emplacement. For all other sites, entrapment near the wet solidus (~ 650 °C) at pressures equivalent to the depths of intrusion (3 – 5 kbar) is inferred in view of the absence of down-temperature replacement of igneous minerals along vein margins. These conditions overlap pressures at ~ 650 °C estimated from inclusion densities. Fluid entrapment is thus interpreted to be at depths greater than those at which condensation of brine might take place from rising low-salinity fluids.

At all sites, the cation load of these low-salinity fluids are significantly different to those summarised above and can in contrast be described as Na > K > Ca > Fe. Potassium/(K+Na) ratios are most commonly around 0.1, but are at some sites as high as about 0.7. Concentrations of Fe and Ca are below limits of detection in many inclusions, but can be constrained to be at most a few 100's ppm, or in many cases lower. Compared to the experimental ratios, K/(K+Na) ratios extend to significantly lower values than experimental granitic magmatic-hydrothermal fluids, and Fe contents are at least an order of magnitude lower. Calcium/(Ca+Na) ratios overlap the experimentally determined range.

If we assume that we have not mis-interpreted the context of these fluids, at-source compositional variability can thus be inferred for the composition of hydrothermal fluids derived from intermediate to felsic magmas. It is further indicated that the available experimental results may not be universally applicable. The experiments were of necessity carried out in simplified chemical systems. Chloride was, in particular, the only anion in each set. In view of the dominance of ion-pairing in hydrothermal fluids at magmatic temperatures, additional or alternative anions may be present and may control fluid cation ratios.

#### REFERENCES

Audétat A, Pettke T, Heinrich CA and Bodnar R J (2008) The composition of magmatic-hydrothermal fluids in barren and mineralized intrusions. Economic Geology 103, 877-908.

Landtwing M R, Furrer C, Redmond P B, Pettke T, Guillong M and Heinrich C A (2010) The Bingham Canyon porphyry Cu-Mo-Au deposit. III: Zoned copper-gold ore deposition by magmatic vapor expansion. Economic Geology 105, 91-118.

Orville P M (1963) Alkali ion exchange between vapor and feldspar phases. American Journal of Science 261, 201-237.

Rusk B G, Reed M H, Dilles J H, Klemm L M and Heinrich C A (2004) Compositions of magmatic hydrothermal fluids determined by LA-ICP-MS of fluid inclusions from the porphyry copper-molybdenum deposit at Butte, MT. Chemical Geology 210, 173-199.

Shmulovich K I and Graham C (2008) Plagioclase-aqueous solution equilibrium: concentration dependence, Petrology 16, 177-192.

Simon A C, Pettke T, Candela P A, Piccoli P M and Heinrich C A (2004) Magnetite solubility and iron transport in magmatic-hydrothermal environments. Geochimica et Cosmochimica Acta 68, 4905-4914.

Stevanova E, Dreisner T, Zajacz A, Heinrich C A, Petrov P and Vasilev Z (2014) Melt and fluid inclusions in hydrothermal veins: The magmatic to hydrothermal evolution of the Elastite porphyry Cu-Au deposit, Bulgaria. Economic Geology 109, 1359-1381.

# Fluid Inclusion constraints on the character and role of fluids in the genesis of syenite-related rare metal deposits: evidence from Thor Lake, NWT, Canada.

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Rare metal deposits (REE, Zr, Nb) associated with alkaline granites and nepheline syenites have generally been affected by water-rock interaction, which in many cases has significantly modified the character and grade of mineralization. Compared to many other deposit types, little is known about the nature of the fluids in these systems and their role in the redistribution and concentration of the rare metals. An important question is whether these fluids in fact contain dissolved rare metals or whether they simply act to recrystallize primary assemblages.

We have studied fluid inclusions in the rare metal deposits at Thor Lake, NWT, in order to characterize the physicochemical characteristics of the fluids and assess whether they carried dissolved rare metals and at what concentrations. The mineralization at Thor Lake occurs principally in two zones, both of which are enriched in REE, Nb, Zr, Ta, and Ga: these are the Nechalacho deposit and the T Zone. The T Zone is also characterized by high concentrations of Li and Be. The Nechalacho deposit is hosted by the Nechalacho layered complex, a thick sequence of aegirine-nepheline syenites. The T Zone is smaller, sits above the Nechalcho Complex, and comprises a pegmatite hosted by granite and syenite. Both zones experienced extensive hydrothermal alteration. Essentially no primary silicates or rare-metal minerals remain in either deposit, the exception being some alkali feldspars. This reflects extreme disequilbrium between the original rock and the fluids.

The almost ubiquitous replacement of the primary mineralogy by secondary assemblages has resulted in the formation of abundant pseudomorphs in both the T Zone and the Nechalacho deposit. In the T Zone in particular, these are hosted by optically-continuous coarse-grained quartz. Most pseudomorphs are defined by concentrations of fine- to medium-grained rare-metal minerals, phenakite, K-feldspar or Fe and Ti oxides. Rare-metal minerals include zircon, bastnäsite-(Ce), and columbite-(Fe). These pseudomorphs contain fluid inclusion assemblages (FIAs) that are absent from the surrounding quartz or define the boundaries of the pseudomorphs (Fig. 1a) and are therefore considered primary. Some pseudomorphs are defined by fluid inclusions alone (Fig, 1b). Primary FIAs also define growth zones in quartz that is associated with either bastnäsite-(Ce) or xenotime-(Y), and possible primary inclusions occur in threedimensional arrays in bastnäsite.

In the T Zone, all of these FIAs comprise aqueous, liquid-rich inclusions, with or without trapped solids; CO<sub>2</sub> and CH<sub>4</sub> are present in trace amounts in some FIAs. Homogenization temperatures and salinities of Inclusions related to precipitation of zircon range from 100 to 400°C and from 12 to 24 wt. % NaClequiv, respectively. Cathodoluminescence imaging of quartz in zircon-dominated pseudomorphs indicates that the character of the fluid evolved during development of these pseudomorphs, which is reflected in the variable temperature and salinity data. Homogenization temperatures and salinities of inclusions responsible for bastnäsite-(Ce) precipitation range from 219 to 332°C and from 4 to 27 wt. % NaCleauiv, respectively. The FIAs related to replacement of K-feldspar, and precipitation of xenotime-(Y) and late phenakite all have low homogenization temperatures (≤180 °C) and moderate salinities (≥ 18 wt. % NaClequiv). Trapping conditions were estimated using microthermometric data, Ti-in-guartz thermometry and quartz-polylithionite oxygen isotope thermometry. The trapping temperature-pressure range for FIAs that define Ti oxide-dominated pseudomorphs (342 - 404 °C and 0.4 - 1.9 kbar), calculated using isochoric projections and TitaniQ geothermometry, is consistent with the conditions obtained using isochores and quartz-polylithionite oxygen isotope thermometry (360 °C and 0.7 - 1.3 kbar). These pressures are lower than previous estimates for the emplacement of granite and syenite in the western lobe of the complex. Estimated temperatures for Zr mineralization range from ~ 150 °C to 500 °C, whereas REE mineralization (principally bastnäsite) occurred from ~ 250 °C to 400 °C, and temperatures of Be and Y mineralization

were < 250 °C. These data illustrate that hydrothermal modification of the the T Zone was not caused by a single fluid event and that the fluids responsible for rare metal mineralization in the T Zone had variable character, both in terms of temperature and salinity. The limited data available for the Nechalacho deposit indicate that fluids responsible for alteration and mobilization of rare metals had comparable salinities (8-13 wt. % NaCl<sub>equiv</sub>) and temperatures ( $T_h$  = 200-400°C) to those that permeated the T Zone.

Both EDS analysis of evaporate mounds and laser ablation-ICP-MS analysis of individual inclusions from the T Zone show that the mineralizing fluids were dominated by Na and Cl, with lesser K and trace amounts of Ca and S. This suggests that the fluorite precipitation hypothesis proposed for many rare-metal deposits is not applicable to the mineralization in the T Zone. Analysis of individual inclusions demonstrates that significant rare metals were dissolved in the fluids that permeated the T Zone. Fluids with temperatures and salinities ranging from ~ 150 to 250 °C and from ~ 20 to 25 wt. % NaCl<sub>equiv</sub>, respectively, contain the highest Ti (2764 ppm), Nb (286 ppm), Zr (55 ppm), Y (263 ppm) and total LREE (653 ppm) concentrations.

The character of fluids in rare metal deposits, sensu lato, are highly variable, with a wide range of temperatures, salinities, and CO<sub>2</sub> contents reported. To some extent, however, these properties correlate with their igneous environment: granite vs. syenite vs. carbonatite. For example, compared to granite-related deposits, syenite-related deposits do not contain hypersaline fluids (no halite-saturated inclusions have been reported) and temperatures tend to be lower (up to ~ 400°C). In addition, syenite-related systems are essentially devoid of CO<sub>2</sub>. In syenite-related systems, however, salinities are quite variable; from near 0 to 30 wt. % NaCl<sub>equiv</sub>. The character of the fluids at Thor Lake are generally consistent with temperatures and salinity data from other syenite-related systems, but demonstrate that rare metals such as Nb, Zr, Y and REE were dissolved in the relatively low-temperature fluids that affected these deposits.



Fig 1. a) Edge of a phenkite-bearing pseudomorph showing abundant fluid inclusions inside the pseudomorph and inclusion-free quartz outside of the pseudomorph. Qtz = quartz, Phk = phenakite, FI = fluid inclusion. b) pseudomorph in quartz after K-feldspar defined by a high density of fluid inclusions.

### Preliminary results of trace element abundances in Permian seawater from LA-ICP-MS analysis of fluid inclusions in halite

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It has been known since the late 1970's that the chemical composition of seawater has changed during Earth's history. The basis for this distinction was recognition of the regular distribution of primary calcite and aragonite ooids in geologic time, which led to the designation of 'aragonite' and 'calcite' seas (e.g. Sandberg, 1983). The major element content of paleo-seawater shows variations that coincide with these periods. For instance, a high molar ratio of  $Mg^{2+}/Ca^{2+}$  (>2) in seawater correlates with the precipitation of aragonite, whereas low seawater  $Mg^{2+}/Ca^{2+}$  (<2) coincides with the precipitation of calcite. Furthermore, previous studies show that during the Phanerozoic the oceans have undergone two oscillations in majorion chemistry between SO<sub>4</sub>-rich and Ca-rich seas during periods of 'aragonite' and 'calcite' seas, respectively (e.g. Horita et al., 2002). However, our knowledge of how the minor and trace element composition of ancient seawater has varied during the evolution of Earth, if at all, is still deficient.

Minor and trace elements that show multiple valence states over the range of oxidation conditions expected on Earth (e.g., Fe, Mn, U) may be good indicators for the evolution of the oxidation state of the atmosphere and ancient seawater, since the solubility of these ions is highly dependent on the oxidation state. For example, iron is more soluble in its reduced Fe<sup>2+</sup> (ferrous) form than in its oxidized Fe<sup>3+</sup> (ferric) form, while uranium shows the opposite behavior. Analysis of primary fluid inclusions (FI) in halite can provide direct information about the chemical composition of evaporating seawater from which the salt crystallized. The major element concentrations of Permian seawater are similar to those of modern seawater. Thus, FI in Permian halites are good targets to study the minor and trace element composition of ancient seawater for comparison with present-day seawater.

The goal of this study is to develop a methodology to detect and guantify ratios of minor and trace elements (Rb, Sr, Mo, Ba, Li, B, V, U, Fe, Mn, Se, Cr, Cu) in seawater based on LA-ICP-MS analysis of primary marine halites. The samples used to develop and test the methodology are from the Permian Salado Formation, New Mexico. FI in these Permian evaporites have been studied in detail by previous workers, and the major element chemistry of the paleo-seawater trapped in the FI is well established. The measured FI were selected from different FI assemblages in chevron structures, are 15-200 µm in maximum dimension, contain only a single (brine) phase and have negative crystal shapes. The primary FI bands are separated by inclusion-free halite zones and represent distinct time steps of halite growth and, therefore, may show slightly different parent brine compositions due to the varying degrees of saturation along the evaporation path. Although the concentrations of some of the elements may have been modified from original seawater concentrations during the initial stages of seawater evaporation as calcite and/or gypsum precipitate, the measured minor and trace elements behave conservatively during halite deposition as none of these elements are incorporated into the halite structure. Thus, the FI preserve the element ratios present in the original parent seawater, even if the absolute concentration of these elements in the brine increases during halite precipitation.

Our preliminary results show an  $Mg^{2+}/Ca^{2+}$  ratio in the fluid inclusions of 117±19 (Fig. 1), which corresponds to the beginning of halite precipitation during evaporation of modern seawater at a brine concentration of approximately 13 times that of seawater, based on the evaporation path reported by McCaffrey et al. (1987). Furthermore, we detected B, Rb, Sr, Li and Se in all of the individual FI with a diameter greater than ~45 µm. The Mg<sup>2+</sup>/Li<sup>+</sup> ratio is also consistent with the few data previously reported from FI in Salado Formation halite by Horita et al. (1991).

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Fig. 1. Mg<sup>2+</sup>/Ca<sup>2+</sup> ratio in the different fluid inclusion assemblages (FIA). Lines represent the minimum and maximum values and red squares show the average values. Dashed lines indicate Mg<sup>2+</sup>/Ca<sup>2+</sup> ratio at a brine concentration of approximately 12.6 and 13.2 times that of modern seawater (McCaffrey et al., 1987).

#### REFERENCES

McCaffrey, M.A., Lazar, B. & Holland, H.D. (1987) The evaporation path of seawater and the coprecipitation of Br<sup>-</sup> and K<sup>+</sup> with halite. Journal of Sedimentary Petrology. 57. 928–937.

Horita J., Friedman T.J., Lazar B. & Holland, H.D. (1991) The composition of Permian seawater. Geochimica et Cosmochimica Acta. 55. 417–432.

Horita, J., Zimmermann, H. & Holland, H.D. (2002) Chemical evolution of seawater during the Phanerozoic: Implications from the record of marine evaporites. Geochimica et Cosmochimica Acta. 66/21. 3733–3756.

Sandberg, P.A. (1983) An oscillating trend in Phanerozoic non-skeletal carbonate mineralogy. Nature. 305. 19–22.

### Fluid inclusion and sulfur isotope studies of a new kind of Zn-Cu-rich MVT orebody at the Lamotte Sandstone/Bonneterre Dolomite contact, Viburnum Trend district, southeast Missouri: Evidence for multiple sulfur sources and metal-specific fluids

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MVT deposits of the Viburnum Trend are typically lead-dominant (Pb:Zn > 5) and occur mainly in the reef-grainstone facies of the upper Bonneterre Dolomite (Cambrian). Recent drilling/mining has encountered economic mineralization within the lower Bonneterre Dolomite of the Brushy Creek mine, more than 30 m below the main ore-bearing horizon of the district. These ores are more zinc- and copper-rich than typical deposits (Zn:Pb > 2 and Cu up to 8 wt. %), with notable enrichments in Ni, Co, and Ag. There is pronounced vertical zoning of Ni-Co, Cu, Zn and Pb with increasing distance above the underlying Lamotte Sandstone (Fig. 1, Cavender et al., 2016).

The ores display frequent breccia textures at the meso- and micro-scale and are composed dominantly of multiple generations of chalcopyrite and sphalerite supported by clay (insoluble residue). These are cemented by subsequent generations of sulfides and carbonates, resulting in massive, high-grade ore. Cathodoluminescence microscopy reveals that ore is associated with two generations of dolomite cement that predate the regional dolomite cement associated with main-stage Pb-Zn mineralization in the Viburnum Trend (Cavender et al., 2016).

The ores appear to be localized along early zones of fracture-enhanced porosity and permeability within the Lamotte Sandstone, which promoted extreme dissolution of host rocks at the base of the Bonneterre Dolomite. The presence of distinct Ni- and Ni-Co-rich areas and the spatial variability of sphalerite types across the orebody indicate that there were likely multiple sites of ore fluid introduction whose influence varied with time during development of the ores. Fluid inclusion and sulfur isotope studies were undertaken to assess whether the ores reflect a single fluid that evolved from Cu-Ni-Co-rich to Zn-rich to Pb-rich or are instead products of distinct fluids unrelated to the main Pb-rich ores of the district.

The  $\delta^{34}$ S values of ore minerals (early pyrite and chalcopyrite, -7 to +5‰; early sphalerite +6 to +15‰; main sphalerite, +7 to +17‰) indicate deposition from fluids that utilized isotopically distinct sulfide reservoirs. Low- $\delta^{34}$ S sulfur sources for early ores likely included sulfide in local brines within the Lamotte Sandstone and diagenetic sulfide minerals within the basal units of the Bonneterre Dolomite. A trend of increasing  $\delta^{34}$ S values of ore sulfides (from -5 toward +17‰) with vertical distance above the Lamotte/Bonneterre contact indicates that as the ore fluid system worked its way upward, it breached less permeable units in the lower Bonneterre, allowing incorporation of high- $\delta^{34}$ S sulfide from brines present higher in the stratigraphic section (Fig. 1).

Sphalerite-hosted fluid inclusions from the lower orebody record the highest K/Na and Mg/Na ratios in the southeast Missouri MVT district and elevated Sr/Na and Ba/Na ratios. These fluids appear to be geochemically distinct from those that formed the upper orebodies (Wenz et al., 2012). Paragenetic trends indicate distinct compositions are associated with specific generations of sphalerite, which may reflect unique fluids whose migration pathways varied with time.

The episodic nature of ore introduction in the lower section orebody points to a system in which fluid mixing would have been highly variable, both temporally and spatially. Reaction path models require mixing of multiple, metal-specific and sulfide-bearing fluids in order to form the orebody. The sequence and concentrations of metal sulfides, as well as distinct fluid inclusion chemistries, are inconsistent with ore formation from a single, evolving metal-bearing fluid.

#### REFERENCES

Cavender, B.D., Shelton, K.L., and Schiffbauer, J.D. (2016) An atypical orebody in the Brushy
Creek mine, Viburnum Trend, MVT district, Missouri: Early Cu-(Ni-Co)-Zn-rich ores at the Lamotte Sandstone/Bonneterre Dolomite contact. Economic Geology. v. 111, p. 259-269. Wenz, Z.J., Appold, M.S., Shelton, K.L., and Tesfaye, S. (2012) Geochemistry of Mississippi Valley-type mineralizing fluids of the Ozark Plateau: A regional synthesis. American Journal of Science. v. 312, p. 22-80.







Fig. 2. Box and whisker plots showing K/Na, Mg/Na, Sr/Na and Ba/Na molar ratios for sphalerite-hosted fluid inclusions from the Viburnum Trend (VT) and the lower ore zone (LOZ) of the Brushy Creek mine.



Fig. 3. Reaction path model at  $140^{\circ}$ C for mixing of a metalchloride brine with an H<sub>2</sub>S-bearing fluid. Single fluid models and models with lead in solution are incompatible with the observed mineral paragenesis and Cu-Zn metal zoning.

### Constraints from fluid inclusions on MVT ore fluid metal concentrations predicted from solid solution metal concentrations in ore-stage calcite

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Mississippi-Valley-type (MVT) ore deposits represent enrichments of Zn, Pb, Ba, and F in the Earth's crust that are orders of magnitude greater than crustal averages. Fundamental to understanding how these enrichments originated is knowing the concentrations of these elements in the ore fluids. Because fluid inclusions can be direct samples of ore fluids, much of the previous effort in determining Zn, Pb, Ba, and F concentrations in MVT ore fluids has focused on analyzing fluid inclusions using a variety of methods. However, each of these methods has serious technical limitations, leaving the concentrations, particularly of Zn, Pb, and F, ambiguous. For example, bulk crush leachate methods are prone to contamination from secondary fluid inclusions and the host matrix, making it difficult to identify the signal from the primary fluid inclusions. Synchrotron X-ray fluorescence has been used successfully to analyze individual fluid inclusions hosted mainly in guartz. However, guartz is rare or absent in many MVT deposits or does not overlap sulfide mineral precipitation temporally. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has been used successfully to analyze individual fluid inclusions in a wider variety of minerals, including sphalerite and fluorite, typically the only transparent ore minerals in MVT deposits. These analyses have yielded reliable information about Ba concentrations, which are typically on the order of 10's of ppm. However, the high ionization potential of F prevents it from being measured by LA-ICP-MS. In addition, it is not clear whether the high Pb, Zn, and Cu signals in many fluorite-hosted fluid inclusions and the high Pb signals in many sphalerite-hosted fluid inclusions observed in LA-ICP-MS analyses represent aqueous solute or mineral accidentals. Given these problems, the present study was undertaken in order to calculate MVT ore fluid metal concentrations based on solid solution metal concentrations measured in ore-stage calcites.

Prediction of the ore fluid concentrations of Mg, Zn, Fe, Mn, Sr, Ba, and Pb were made using the experimental distribution coefficients derived in Rimstidt et al. (1998) at 100° C in combination with the compositions of ore-stage calcites from the Illinois-Kentucky and Central-Tennessee MVT districts, which were measured in the present study. Predicted Mg and Mn ore fluid concentrations were in the 100's of ppm and 1's to 10's of ppm, respectively, which agreed well with available fluid inclusion data (Fig. 1a) (Pelch et al. 2015). These elements form carbonate minerals with the calcite structure (magnesite and rhodochrosite), as do Zn and Fe (smithsonite and siderite). Therefore the 1's of ppm Zn and 0.1's to 1's of ppm Fe ore fluid concentrations predicted in this study are also likely to be correct (Fig. 1b). Conversely, the predicted Ba and Sr ore fluid concentrations, 10's to 100's of ppm and 0.1's to 1's of ppm, respectively, were orders of magnitude lower than data from previous fluid inclusion studies (Pelch et al. 2015). These elements, along with Pb, form carbonate minerals with the aragonite structure (strontianite, witherite, and cerussite); therefore the ore fluid concentrations in the 1's of ppm for Pb predicted in this study are likely to be inaccurate.

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Fig. 1. (A) Comparison of measured and predicted ore fluid concentrations of Mg and Mn, Measured concentrations are from fluid inclusions analyzed by Pelch et al. (2015). (B) Predicted ore fluid concentrations of Fe and Zn compared to Fe and Zn concentrations in sedimentary brines reported by Yardley (2005).

#### REFERENCES

Rimstidt, J.D., Balog, A., and Webb, J. (1998) Distribution of trace elements between carbonate minerals and aqueous solutions. Geochimica et Cosmochimica Acta, v. 62, pp. 1851-1863.

Pelch, M. A., Appold, M. S., Emsbo, P., & Bodnar, R. J. (2015) Constraints from Fluid Inclusion Compositions on the Origin of Mississippi Valley-Type Mineralization in the Illinois-Kentucky District. Economic Geology. v.110, pp. 787-808.

Yardley, B. W. (2005) 100th anniversary special paper: metal concentrations in crustal fluids and their relationship to ore formation. Economic Geology, v. 100, pp. 613-632.

## Liquidus relations in multi-component, saline aqueous fluid inclusions: Application to salinity estimation and LA-ICPMS analysis.

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Geologic fluids commonly contain appreciable concentrations of multiple salts in addition to NaCl, including chlorides of  $K^*$ ,  $Ca^{2*}$ , and  $Fe^{2*}$  and  $Mg^{2*}$ , as well as sulfates and other (typically minor) anions. Interpretations of microthermometric data are commonly based on vapor-saturated liquidus relations of relatively simple systems such as H<sub>2</sub>O-NaCl or H<sub>2</sub>O-NaCl-CaCl<sub>2</sub>, because information on the phase relations of other (particularly, more complex) systems is rare. Here, we review and reassess the compositional information that can be obtained from microthermometric measurements in multicomponent chloride-dominated aqueous systems. To do so, we investigate the systematics of vapor-saturated liquidus phase equilibria in complex multicomponent electrolyte solutions through thermodynamic modeling based on Pitzer's equations (Steele-MacInnis et al., 2016). We focus on low-salinity, chloridedominated fluids, where ice is the liquidus phase, but also compare topologies of salts and salt-hydrates at higher salinities, and investigate the effects of other anions. For chloride-dominated systems, our results identify generic classes of fluids on the basis of measured ice and hydrohalite dissolution temperatures. In such systems, we can identify whether the chloride-salts present are predominantly monovalent (Na ± K), or mixtures of monovalent and divalent cation chlorides. However, two microthermometric measurements do not allow unequivocal determination of the identity of salts that are present in addition to NaCl. For systems in which other anions (e.g., SO42-) occur as major solutes, additional considerations arise in interpreting microthermometric measurements. Reasonable quantification of multiple cation (and/or anion) ratios from microthermometry is possible in large, easily observed inclusions where additional phase changes can be observed, and we present examples of fluid inclusion microthermometric analysis involving measurement of dissolution temperatures of multiple salts and salt-hydrates plus ice. In the case of chloride-dominated inclusions, we present methods suitable for combining microthermometric measurements with generic H<sub>2</sub>O-(Na,K)Cl- $\Sigma X^{n+}$ Cl<sub>n</sub> phase stability relations and microanalytical determination of cation ratios (e.g., LA-ICPMS analysis), to obtain robust compositional results for multi-salt aqueous fluid inclusions.

#### REFERENCES

Steele-MacInnis, M., Ridley, J., Lecumberri-Sanchez, P., Schlegel, T.U., Heinrich, C.A. (2016) Application of low-temperature microthermometric data for interpreting multicomponent fluid inclusion compositions. Earth Science Reviews (in press).

### Chemical geothermometry applied to adularia-sericite epithermal Au-Ag deposits: A case study from the Hauraki Goldfield, New Zealand

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The Hauraki Goldfield on the North Island of New Zealand is a classic adularia-sericite epithermal Au-Ag province with more than 50 deposits and prospects. The shallow parts of the deposits contain crustiform to colloform quartz veins with adularia, platy calcite, electrum and acanthite (Christie et al., 2007). They contain low salinity (<4.2 wt % NaCl equiv.) near neutral pH alkali chloride waters that were trapped at temperatures between 190 and 265°C. The deeper parts of the deposits are characterized by coarse-grained quartz veins enriched in base-metal sulphide minerals. They contain moderately saline (<7 wt % NaCl equiv.) near-neutral to slightly acid H<sub>2</sub>O-NaCl±CO<sub>2</sub> fluids that were trapped at temperatures between 240 and 290°C. The Hauraki Goldfield is an ideal locality to test various chemical geothermometers that are commonly used in exploration for geothermal resources such as Na-K (Fournier, 1979; Giggenbach, 1988), Na-K-Ca (Fournier & Truesdell, 1973), Na-Li (Fouillac & Michard, 1981), K-Mg (Giggenbach et al. 1988), and silica (Fournier & Potter, 1982). Microthermometry and LA-ICP-MS analyses of fluid inclusions provided the basis for comparisons of homogenization temperatures to chemical thermometers in primary (P), pseudosecondary (PS), and secondary (S) fluid inclusions in ore and gangue minerals (Table 1).

The Na/K geothermometer is based on temperature-dependant cation exchange reactions between albite and K-feldspar. It yielded temperatures of ~300°C, which reflects the deep reservoir fluid temperature rather than the formation temperature of quartz veins. However, this geothermometer can be affected by accidentally trapped clay and/or adularia crystals.

The Na-K-Ca geothermometer is controlled by equilibrium between alkali feldspars and Ca-bearing minerals. It gave unrealistically high temperatures (~360-680°C) in the shallow veins due to remove of Ca by precipitation of calcite from boiling fluids.

The Li-Na geothermometer is controlled by cation exchange reactions with clay minerals and zeolites rather than formation of discrete mineral phases. The fluid inclusions studied commonly contain accidentally trapped Li-bearing clay minerals, so this geothermometer has very limited application.

The K-Mg geothermometer requires fluid equilibration between K-feldspar, K-mica, clinochlore, and chalcedony. This geothermometer was not useful because Mg concentrations were mostly below the detection limit.

The silica geothermometer is controlled by SiO<sub>2</sub> solubility and can only be applied to inclusions in sulphide or carbonate minerals. Although SiO<sub>2</sub> solubility increases with increasing pH, in acid to near-neutral fluids the geothermometer is not significantly affected by pH changes. Because SiO<sub>2</sub> can be deposited in different forms (quartz, chalcedony,  $\alpha$ -cristobalite,  $\beta$ - cristobalite, and amorphous SiO<sub>2</sub>), the geothermometer could not be applied unambiguously. Therefore, we selected only inclusions whose intersections of the homogenization temperatures and measured SiO<sub>2</sub> concentrations fall within the stability field of quartz. The homogenization temperature represents the lowest possible formation temperature, and if the intersection falls within the stability field of quartz, that implies that the fluid was in equilibrium with quartz. Such inclusions were abundant in the deeply seated Tui deposit (~1400 m below paleowater table). In contrast, fluid inclusions hosted by sphalerite in the Waihi system (~500 m below paleowater table) were in equilibrium with microcrystalline varieties of  $SiO_2$  and the quartz geothermometer could not be applied to them.

Alkali and alkaline earth geothermometers reflect the deep reservoir fluid temperature which can significantly differ from quartz vein formation temperature, especially in veins deposited from adiabatically boiling fluids. In contrast, the quartz geothermometer gives formation temperatures, but it can be applied only to fluid inclusions hosted by sulphide or carbonate minerals deposited in chemical equilibrium with quartz.

Table 1. The summary of chemical geothermometry data (°C) obtained from ore and gangue minerals in adularia-sericite epithermal Ag-Au deposits of the Hauraki Goldfield, New Zealand.

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Ore deposit	Mineral	P/PS/S	Na-K*	Na-K**	Na-K-Ca	Na-Li	Quartz
Karangahake	Quartz	PS	286±67	284±59	449±83	-	-
Waitekauri	Quartz	Р	290±16	289±14	-	-	-
		PS	316±30	311±26	530±41	-	-
		S	281±74	280±65	474±120	-	-
Waihi (shallow)	Quartz	S	283±60	282±53	439±72	352±62	-
Waihi (deep)	Quartz	Р	289±29	288±25	472±34	298±100	-
		PS	308±29	304±25	529±60	275±104	-
		S	161±82	172±75	312±94	265±135	-
Waihi (deep)	Calcite	Р	321±53	315±45		334±45	-
		PS	319±7	314±6	-	320±17	-
		S	275±10	276±9	-	325±13	-
Waihi (deep)	Sphalerite	Р	304±39	300±34	510±61	171±15	
		PS	352±54	342±45	-	225±2	-
		S	321±33	316±28	556±41	-	-
Tui	Early quartz	Р	309±14	316±12	335±3	291±37	-
Tui	Late quartz	Р	217±67	231±62	416±131	-	-
Tui	Sphalerite	Р	284±16	294±14	257±10	318±12	265±10
		PS	303±16	312±15	282±7	328±23	-
		S	307±23	314±21	297±16	327±19	-

\*Fournier (1979), \*\*Giggenbach (1988)

#### REFERENCES

Christie, A.B., Simpson, M.P., Brathwaite, R.L., Mauk, J.L., Simmons, S.F. (2007) Epithermal Au-Ag and related deposits of the Hauraki goldfield, Coromandel volcanic zone, New Zealand. Economic Geology, 102, 785-816.

Fouillac, R. and Michard, S. (1981) Sodium/lithium ratio in water applied to geothermometry of geothermal reservoirs. Geothermics, 10, 55-70.

Fournier, R.O. (1979) A revised equation for the Na/K geothermometer. Geothermal Resources Council Transactions. 3, 221-224.

Fournier, R.O., Potter, R.W. II, (1982) A revised and expanded silica (quartz) geothermometer. Geothermal Resources Council Bulletin, 11-10, 3-12.

Fournier, R.O., Truesdell, A.H. (1973) An empirical Na-K-Ca geothermometer for natural waters. Geochimica et Cosmochimica Acta, 37, 1255-1275.

Giggenbach, W.F. (1988) Geothermal solute equilibria. Geochimica et Cosmochimica Acta, 52, 2749-2765.

## Partitioning of Na and K between liquid and vapor in the H<sub>2</sub>O-NaCI-KCI system at 600-800°C and 500-1000 bars

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Hydrothermal fluids are responsible for transporting and depositing ore-forming components and the agent that produces the characteristic alteration assemblages observed in porphyry copper deposits (PCD). One of the major depositional mechanisms in PCD systems is phase separation, whereby an originally single-phase magmatic-hydrothermal fluid undergoes immiscibility to produce a high salinity liquid in equilibrium with a low salinity vapor [1]. Studies of fluid inclusions have shown that sodium and potassium are the common major cations in hydrothermal fluids associated with PCD, and the H<sub>2</sub>O-NaCl-KCI system thus provides a good proxy for the PVTX properties of these fluids [2]. During phase separation, the single phase fluid will split into two coexisting immiscible fluid phases, a high density, high-salinity liquid phase and a low density, low-salinity vapor phase. Owing to their different densities and relative buoyancies, the liquid and vapor physically separate, with vapor moving upwards into the shallow parts of the system and the liquid phase "ponding" at depth. As such, it is necessary to better understand the compositions of the two fluid phases in order constrain their roles in alteration and mineralization. The major element composition, which is controlled by the partitioning behavior of the major components between the liquid and vapor phases during phase separation, will influence the type and intensity of alteration. Thus, understanding how sodium and potassium partition between the two fluid phases during phase separation at PT conditions associated with PCD formation will advance our understanding of the conditions associated with the alteration processes characteristic of this important class of ore deposit.

In this study, the partitioning behavior of sodium and potassium between two immiscible fluid phases during phase separation was determined for the H<sub>2</sub>O-NaCl-KCl system at 600-800°C, and 500-1000 bars, for fluids with an initial Na:K molar ratio of 3:1, 2:1, 1:1, 1:2, and 1:3 using the synthetic fluid inclusion technique. Some FI trapped the low salinity vapor phase and at room temperature contain a large vapor bubble and a small amount of liquid that condensed from the vapor during cooling from the trapping temperature to room temperature, as shown in the lower left of Figure 1. FI that trapped the high salinity liquid phase become saturated in halite and sylvite as the sample is quenched, and precipitate daughter minerals of each salt, as shown by the FI in the upper right portion of Figure 1. The compositions of the vapor-rich FI were obtained by cooling the inclusions and subsequently heating them and measuring the dissolution temperature of sylvite and the melting temperature of ice. The compositions of the liquid-rich FI were determined by



Figure 1: Photomicrograph of FI that trapped a low salinity vapor phase (lower left) and FI that trapped a high salinity liquid phase (Upper right).

heating the FI and measuring the dissolution temperatures of the daughter minerals (halite and sylvite). Compositions were calculated from the microthermometric data using the FORTRAN program "SALTY"

[2]. The measured salinities were then used to calculate the partition coefficient between the liquid and



vapor phases for sodium  $(K_{Na}^{L/V})$  and potassium  $(K_{K}^{L/V})$ . The results of the partitioning calculations are shown in Figure 2. The partitioning of sodium and potassium between the liquid and vapor phases was found to be nearly unity, with potassium slightly favoring the liquid phase and sodium slightly favoring the vapor phase.

Figure 2: Partition coefficient of potassium vs the partition coefficient of sodium. The 1:1 line indciates no preference for the liquid or vapor phase.

#### REFERENCES

- [1] Williams-Jones, A. E., and Heinrich, C. A. (2005) Vapor transport of metals and the formation of magmatic-hydrothermal ore deposits. Economic Geology. 100. 1287-1312.
- [2] Roedder, E. (1971) Fluid inclusion studies on the porphyry-type ore deposits at Bingham, Utah, Butte, Montana, and Climax, Colorado. Economic Geology. 66. 98-120.
- [3] Bodnar J., Sterner S., Hall D. (1989) SALTY: A FORTRAN program to calculate fluid inclusions in the system NaCl-KCl-H<sub>2</sub>O. Computers & Geosciences. 15. 19-41.

### Petrology and geochemistry of Upper Cambrian and Lower Ordovician (Arbuckle Group) carbonates, NE Oklahoma and SW Missouri

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The Arbuckle Group (Upper Cambrian and Lower Ordovician) carbonates in Oklahoma are an important petroleum reservoir and also are used to store petroleum waste-water. The Arbuckle also may have sourced all or part of the hydrocarbons in many of the overlying younger oil fields in Oklahoma, including those in Silurian and Mississippian rocks. Additionally the Arbuckle may have been a major conduit for metalliferous fluids affecting the Ozark region and contributing to the Tri-State mineral district of Oklahoma, Kansas and Missouri. This study focuses on the petrography and diagenesis of Arbuckle Group strata on the Ozark Platform in northeasatern Oklahoma and southwestern Missouri.

Northeast Oklahoma and southwest Missouri are part of the stable cratonic interior of North America. In this region the Ozark Uplift is the primary geological feature and is bounded by the Illinois Basin to the northeast, Forest City Basin to the northwest, Arkoma Basin to the south, and Reelfoot Rift to the southeast (He et al., 1997; Fig. 1). The Arbuckle Group was deposited under epeiric sea conditions on a shallow water platform. These strata reflect a series of large and small-scale (3<sup>rd</sup> to 5<sup>th</sup> order) depositional cycles that are further defined by regional and sub-regional unconformities.

Three subsurface cores cutting Arbuckle strata in northeast Oklahoma and southwest Missouri were studied. The Arbuckle section can be characterized as cyclic, cherty dolomite, occasionally interbedded with thin, quartzic sandstone. Subtidal to peritidal lithologies encountered consist of: algal stromatolites, thrombolite boundstones, tidal-flat laminates, ooid grainstones, peloidal wackestones, burrowed mudstones and quartz sandstones (He, et al., 1997; Overstreet et al., 2003). Replacement dolomite throughout the Arbuckle Group in the study area display mainly dark gray, fine to coarse crystalline, planar to nonplanar textures. Coarse crystalline rhombohedral and saddle dolomite cement fills the majority of fracture and vug porosity. Dolomite cement is occasionally followed by quartz and calcite cement. The dolomite cements display disctinctive cathodoluminescent (CL) zonation consisting of a bright, mottled CL center followed by three to five CL zones varying from non-CL to bright CL. Calcite cement displays bright to less-bright CL in thin multiple zones. Quartz cement has no response to CL.

Ratios of <sup>87</sup>Sr/<sup>86</sup>Sr for replacement dolomite and dolomite cement range from 0.7089 to 0.7106. The majority of the samples, including the replacement dolomite, are more radiogenic than expected for dolomite in equilibrium with Upper Cambrian and Lower Ordovician seawater (<sup>87</sup>Sr/<sup>86</sup>Sr values >0.7092) indicating likely interaction with continental basement or siliciclastic rocks derived from continental basement. Carbon and oxygen isotope data are not yet available at this writing.

Two-phase (liquid and vapor) aqueous inclusions were observed in dolomite cements. Primary inclusions homogenize between 83° to 169°C and have salinities ranging from 6 to 28 equivalent weight % NaCl (Fig. 2). In the lower part of the Arbuckle Group section the majority of the inclusions homogenized between 84° to 143°C with salinities ranging from 18 to 24 weight % NaCL. In the upper part of the section of the Arbuckle Group the inclusions homogenized at higher temperatures ranging from 125° to 169°C with the salinities ranging from 6 to 13 equivalent weight % NaCl. The data seem to indicate a gradual increase in the influence of the more saline fluid end-member higher in the section.

The fluid inclusion data resembles that of Mohammadi et al. (2016) in the overlying Mississippian section in that saline and dilute fluid end-member(s) exist. However, the dilute end-member fluid in this study is more saline that that observed in Mississippian strata (Mohammadi et al., 2016). The fluid inclusion data here (Fig. 2) more closely resembles that of Shelton et al. (1992) for the Bonneterre Dolomite to the northeast. They observed three possible fluids end-members: a cooler, saline fluid, a warmer, saline fluid, and a warm, dilute fluid. These conclusions remain tentative until further fluid inclusion and stable carbon and oxygen isotope data are collected.

#### REFERENCES

- He, Z., Gregg, J. M., Shelton, K. L., and Palmer, J. R., 1997, Sedimentary facies control of fluid flow and mineralization in Cambro-Ordovician strata, southern Missouri, in Montanez, I. P., Gregg, J. M., and Shelton, K. L., eds., Basin-wide diagenetic patterns: integrated petrological, geochemical, and hydrologic considerations: SEPM Special Publication no. 57, p. 81-99.
- Mohammadi, S., Gregg, J. M., Shelton, K. L., Appold, M. S., and Puckette, J. O. (2016) Influence of late diagenetic fluids on Mississippian carbonate rocks on the Cherokee Ozark Platform, NE Oklahoma, NW Arkansas, SW Missouri, and SE Kansas. In G. M. Grammer, J. M. Gregg, J. O. Puckette, P. Jaiswal, M. Pranter, S. J. Mazzullo, and R. H. Goldstein, eds. Mississippian Reservoirs of the Mid-Continent, U.S.A. American Association of Petroleum Geologists Memoir. in editorial review.
- Overstreet, R. B., Oboh-Ikuenobe, F. E., and Gregg, J. M., 2002, Sequence stratigraphy and depositional facies of Lower Ordovician cyclic carbonates, Southern Missouri: Journal of Sedimentary Research, p. 421-433.
- Shelton, K. L., R. M. Bauer, and J. M. Gregg, 1992, Fluid-inclusion studies of regionally extensive epigenetic dolomites, Bonneterre Dolomite (Cambrian), southeast Missouri: Evidence of multiple fluids during dolomitization and lead-zinc mineralization: Geological Society of America Bulletin, v. 104, p. 675-683.



Fig. 1. Geologic map of the Ozark Uplift with locations of cores that were used in this study (modified from Shelton et al., 1992).



Fig. 2. Fluid inclusion assemblages plotted as salinity versus homogenization temperature. The three fluid end-members of Shelton et al. (1992) are shown.

# Ore Genesis of the Keyinbulake Cu-Zn Deposit, Altay, China: Ore Textures, CO2-rich Inclusions, and Isotope Geochemistry

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The Keyinbulake copper-zinc deposit, located in the Chonghuer basin of the southern Altaids, is one the important deposits in Altay area, Xinjiang. The strata in the deposit area are mainly Lower Devonian Kangbutiebao Formation and Middle Devonian Altay Formation, and the Keyinbulake deposit is hosted in metamorphic tuff and rhyolite of Lower Devonian Kangbutiebao formation with LA-ICP-MS zircon U-Pb ages of 385.3±1.2Ma (tuff) and 398.1±1.8Ma~405.6±2.2Ma (rhyolite) (Chai et al., 2012). There is Permian mica granite with zircon U-Pb age of 278.6±3.5Ma (Li et al., 2012). Ore bodies mainly occur in the Kangbutiebao formation near the Permian granite, and are controlled by the NW-trending Qiongkuer fault and Taerlang-Hailiutan fault. The ore minerals are mainly pyrite, chalcopyrite, sphalerite and pyrrhotite.Two mineralization periods can be identified based on field geology and ore textures: submarine volcanic sedimentary exhalation period and metamorphic hydrothermal superimposition period. The later period could be further divided into two stages : an early bedded foliated quartz vein stage (Q1) and a late pyrite-chalcopyrite quartz veins(Q2) cross-cutting the foliation.



Fig. 1 Geological map (A) (Modified after Yang et al., 2010) and characteristics of ores (B, C, D, E, F, G) from the Keyinbulake Cu-Zn deposit, Xinjiang, China

A-Geological map showing the distibution of ore bodies; B-Banded Zn-Cu ores with quartz vein parallel to the foliation (Q1); C-Late quartz veins cross-cutting the foliation of biotite quartz schist; D-Shalerite (Sp) and chalcopyrite (Cp) in massive ore replaced by biotite (Bi), KY112, reflected light; E-Colloidal pyrrhotite (Po) cut by late hydrothermal pyrite (Py), KY114b, reflected light; F-Disseminated chalcopyrite(Cp) and pyrrhotite (Po) occurring along the schistosity of biotite quartz schist, KY119, plane polarized light; G-Brown sphaleite (Sp) and pyrrhotite replaced by biotite (Bi), KY109b, plane polarized light

Fluid inclusions in quartz vein are characterized by CO<sub>2</sub>-rich inclusions, including carbonic fluid inclusions (C-type) and H<sub>2</sub>O-CO<sub>2</sub> inclusions (CW-type). L-V aqueous inclusions (W type) are less seen. Most C and CW types inclusions occur as Fluid Inclusion Assemblage(FIA). The fluid inclusions in Q1 are mainly composed of C-type inclusions both occurring in isolated and in FIA, with solid CO<sub>2</sub> melting temperatures ( $T_{m,CO2}$ ) being from -61.2~-60.3°C (isolated) and -61.0 to -59.1°C (FIA). They have very low homogenization temperatures ( $T_{h,CO2}$ ) that are from -42.3~-38.3°C (isolated) and from -41.4 to -36.0°C (FIA). In the late quartz veins (Q2), fluid inclusions are mainly C and CW types. The values of  $T_{m,CO2}$  for C-type inclusions vary from -60.8 to -58.1°C (FIA) and from -61.6 to -58.9°C (isolated), and values of  $T_{h,CO2}$  vary from -30.0 to -1.6°C (FIA) and from -21.9 to 10.4°C (isolated). The CW-type inclusions (isolated) of Q2 have  $T_{m,CO2}$  from -61.4 to -58.1°C,  $T_{h,CO2}$  from -11.9~5.3°C, and clathrate melting temperatures ( $T_{m,clath}$ ) from 2.9 to 13.1 °C. Only one final homogenization temperature ( $T_{h,tot}$ ) of CW inclusion obtained (312°C) because of decrepitation. The W-type inclusions have ice melting temperatures ( $T_{m,ice}$ ) from -14.2~-2.2°C and  $T_{h,tot}$  from 220~389°C. A Laser Raman microprobe analysis showed that C type inclusions have clear CO<sub>2</sub> spectra peaks Raman shift 1385 cm<sup>-1</sup> and 1278cm<sup>-1</sup>, and N<sub>2</sub> spectra peaks may also be seen at Raman shift 2327 cm<sup>-1</sup>. These features are very similar to the fluid inclusions in orogenic gold mineralization in Altay area (Xu et al. 2015).



Fig.2 Characteristics of CO<sub>2</sub>-rich inclusions in vein quartz from the Keyinbulake Cu-Zn deposit A-C type inclusions occuring as FIA in vein Q1, KY104; B-C type inclusions occuring as isolated in vein Q2, KY105; C- C type inclusions occuring as several FIAs in vein Q2, KY125

The sulfur isotope analysis show that the sulfides (pyrite, pyrrhotite, sphalerite) of the early submarine volcanic sedimentary period have a narrow  $\delta^{34}$ S values varing from 0.2‰ to 2.2‰, and the late metamorphic hydrothermal sulfides (chalcopyrite, pyrite) also have a narrow  $\delta^{34}$ S range of 0.1‰ ~ 0.8‰. reflecting a submarine volcanic magmatic source and an inherited characteristics during late orogenic and metamorphic events. The ratios of lead isotope composition for the early submarine volcanic sedimentary pyrite are 17.919~18.142 (<sup>206</sup>Pb/<sup>204</sup>Pb), 15.489~15.524 (<sup>207</sup>Pb/<sup>204</sup>Pb), and 37.653~37.861 (<sup>208</sup>Pb/<sup>204</sup>Pb), which change very little, indicating that the lead in pyrite belong to old normal lead and was derived from a mantle source, based on the plot of Doe and Zartman (1979). Hydrogen and oxygen isotope analysis show that  $\delta^{18}O_{H2O}$  and  $\delta D$  values of early quartz vein Q1 may be associated with regional metamorphic and magmatic event.

#### REFERENCES

Chai FM, Yang FQ, Liu F, Geng XX, Jiang LP, Lu SJ, Guo XJ and Chen B. (2012) Geochronology and Genesis of Meta-felsic Volcanic Rocks from the Kangbutiebao Formation in Chonghuer Basin on Southern Margin of Altay, Xinjiang. Geological Review, 58(6), 1023-1037 (Chinese with English abstract)

Li XR, Liu F and Yang FQ. (2012) Geological times and its signification of the two-mica syenogranite in the Keyinblak Cu-Zn Deposit Area in Altay, Xinjiang. Xinjiang Geology, 30(1), 5-11 (Chinese)

Xu JH, Yang R, Xiao X, Lin LH. and Mulder DC. (2015) CO<sub>2</sub>-rich inclusions in vein gold–copper mineralization of the Sarekoubu–Qiaxia District, southern Altaides, China: Implication for ore genesis. Journal of Geochemical Exploration 159, 262–277

Yang FQ, Mao JW, Liu F, Dong YG, Chai FM and Geng XX. (2010) Geological characteristics and metallogenesis of the Keyinbulake copper-zinc deposit in Altay, Xinjiang. Acta Geologica Sinica 26, 361-376 (Chinese with English abstract)