# The Sorby Conference on Fluid and Melt Inclusions





**Geochemistry Group** 



Mineral Deposits Studies Group

**VMSG** 

Volcanic & Magmatic Studies Group







Earth & Environment Leeds

# ABSTRACTS

**ECROFI XXIII** 

June 27-29 2015

**University of Leeds, UK** 

# The Sorby Conference on Fluid and Melt Inclusions

# **ECROFI-XXIII**

School of Earth and Environment University of Leeds June 27<sup>th</sup> to 29<sup>th</sup> 2015

Organised by

**Bruce Yardley** 

**David Banks** 

**Jason Harvey** 

**Delia Cangelosi** 

**Matthew Grimshaw** 

Lubomira Tomanikova

The Organisers wish to thank





The Geochemistry Group



The Mineral Deposits Studies Group



Society for Geology Applied to Ore Deposits



WITec GmbH



Volcanic and Magmatic Studies Group

The Sorby Conference on Fluid and Melt Inclusions						
ECROFI-XXIII						
Friday 26th June: Farth and Environment Building						
indu	y 20th 50h					
18:00	) - 20:00 Re	gistration and Ice Breaker Reception.				
Satur	day 27th J	une: Earth and Environment Building				
08.30	) Onwards	Registration				
00.50	, Onwarus,					
		09:00 welcome				
		Analytical Methods				
	09.1	Keynote Presentation				
	05.10	Recent Advances in the Analysis of Volatiles and Eluid-Mobile Elements in Melt				
		Inclusions by Secondary Ion Mass Spectrometry (SIMS)				
		Ian C M De Hoog R W/ Hinton & FIME				
	09.15	Analytical advances in studying melt inclusions: a HR-Raman and FIR-SEM case				
	05.45	study of carbonate melt inclusions in jacunirangite from Kerimasi (Tanzania)				
		Ráka Káldos Tibor Guzmics Tamás Váczi, Adrienn Baris Márta Barkesi Károly				
		Havancsák Zoltán Dankházi. Csaba Szabó				
	10:00	Havalicsak, Zuitali Dalikilazi, Csaba Szabu				
	10:00	Flow Mineral minings crystallize in Multiplase inclusions From OHP Fluid Plase.				
		First in Situ Synchrotron X-ray iviedsurements.				
	10.15	Nadia Malaspina, Matteo Alvaro, Marcello Campione, Fabrizio Nestola				
	10:15	Progress in 3D multiphoton microscopy of fluid inclusions.				
		Robert C. Burruss				
10:30	Coffee Br	eak				
	11:00	Linkam Presentation,				
		Duncan Stacey				
	11:15	Identification of CaCl <sub>2</sub> -bearing daughter minerals in natural inclusions.				
		Svetlana Grishina, Jean Dubessy, Lucas Uriarte, Sergey Goryanov & Igor Yakovlev				
	11:30	In Situ Identification of the S3– Ion in S-rich Hydrothermal Fluids from Synthetic				
		Fluid Inclusions.				
		Nicolas Jacquemet, Damien Guillaume, Antoine Zwick, & Gleb S. Pokrovski				
	11:45	Sulfur forms in the hydrothermal fluids and their role in ore formation.				
		Alexandr S. Borisenko, Andrey A. Borovikov1, Ivan D. Borisenko, Nikolav S.				
		Bortnikov, Vsevolod Yu, Prokofiev, Olga V, Vikent'eva, Gennady N, Gamvanin,				
		Ivan V. Gaskov				
	12:00	The role of illites in determination the age and origin of hydrothermal fluids. Biga				
	12.00	Peninsula NW Turkey				
		Gülcan Bozkava, Ömer Bozkava, I Tongue Livsal, David A, Banks				
	17.1	Reassessment of the Raman densimeter of CO2				
	12.10	Hertor M. Lamadrid Lowell Moore Daniel Moncada Donald Rimstidt & Robert L				
		Bodnar				

12:30 Lunch				
	Magmatic Systems			
13:3	0 Keynote Presentation			
	Volatile concentrations of silicate melt inclusions: Insights into processes in active			
	volcanic systems.			
	Rosario Esposito, Matthew Steele-MacInnis, Lowell R. Moore, and Robert J.			
14.0	Bodnar Bodnar			
14.0	Southern Italy: a Complete Picture Using Melt Inclusion Geochemistry and			
	Volatile Contents			
	Angela L. Doherty, Claudia Cannatelli, Harvey E. Belkin, Robert J. Bodnar, &			
	Benedetto De Vivo			
14::	5 Insights into Pre-Campanian Ignimbrite volcanism in the Campanian Plain			
	(Southern Italy): a Melt Inclusions Approach.			
	Claudia Cannatelli, Angela L. Doherty, Paola Petrosino, Harvey E. Belkin,			
	Giuseppe Rolandi, Annamaria Lima, Stefano Albanese, & Benedetto De Vivo			
14:3	0 Using synthetic fluid inclusions as mini batch reactors to monitor serpentinization			
	reactions in the oceanic lithosphere.			
14.	Hector Wi. Lamadrid, Esther Schwartzenbach, Donaid Rimstldt & Robert J. Bodnar			
14.4	Brian C Tattitch & Ion M. Blundy			
	Bhan C. Tattiten & John W. Blundy			
15:00 Coffee F	reak			
15.00 conce l	i cak			
15.0	The effects of densing the ice on reconstructing the are equative CO2 content.			
15.:	of magmas based on Paman analysis of vanor hubbles in melt inclusions			
	Lowell R. Moore, Héctor M. Lamadrid, Daniel Moncada, Robert I. Bodnar			
15:4	5 Fluid inclusion study of VMS-related stockwork and stratiform deposits in the			
10.	Northern Apennine Ophiolites (Italy).			
	Gabriella B. Kiss, Giorgio Garuti, Federica Zaccarini, Zsuzsanna Kapui			
16:0	0 Fluid inclusion study on LCT pegmatites from Bikita, Zimbabwe craton -			
	constraints on a magmatic-hydrothermal model.			
	Lisa Richter, Thomas Dittrich, Steffen Hagemann, Thomas Seifert & David Banks			
16::	5 Comparison of fluid inclusion studies in cordierite-andalusite-rich leucogranite			
	dykes and tourmaline-bearing aplite-pegmatite dykes (Elba, Italy).			
	Ronald J. Bakker, & Sebastian E. Schilli			
16:30 - 17:00 I	ntroduction to Posters			
17:00 - 18:30 Poster session (note posters to be removed at close of conference on Sunday)				
17:30 Drinks Reception				
19:30 Confere	nce Dinner, University Refectory			

Sunday 28th June: Earth and Environment Building					
Fluids in Porphyry and Epithermal Systems					
	09:00	A Record of Cu-Au Mineralizing Fluids over a 2-km Vertical Range in the Ertsberg East Skarn System, Ertsberg-Grasberg District, Papua, Indonesia,			
		J. Richard Kyle, Matthew Ledvina, & Stefanie Frelinger			
	09:30	Deep porphyry veins at Cerro de Pasco, Peru: Constraints from mineral, fluid and			
		silicate melt inclusions in hydrothermal quartz.			
		Bertrand Rottier, Kalin Kouzmanov, Markus Wälle, Luís Fontboté			
	09:45	Explosive brecciation and base-metal-Au mineralization at Koru, NW Turkey. P-T-			
		x of the hydrothermal fluids.			
		Gülcan Bozkaya & David A. Banks			
	10:00	Fluid Inclusion Characteristics of the Giant Tertiary Kadjaran Porphyry Mo-Cu			
		Deposit, Tethys Metallogenic Belt, Armenia, Lesser Caucasus.			
		Hovakimyan S., Moritz R., Tayan R., Rezeau H.			
	10:15	Properties of fluid inclusions from potassic alteration zone of Karakartal deposit			
		(Erzincan, Central Eastern Turkey).			
		<b>Oguzhan Gümrük</b> , Migraç Akçay & David A. Banks			
10:30 Co	fee brea	k			
	11:00	Hydrothermal evolution from porphyry to epithermal system: Insights from fluid			
		inclusion and stable isotope studies of the Qibaoshan Cu-Au deposit,			
		southeastern North China Craton.			
		Hong-Rui Fan & Wen-Gang Xu, Fang-Fang Hu, Kui-Feng Yang			
	11:15	Porphyry and Epithermal deposits of the Urals: P-T-x-parameters.			
		E.O. Groznova, O.Yu. Plotinskaya, S.S. Abramov, A.A. Borovikov, S. Milovska, J.			
		Luptakova, R. Seltmann			
	11:30	Effect of CO2 on salinity determinations for fluid inclusions from the epithermal			
		environment.			
	11.45	Daniel Moncada, Lowell Moore, Hector M. Lamadrid, Robert J. Bodnar			
	11:45	Turkey: Derphyry / Derphyry Epithermal transition?			
		Turkey: Porphyry / Porphyry-Epithermal transition?			
		Öztaş			
	12:00	Identification of daughter crystals in polyphase fluid inclusions: Implications for			
		fluid chemistry at the Bingham Canyon porphyry deposit, Utah.			
		Simon Kocher & Jamie J. Wilkinson			
	12:15	Mineral Composition of Salt Melt Inclusions of the Porphyry Gold Deposit Biely			
		Vrch (Slovakia).			
		Peter Kodera, Agnes Takács, Tamás Váczi, Jarmila Luptáková & Peter Antal			
12:30 Lur	nch				
	13:30	Hydrosilicate liquids: unconventional agents of metal transport in porphyry ore			
		systems.			
		Jamie J. Wilkinson, Olga Vasyukova, Jamie S. Laird, Chris Ryan & Dima			
		Kamenetsky			

		in Diagenetic and Metamorphic Rocks, Central Alps, Switzerland.
	10:00	PVTX Evolution and Re-equilibration of Prograde and Retrograde Fluid Inclusions
		András Fall, Estibalitz Ukar, Randall Marrett, & Stephen E. Laubach
		Deeply Buried Sandstones.
	09:45	Dauphiné Twin Planes in Quartz Trap Fluid Inclusions and Indicate Paleostress in
		Robert H. Goldstein
		Laura González-Acebrón, MaialenLópez-Elorza, José Ramón Mas, José Arribas,
	09:30	Evolution of Carbonic Fluids in Crack-sealed Quartz veins.
		Larryn W. Diamond & Alexandre Tarantola
	09:00	<i>Reynote Presentation</i> What can we learn from fluid inclusions in ductilely deformed quartz?
	00.00	Kourate Dresentation
		Quartz Voinc
ivioliuay 2		
Monday	9th lune	Michael Sadler Building I G19 (Note Change of Venue)
		U
16:30 Bus	siness M	eeting
	L	
		Jiuhua Xu, Longhua Lin, Rui Yang, Xing Xiao
	10.13	Qiaxia District, Southern Altaides, China.
	16:15	CO2-rich Fluid Inclusions in Vein Gold-Conner Mineralization of the Sarekoubu-
		Alexander A. Pek
	10:00	Fiuld inclusions in Quartz from the Gold Mineralization at a Depth of 10 km.
	16.00	I ODIAS FUSSWINKEI, I NOMAS WAGNER, GRIGORIUS SAKEIIARIS
		the Late Archean Hattu Schist Belt, Eastern Finland.
	15:45	Fluid Inclusion LA-ICPMS Analysis of Ore Fluids from Orogenic Gold Deposits of
	45	Volker Lüders, Reiner Klemd, Thomas Oberthür & Lisa Richter
		of quartz-hosted CO2-rich fluid inclusions.
		Proterozoic gold deposits? Constraints from stable carbon isotopic compositions
	15:30	Different carbon reservoirs of auriferous fluids in African Archean and
15:0	0 Coffee	Break
		Thomas Pettke & Larryn W. Diamond
		Hydrothermal Ore Formation.
		Fluid Inclusion Gold Concentrations: From Analysis to Implications for
	14:30	Keynote Presentation
		Gold Mineralization
14:00 - 14	1:30 Disc	ussion: Fluids in Porphyry and Epithermal Systems.
		M.P. Smith, S.Gleeson, N. Bernal & B.W.D. Yardley
		from fluid inclusions.
	13:45	Source of brines and metal transport in the Kiruna district, Sweden: Evidence

		Sedimentary and Hydrocarbons
-	10:15	Keynote Presentation
		Hydrocarbon inclusions, an efficient proxy for basin modelling through time and
		space.
		Jacques Pironon
10:45 Coffe	ee Brea	k
	11:15	Isotope Geochemistry (87Sr/86Sr, 618O, 634S, 6D), Fluid Inclusion and Raman
		Micro-Spectroscopy of Celestine Deposits from the Evaporitic Sarkısla-Celalli Sub-
		Basin in the Tertiary Sivas Basin, Turkey.
		Ali Ucurum, Cigdem Sahin Demir, Greg B. Arehart, Ernst Pernicka, Ferenc
		Molnar, Ronald J. Bakker
-	11:30	Fluid Inclusion and Pb Isotope Evidence for the Origin of Mississippi Valley-type
		Mineralization in the North American Mid-Continent: Insights from Trace
		Occurrences of Mineralization.
		Joshua D. Field, Martin S. Appold, & Raymond M. Coveney, Jr.
-	11:45	Keynote Presentation
		The role of hydrothermal fluids in the formation of high grade BIF-hosted iron ore
		deposits.
		Steffen G. Hagemann
-	12:15	Constraining the source of Archean fluids involved in the formation of BIF-hosted
		hypogene iron ores in the Yilgarn Craton of Western Australia.
		Paul Duuring, Steffen G. Hagemann, David A. Banks, Christian Schindler &
		Thomas Angerer
12:30 Lunc	h	
		Experimental and Theoretical Studies
	13:30	H2O-NaCl fluid inclusions in wonderland.
		Ronald J. Bakker
1	13:45	Liquid-vapor partitioning behavior of sodium and potassium in the system H2O-
		NaCl-KCl at 600-800OC and 500-750 bars.
		D. Matthew Sublett & Robert J. Bodnar
1	14:00	Microthermometric data of stretched and super-cooled liquid water obtained
		from high-density synthetic fluid inclusions.
		Chen Qiu, Yves Krüger, Max Wilke, Dominik Marti, Jaro Rička, and Martin Frenz
-	14:15	Role of dissolved gases in the formation of liquid inclusions.
		Emilie Bobo, Valérie Dupray, Samuel Petit & Gérard Coquerel
	14:30	The Smaller the Harder: Theorization of a Threshold Size below which Fluid
		Inclusions do not Decrepitate.
		Marcello Campione, Nadia Malaspina, Eduardo Oglialoro, & Maria Luce Frezzotti
	14:45	importance of melt inclusions in study of carbonatites: insight into Kerimasi melt
		evolution.
		<b>HDOR GUZMICS</b> , KEKA KAIGOS, ZOITAN ZAJACZ, USADA SZADO

15:00 Close of Meeting Coffee					
15:30 North Pennine Mineralization Logistics of field trip and examination of mineralized samples.					
Poster Presentations					
How microthermometry and eq. mass fraction NaCl can spoil your highly sophisticated LA-ICP-MS					
data of fluid inclusions					
Ronald J. Bakker					
Composition and metal-bearing capacity of the ore-forming fluids of the Late Mesozoic alkaline					
complexes in the Aldan shield (Russia)					
Andrey A. Boroikov, Alexandr S. Borisenko, Ivan V. Gaskov, Ivan D. Borisenko, Anna G.					
Doroshkevich, Nikolay V. Vladykin, Ilia R. Prokopiev					
Evidence of sulphate-rich fluid associated with an enriched heavy rare earth element carbonatite,					
Huanglongpu deposit, China					
Delia Cangelosi, Martin Smith, Bruce Yardley and David Banks					
Magmatic CO2-H2O-S fluids at Mt. Somma-Vesuvius: Insights from shrinkage bubbles of melt					
inclusions					
Rosario Esposito, Hector La Madrid, Leonid V. Danyushevsky, Daniele Redi, Claudia Cannatelli,					
Matthew Steele-Macinnis, Annamaria Lima, Robert J. Bodnar, Benedetto De Vivo					
Fluid Chemistry of High Grade Iron Mineralization at Picarrao-Liberdade Deposit, Brazil					
Sylvio D. Gomes, Rosaline C. Figueiredo e Silva, Carlos A. Rosieri, Lydia IVI. Lobalo, Sterien					
Hagemann & David A. Banks					
Adel Mady Afify <sup>1</sup> , Laura González-Acebrón, María Esther Sanz-Montero & Jose Pedro Calvo					
Development of a denosit model for the giant gold orebody at Lone Star in the Klondike. Yukon					
Matthew Grimshaw. Rob Chapman and Graham McLeod					
Fluid inclusion studies on rare metal enriched pegmatites					
Marieta Freitas, Alexandra Carolino, Alexandra Guedes & Fernando Noronha					
The Sulphur Isotopes and Fluid Inclusion Characteristics of the Madenköy (İmranlı) Cu-Pb-Zn±Ag					
Mineralization, Sivas, Turkey					
Serkan Şenkaya & Nurullah Hanilçi					
Polymineralic Inclusions Representing In Situ Melting in Garnet of Eclogite-Facies Metapelites during					
Uplift and Heating					
Petra Herms, Andreas Möller, Peter Appel & Peter Raase					
Fluid inclusions in apatite indicate low-temperature, metasomatic-infiltration origin of the Evate					
carbonatite deposit (Mozambique)					
Vratislav Hurai, Monika Huraiová					
CH4-N2-CO2-H2O-NaCl fluid inclusions in Praid salt rock, (Transylvania, Romania)					
Orsolya R. Katai, <b>Réka Kaldos</b> , Attila Toth, Csaba Szabo					
Genetical study of the fluorite veins of Pecsely (Balaton Highland, Transdanublan Mountain Range,					
INVV-Muligary)					
<b>230236 WORRER</b> , Gabriella D. NISS, ISLVAII DURKI, Tarrias Valzi, Federica Zaccarini, & ISLVAII DOdony					
António Moura Jens Götze Stuart Kearns					
P-T-X conditions of hydrothermal fluids of hase-metal-gold mineralization at the Teshibdere deposit					
Riga Peninsula. NW Turkey					
<b>Fatih Ozbas,</b> Gulcan Bozkaya and David A Banks					
,					

Fluid inclusion study in metamorphic veins from the Luarca sector (Asturias, northern Spain): role of fluid pressure in veining

Jorge Pérez-Alonso, Mercedes Fuertes-Fuente & Fernando Bastida

Mineralizing Fluids of Two Stage Au Mineralization of Pionersky Ore Cluster, North-East Russia **Vsevolod Yu. Prokofiev**, Alexandr V. Volkov, Evgeniya E. Tyukova

Cyclic injection of metal-rich high-salinity magmatic fluids leading to the formation of the giant base metal deposit of Cerro de Pasco, Peru

Bertrand Rottier, Kalin Kouzmanov, Markus Wälle, Lluís Fontboté

Preliminary Microthermometric Data of Hayriye, Iclaliye Mineralizations in (Inegöl-Bursa).

Hüseyin Sendir, Kadir Sarıiz,

Fluid mixing and fault-valve action in the formation of the Nalunaq Gold deposit, Greenland. **M.P. Smith**, D.A. Banks, F. Bowers

Fluid inclusion studies constrain conditions of Cu mineralization in Cerro Colorado Mine, Northern Chile

Debbie P.W. Tsang, Brian Tattitch & Simon Wallis

Methodology and Application of Evaporate Mound SEM-EDS analysis to Quantify the Solute Chemistry of Quartz-hosted Fluid Inclusions in a Mineralized Granitic Batholith

Fergus Tweedale, Jacob Hanley, Daniel Kontak, and Neil Rogers

# Keynote Presentations

# What can we learn from fluid inclusions in ductilely deformed quartz?

Larryn W. Diamond<sup>1</sup> & Alexandre Tarantola<sup>2</sup>

<sup>1</sup>Rock–Water Interaction Group, Institute of Geological Sciences, University of Bern, Baltzerstrasse 3, CH-3012 Bern, Switzerland. diamond@geo.unibe.ch <sup>2</sup>Université de Lorgeire, CNPS, CRECU, CooRespondence Jah, BP 220, E 54506, Ven doorway, Jak Neney, Coder,

<sup>2</sup>Université de Lorraine, CNRS, CREGU, GeoRessources lab., BP 239, F-54506, Vandoeuvre-lès-Nancy Cedex, France. alexandre.tarantola@univ-lorraine.fr

## Introduction

It is well known that recrystallization of quartz subgrains and migration of grain boundaries at high degrees of ductile shear strain obliterates any pre-existing fluid inclusions [1]. Their contents are leaked to the grain boundaries. Fully recrystallized mylonites are therefore devoid of pre-deformation fluid inclusions.

In contrast, fluid inclusions are commonly abundant in hydrothermal quartz crystals that have been only weakly deformed by intracrystalline mechanisms in the ductile regime. Examples shear are quartz porphyroclasts in hydrothermal veins in shear zones, many of which host ore deposits. Inclusions that clearly post-date the ductile deformation in such samples pose no special problems in interpretation, as the standard approach to fluid inclusion studies provides an adequate framework for their analysis. However, attempts to interpret the properties of older, pre- or syn-deformation inclusions face serious obstacles. First. normal petrographic indicators for the primary or secondary origin of fluid inclusions are often having been eradicated absent. bv intracrystalline deformation. Second. as intracrystalline deformation intensifies (manifested by greater intensity of undulose optical extinction and greater frequency of deformation lamellae and subgrains), the size of fluid inclusions decreases while the number of inclusions increases. Ductile deformation evidently has a profound effect on pre-existing fluid inclusions. Thus, quartz crystals that have undergone only about 10-20% of ductile strain  $(\Delta L/L)$  appear macroscopically milky because they are densely packed with myriad tiny inclusions. Frustratingly, the inclusions cannot be assigned to crystal growth zones or to traces of healed fractures and so their age relative to deformation and mineral precipitation events cannot be established with certainty. Equally confusing is the fact that their microthermometric values typically span inexplicably wide ranges. The literature on shear-zone hosted orogenic gold deposits is full of photographs of such fluid inclusions in quartz porphyroclasts (e.g. Fig. 1).



Figure 1. Hydrothermal quartz that has been weakly deformed in the ductile regime. Relatively large, irregular-shaped fluid inclusions occur with clusters of tiny equant inclusions. Sample from the Packsack orogenic gold deposit, Manitoba.

#### **Research questions and approach**

The obvious questions that arise are: (1) What systematic changes in shape, size, chemical composition (X) and density (or molar volume,  $V_{\rm m}$ ) are induced in fluid inclusions by progressive shear deformation of the host quartz crystal? (2) Are pre-deformation inclusions and their original  $V_{\rm m}$ -X properties ever preserved and how can such inclusions be recognized? (3) Do "sheared" fluid inclusions preserve information about the conditions of deformation?

To begin answering these questions we undertook a project with a 2-step approach: (1) subject natural, undeformed, inclusion-bearing quartz samples to low degrees of ductile shear in the laboratory, then (2) compare the deformed inclusions and their modified properties with naturally deformed samples.

#### **Deformation experiments**

For the experiments [2,3,4] we chose freely grown quartz crystals containing large CO<sub>2</sub>-H<sub>2</sub>O-NaCl inclusions from an undeformed orogenic gold vein and a control sample with H<sub>2</sub>O–NaCl inclusions. After photographing the inclusions and performing microthermometry, we placed the samples in a Griggs pistoncylinder apparatus. High temperatures (700-900 °C) were required to achieve incipient plastic behaviour, so high confining pressures  $(\sigma_3 = 600-1150 \text{ MPa})$  were required to keep the fluid inclusions on their original isochores during run-up and run-down and thereby avoid decrepitation or stretching. Small degrees of pure shear strain (1–15%  $\Delta L/L$ ) were induced in the samples by applying high axial compression ( $\sigma_1 = 700-1500$  MPa, equal to differential stresses of  $\sigma_1 - \sigma_3 = 250-500$  MPa) at strain rates of  $10^{-8}$  to  $10^{-9}$  s<sup>-1</sup>. These *P*-*T* conditions and strain rates are far more extreme than those that cause comparable degrees of shear strain in nature.

The deformed crystals display undulose optical extinction and bands of c-axis misorientation but no subgrains. All nine experiments show the same systematic results. Textural changes are summarized in Fig. 2. Some precursor inclusions became irregular in shape but otherwise remained intact. Other more deformed inclusions became dismembered into discoid *clusters* in which the irregular-shaped relict of a precursor inclusion is surrounded by a planar halo of tiny, newformed, neonate inclusions. All the planar clusters lie within a crystallographic plane subperpendicular to the orientation of  $\sigma_1$ . The alignment of all the hundreds of planar clusters within this lattice plane (rhomb or prism, according to the orientation of the crystal in the experiment) defines a macroscopic cleavage within the samples.

As far as  $V_m$ -X changes are concerned, *intact* inclusions retain the properties of the

precursors but *relict* inclusions adopt new disequilibrium  $V_{\rm m}$  values unrelated to the P-Tconditions of deformation. The neonate inclusions inherit the CO<sub>2</sub>/NaCl ratios of the precursor inclusions but their salinities are consistently elevated, demonstrating loss of H<sub>2</sub>O to the surrounding quartz during deformation. Their  $V_{\rm m}$  values (and hence their  $T_{\rm h}$  values) spread over wide ranges. A surprising result is that the lowest  $V_{\rm m}$  values (i.e. highest densities) of the neonates are in equilibrium with the pressure defined by  $\sigma_1$  at the temperature of the experiment. That is to say, the isochores of the densest neonates pass through the pressure value of  $\sigma_1$  at  $T_{exp}$ . We had expected reequilibration towards the mean stress of the experiment  $(\sigma_1 + \sigma_3)/2$ , but this is not the case.



*Figure 2. Textural changes induced by shear deformation of fluid inclusions in quartz.* 

## **Comparison with natural samples**

For the second step in our approach [5] we sampled a weakly deformed, hydrothermalmetamorphic quartz vein from the Grimsel Pass, Aar Massif, Central Alps, Switzerland. The vein sits within a slice of Pre-Variscan gneisses bounded by major strike-slip shear zones. Some 95 vol.% of the vein consists of cm-size crystals that are rich in CO<sub>2</sub>-NaCl-H<sub>2</sub>O inclusions and that display undulose optical extinction, deformation lamellae, bands of c-axis misorientation and domains of subgrains. The remaining 5 vol.% of the vein is made up of ribbons of rotated and recrystallized subgrains (devoid of fluid inclusions) along the margins of the large quartz crystals. All these features indicate that the large crystals that still contain fluid inclusions experienced only about 5% ( $\Delta L/L$ )

intracrystalline ductile strain, comparable to that in the piston-cylinder experiments.

Our first surprise was that the fluid inclusion textures in the Grimsel vein look essentially identical to those in our experimental products (Figs. 3–5). None of the textural features noted in the experiments are missing from the natural samples and vice versa. As the natural samples contain more inclusions, the macroscopic cleavage due to alignment of the planar inclusion clusters is even more prominent. Moreover, the pattern of microthermometric data shown by the various inclusion types (intact, relict and neonate) in the Grimsel vein is the same as that in the experiments.



*Figure 3.* Comparison of intact inclusions in experimentally and naturally strained quartz.

# What we can learn from fluid inclusions in ductilely deformed quartz?

We propose that the striking one-to-one correspondence in textural and  $V_m-X$  properties between the experimental and natural inclusions justifies interpreting the Grimsel samples – and by extension all other natural quartz samples affected by weak ductile deformation – in terms of the experimental results. Accordingly, we suggest that the following 6 kinds of information can be obtained by applying the experimental "rules" to naturally deformed inclusions:



**Figure 4.** Comparison of dismembered inclusion clusters in experimentally and naturally strained quartz, viewed along  $\sigma_1$ .



**Figure 5.** Comparison of dismembered inclusion clusters in experimentally and naturally strained quartz, viewed into the plane containing  $\sigma_1$  and  $\sigma_3$ .

(1) Planar arrays of dismembered fluid inclusions defining a penetrative cleavage in quartz are diagnostic of small degrees of intracrystalline plastic deformation.

- (2) All types of deformed inclusions (intact, relict and neonate) preserve the predeformation concentration ratios of gases to electrolytes.
- (3) The salinity and  $V_{\rm m}$  of the central *relict* inclusion in each cluster cannot be used to determine the properties of the fluid that was trapped in the inclusions prior to deformation. Similarly, the systematically elevated salinity of the neonate inclusions is an artefact of the deformation and thus it provides no more than a maximum value for the salinity of the precursor inclusions.
- (4) Analysis of *intact* inclusions in deformed samples yields the pre-deformation properties of the fluid inclusions.
- (5) The orientation of  $\sigma_1$  at the time of ductile deformation can be derived from the pole to the cleavage plane within which the dismembered inclusions are aligned. This interpretation is the reverse of what would be deduced if the cleavage planes were to be erroneously interpreted as tensile (mode-I) fractures formed in the brittle regime.
- (6) The density of the densest *neonate* inclusions, as obtained by microthermometry and thermodynamic modelling, reflects the pressure value of  $\sigma_1$  at the temperature of ductile deformation.

#### Neonate inclusions as paleopiezometers

We applied the above rules to reconstruct the P-T-deformation history of the Grimsel vein [5]. A prerequisite for this task was to know from independent data the  $P_{\text{lithostatic}}$ -T path of the host rocks of the vein. We intersected the isochores of the *intact* inclusions with the  $P_{\text{lith}}$ -T path to derive the formation conditions of the vein at 430–460 °C and 510–330 MPa. We deduced the subsequent ductile strike-slip deformation to have occurred above the trapping temperature of undeformed secondary inclusions (350 °C) in the vein. Having thus bracketed the ductile event to 350-430 °C, we assumed  $\sigma_2$  was equal to  $P_{\text{lith}}$ , as given by the  $P_{\text{lith}}$ -T path. We then estimated  $\sigma_3$  from the minimum P required to avoid decrepitation of the intact inclusions, as determined in our experiments. Finally, we obtained a range of Pvalues for  $\sigma_1$  during the ductile deformation by intersecting the densest neonate isochore with T = 350-430 °C. From these data were able to calculate the differential stress during the

ductile deformation:  $(\sigma_1 - \sigma_3) \approx 300$  MPa. Thus, as well as allowing reconstruction of the  $V_m - X$ properties of the pre-deformation fluid, this fluid inclusion methodology involving neonate isochores serves as a novel paleopiezometer for weakly deformed quartz.

#### **Future work**

We are now interested in tracking how fluid inclusion properties evolve at higher degrees of strain. Our suspicion is that all intact and relict inclusions become entirely dismembered, leaving only huge numbers of tiny inclusions that have densities neonate commensurate with  $\sigma_i$ , presumably like those in Fig. 1. Eventually, as strain increases further, mechanisms such as subgrain rotation recrystallization and grain-boundary migration consume the porphyroblasts and obliterate the fluid inclusions. Sampling weakly deformed porphyroblasts is therefore the key to extracting fluid inclusion information from ductilely deformed quartz-bearing rocks.

#### References

[1] Kerrich R. (1976) Some effects of tectonic recrystallization on fluid inclusions in vein quartz. Contrib. Mineral. Petrol. 59, 195–202.

[2] 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. Contrib. Mineral. Petrol. 160, 825-843.

[3] Diamond L.W., Tarantola A. & Stünitz H. (2010) Modification of fluid inclusions in quartz by deviatoric stress II: Experimentally induced changes in inclusion volume and composition. Contrib. Mineral. Petrol. 160, 845-864.

[4] Tarantola A., Diamond L.W., Stünitz H., Thust A. & Pec M. (2012) Modification of fluid inclusions in quartz by deviatoric stress. III: Influence of principal stresses on inclusion density and orientation. Contrib. Mineral. Petrol. 164, 537–550.

[5] Diamond L.W. & Tarantola A. (2015) Interpretation of fluid inclusions in quartz ductile deformed bv weak shearing: Reconstruction of differential stress magnitudes and pre-deformation fluid properties. Earth & Letters, 107-119. **Planetary** Sci. 417,

# Volatile concentrations of silicate melt inclusions: Insights into processes in active volcanic systems.

Rosario Esposito<sup>1</sup>, Matthew Steele-MacInnis<sup>2</sup>, Lowell R. Moore<sup>3</sup>, and Robert J. Bodnar<sup>3</sup>,

<sup>1</sup>Department of Earth, Planetary and Space Science, UCLA, Los Angeles, CA 90095-1567 USA <u>r.esposito@epss.ucla.edu</u>

<sup>2</sup>Institute for Geochemistry and Petrology, ETH Zürich, Clausiusstrasse 25, NW CH 8092 Zurich (Switzerland) <sup>3</sup>Fluids Research Laboratory, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061 USA

In recent years, much research has focused on gaining a better understanding of volatile evolution in active volcanic systems using melt inclusions (MI). MI represent aliquots of melt trapped during crystal growth or healing of fractures in minerals (and more rarely during crystal dissolution) and represent the only method available to directly measure volatile contents of deep, undegassed melts. Ideally, the trapped melt is representative of the melt in equilibrium with the host crystal at the moment of trapping. As such, the volatile contents of MI, coupled with the melt (glass) compositions, can be used to estimate depths of inclusion trapping and crystal formation, based on experimental vapor solubility models for silicate melts. In addition, the volatile contents of MI can be used to determine magma dynamics of past eruptions, in an effort to better predict the style of future eruptions. Volatile contents recorded by MI have also been used to infer processes occurring in volcanic plumbing systems, such as volatile fluxing from a deep source region to shallow reservoirs. magma Also, MI volatile concentrations were used to estimate the magmatic volatile input for the global volatile cycles MI [1 and references therein].

In the literature, a common feature of MI volatile concentration data is the high intrasample variability within a typical meltinclusion sample dataset (Fig. 1). For example, CO<sub>2</sub> concentrations in the glass phase contained in silicate MI commonly vary over two to three orders of magnitude, within a typical melt inclusion sample. Such variability may represent variations in pressure, temperature, oxidation state, and/or melt composition during MI entrapment in the magma reservoir or plumbing system. Such variability may thus provide insights into magmatic processes such as cooling, ascent, fractionation, etc. For instance, in many studies, the large variability of CO<sub>2</sub> relative to

the H<sub>2</sub>O concentrations in the glass phase of silicate MI has been interpreted as a record of magma ascent through the crust, owing to the greater pressure-sensitivity of CO<sub>2</sub> solubility relative to that of H<sub>2</sub>O in silicate melts (Fig. 1). Thus, if a silicate melt was saturated in CO<sub>2</sub>rich vapor during its ascent, then CO<sub>2</sub>-rich MI would represent melt trapped at greater depths, while CO<sub>2</sub>-poor MI would represent melt trapped at shallower depths (Fig. 1 a). Note, however, that interpretation of magmatic degassing via ascent (referred to in literature "degassing path") relies on the as a fundamental assumption that the trapped melt was saturated in volatiles.

Although MI data provide numerous key insights into pre-eruptive volatile systematics, several recent studies have reported that the variability in MI volatile contents may be a result of modifications of MI after trapping (Fig. 1 b and c). As such, these recent studies recommend special caution in interpreting MI volatile data. For example, post entrapment crystallization (PEC) at the host/MI interface can lead to formation of a vapor bubble in the inclusion, especially if the melt was vaporsaturated at the moment of trapping (see [2]. and references therein). The formation of vapor bubbles in MI a can strongly affect the concentrations of volatiles remaining in the melt (or glass, when analyzed at ambient conditions). If several MI trapped the same melt, but were affected by different proportions of PEC (e.g., different thermal path after trapping), then the resulting  $CO_2$  vs.  $H_2O$  trends in the MI glasses may be similar to trends produced by degassing (arrows in Fig. 1 b). Moreover, other recent studies have reported that MI may experience either loss or gain of volatiles (especially H) after trapping by diffusional re-equilibration with the surrounding melt (see [3], and references therein). It is important to note that diffusiveloss of volatiles from the MI can significantly

lower the internal pressure of MI and trigger the formation of a vapor bubble. Furthermore, the formation of vapor bubbles after trapping is promoted by differential thermal contraction between melt and host (see [4], and references therein). All processes that lead to formation of a vapor bubble after trapping will affect the volatile contents of volatiles dissolved in the melt (=glass, at the time of analysis). In particular, CO<sub>2</sub> will be preferentially lost to these bubbles, which may produce trends mimicking degassing paths (termed "pseudodegassing paths") if only the volatile contents of the glass are considered. Recently, Esposito et al. [5] reported a method to reconstruct the original volatile contents of bubble-bearing MI (Fig. 1 c). Esposito et al. [5] analyzed both the CO<sub>2</sub> contents of the vapor bubble (using Raman spectroscopy) and of the glass (using secondary ion mass spectrometry) of bubblebearing MI from the Solchiaro eruption in the Phlegrean Volcanic District. Mass balance calculations showed that ca. 64% of the original CO<sub>2</sub> was contained in the vapor phase, whereas only ca. 36% of the CO<sub>2</sub> remained in the glass phase. Likewise, Hartley et al. [6] recently reported similar percentages of CO<sub>2</sub> contained in the bubbles of bubble-bearing MI from the Laki eruption (Iceland). Finally, Moore et al. [4] reported that MI vapor bubbles may contain up to 90% of the CO<sub>2</sub> budget of some volcanic MI. These studies highlight the importance of analyzing the volatile contents of vapor bubbles, especially in order to characterize the evolution of volatiles in volcanic systems based on bubblebearing MI.

In this study, we present methods that can be used to assess the reliability of volatile contents of MI, which in turn can be used to draw rigorous interpretations of magmatic processes. Firstly, we highlight the importance of petrographic examination of MI to collect defensible Detailed data. petrographic information is vital for interpreting the intrasample variability commonly exhibited by MI [7]. For instance, the selected MI must be described before being exposed to the surface. If not, the volume of the MI cannot be accurately assessed and the presence of bubbles (plus trapped and/or daughter crystals) can be missed and the interpretation of geochemical data will suffer. The most important petrographic information is the

observation of melt inclusion assemblages (MIA; see [8] and references therein) which represent groups of MI all trapped at the same time, and thus under the same physical and chemical conditions (e.g., MI trapped along a growth zone of a phenocryst). Because variability in MI volatile contents is common in MI studies, the MIA concept allows one to decipher whether this variability represents real variations in the trapping conditions, or rather reflects post-entrapment modifications, similar to the analogous FIA (Fluid Inclusion Assemblage [9]) concept applied to fluid inclusions. Thus, in order for MI to provide reliable information concerning the preeruptive volatile content, the MI must obey Roedder's (Sorby's) Rules: Namely, the MI must have trapped a single homogeneous melt phase, the volume of the MI must remain constant after trapping, and nothing can be added or lost from the MI after trapping. If MI in a single MIA show the same volatile contents and other properties, an inclusionist can be confident that those MI contain representative samples of the melt in equilibrium with the growing phenocryst.

An advantage of studying groups of MI originally trapping the same melt (MIA) is that it allows investigation of which processes contributed to modifications of MI. For instance. it has been suggested that correlations between MI size and element concentrations may shed light on whether significant element loss/gain occured by diffusion. In particular, if absence of a sizeconcentration correlation is thought to corroborate absence of significant effect of Hloss, because smaller MI are expected to be more strongly affected by this process [11]. However, this argument assumes that all the analyzed MI trapped the same melt. If the MI actually trapped volatile saturated melts at different depths, then the latter assumption would not be valid. If MI within a single MIA show variable volatile concentrations, an inclusionist should question whether these MI record a representative composition. However, locating MIA can be challenging, especially in juvenile phenocrysts, and therefore we propose alternative means to establish time correlations among studied MI (e.g., cathodoluminescence imaging). Furthermore, we highlight the importance of bubbles in bubble-bearing MI, and methods to estimate the original  $CO_2$ 



Figure 1: H<sub>2</sub>O-CO<sub>2</sub> systematics of MI from three eruptions. Fig. 1a: bubble-bearing, bubble-free, and anomalous MI hosted in olivine from the Solchiaro eruption (Italy) (figure modified after [5]). The arrow indicates an open degasing path. CO<sub>2</sub>-rich MI were interpreted as trapped at great depths while CO<sub>2</sub>-poor MI were trapped at shallower depths. Fig. 1 b: MI hosted in quartz from Pine Grove (US) [10]. Solid arrow represents the trend defined by different degrees of PEC, while the dashed arrow represents a degassing path as calculated by [10] (figure modified after [2]. Fig.1c: MI hosted in olivine from Seguam eruption (Aleutian Islands, US) [4]. Noticed that filled symbols represent reconstructed volatile contents of bubblebearing MI (figure modified after [4]).

concentration of bubble-bearing MI [4]. Finally, we review the importance of major/trace element compositions of MI and mineral hosts in interpreting the volatile content of MI.

#### Acknowledgements

R. Esposito thanks B. De Vivo and C. Manning research groups for the continuous source of ideas and scientific support.

#### References

[1] 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.

[2] Steele-MacInnis M.J., Esposito R., & Bodnar R.J. (2011) Thermodynamic model for the effect of post-entrapment crystallization on the  $H_2O$ -CO<sub>2</sub> systematics of volatile saturated silicate melt inclusions, Journal of Petrology, 52(12), 2461-2482.

[3] Lloyd A., Plank T., Ruprecht P., Hauri E., & Rose W. (2013) Volatile loss from melt inclusions in pyroclasts of differing sizes, Contributions to Mineralogy and Petrology, 165(1), 129-153.

[4] Moore L.R., Gazel E., Tuohy R., Lloyd A., Esposito R., Steele-MacInnis M.J., Hauri E. H., Wallace P., Plank T., & Bodnar, R.J. (2015) Bubbles matter: An assessment of the contribution of vapor bubbles to melt inclusion volatile budgets, American Mineralogist, 100, 806-823.

[5] Esposito R., Bodnar R.J., Danyushevsky L.V., De Vivo B., Fedele L., Hunter J., Lima A., & Shimizu N. (2011) Volatile Evolution of Magma Associated with the Solchiaro Eruption in the Phlegrean Volcanic District (Italy), Journal of Petrology, 52(12), 2431-2460.

[6] Hartley M.E., Maclennan J., Edmonds M., & Thordarson T., (2014) Reconstructing the deep  $CO_2$  degassing behaviour of large basaltic fissure eruptions, Earth and Planetary Science Letters, 393(0), 120-131.

[7] Roedder E. (1979) Origin and significance of magmatic inclusions. Bulletin de Mineralogie, 102(5-6), 487-510.

[8] Bodnar R.J., & Student J.J. (2006) Melt inclusions in plutonic rocks: Petrography and microthermometry, in Melt Inclusions in Plutonic Rocks, J.D. Webster, Editor, Mineralogical Association of Canada: Montreal, Quebec, Canada, 1-25.

[9] Goldstein D.J., & Reynolds D.C. (1994) Systematics of fluid inclusions in diagenetic minerals, SEPM (Society for Sedimentary Geology) Short Course Notes, 31, 1-199. [10] Lowenstern J.B. (1994) Dissolved volatile concentrations in an ore-forming magma, Geology, 22(10), 893-896.

[11] Qin Z., Lu F., & Anderson A.T. (1992) Diffusive reequilibration of melt and fluid inclusions, American Mineralogist, 77(5-6), 565-576.

# The role of hydrothermal fluids in the formation of high grade BIF-hosted iron ore deposits

## Steffen G. Hagemann

Centre for Exploration Targeting, School of Earth and Environment, University of Western Australia, Australia. steffen.hagemann@uwa.edu.au

#### Introduction

The BIF-hosted iron ore system represents the world's largest and highest grade iron ore districts and deposits. BIF, the precursor to low- and high-grade BIF hosted iron ore, consists of Archean and Paleoproterozoic Algoma-type BIF (e.g., Serra Norte iron ore district in the Carajás Mineral Province), Proterozoic Lake Superior-type BIF (e.g., deposits in the Hamersley Province and Kaapvaal craton), and Neoproterozoic Rapitan-type banded iron formations (e.g., the Urucum iron ore district).

In most large BIF districts and high-grade iron ore deposits, three major hypogene and one supergene metasomatic processes, which result in distinct ore stages, are observed: (1) silica leaching and formation of magnetite and locally carbonate; (2) oxidation of magnetite to hematite (martitisation), further dissolution of quartz and formation of carbonate, (3) further martitisation, replacement of Fe silicates by hematite, new microplaty hematite and specular hematite formation and dissolution of carbonates; and (4) replacement of magnetite and any remaining carbonate by goethite and hematite and formation of fibrous quartz and clay minerals.

# Hydrothermal fluids involved in the evolution of hypogene and supergene iron ore

The critical processes that caused the transformation of BIF to high-grade iron ore are ultimately caused by external hydrothermal fluids that circulated along fluid pathways (structures) and interacted with the BIF. These hypogene and supergene fluids are paramount for the formation of high-grade BIF-hosted iron ore because of the enormous amount of: (1) silica-undersaturated alkaline fluids necessary to dissolve quartz in BIF, (2) oxidized fluids that causes the oxidation of magnetite to hematite, (3) alkalic fluids that

are necessary to form widespread metasomatic carbonate, (4) carbonate-undersaturated fluids that dissolves the diagenetic and metasomatic carbonates, and (5) oxidized fluids to form hematite in the hypogene- and supergeneenriched zone and clay minerals in the supergene zone. In recent years a variety of researchers have attempted to constrain the fluid chemistry through fluid inclusions trapped in quartz-carbonate veins and hematite (Figures 1 and 2), stable isotope investigations on carbonates, silicates, oxides and microchemistry of oxides (Hagemann et al., 1999; Rosière and Rios, 2004; Figueiredo e Silva et al., 2009; 2013; Hensler et al., 2014). One of the results of these investigations is that there is no single fluid reservoir responsible for the upgrade of BIF to iron ore. Rather multiple fluid sources, depending on the geodynamic setting, crustal depth level and proximity of igneous intrusions to BIF at the time of metasomatism, as well as fluid-rock reactions are involved in facilitating the critical upgrade processes. The hydrothermal fluids include: deep (hypogene), mainly basinal brines, or magmatic fluids and shallow ancient meteoric fluids, as well as recent supergene fluids (Hagemann et al., 1999; Taylor et al., 2001; Thorne et al., 2004; 2014; Figueiredo e Silva et al., 2008; 2013.



**Figure 1** Irregular clusters of primary fluid inclusions are trapped in dolomite in equilibrium with microplaty hematite.



*Figure 2* Liquid-rich fluid inclusions trapped in hematite (from Rosiere and Rios (2004).

#### Modelling

McLellan et al. (2004), Oliver et al. (2007) and McLellan and Oliver (2008) conducted finite difference modelling of fluid flow during extensional deformation in a mountain range and showed that surface fluids are drawn towards areas of failure and focus into the centre of the mountain. The formation of normal faults provides excellent focussed fluid pathways in which mechanical and geological conditions are particularly conductive to both upward and downward fluid flow events. Upward flow from the base of the fault within the model is favoured by low permeability basement materials and supra-hydrostatic pressures. Downward migration of fluids becomes more prominent as extension progresses and upward fluid flow from the base diminishes. Importantly, sedimentary layering, as seen in the BIF units, allows lateral fluid flow, such that sites of potential fluid mixing can be located within permeable iron ore close to fault zones (McLellan et al., 2004). These simulations are considered to be compatible with paragenetic, fluid inclusion and stable isotope models for Lake Superior type, and probably also for Algoma type, BIF deposits, which both predict synchronous fluid flow of upwards and downwards fluids during the hypogene upgrade of BIF to high-grade iron ore (see references in Thorne et al., 2008).

Recently, Evans et al. (2013) apply thermodynamic and mass balance constraints to Lake Superior BIF-hosted iron ore deposits to predict the conditions responsible for the removal of quantities of silica from unenriched BIF. These authors propose the involvement of up- or downward moving high-pH (>9), hypersaline brines. These hypersaline fluids may be sourced from density- or topographydriven basinal brines or evaporitic fluids, sourced from marginal platforms during extensional faulting and orogenic collapse. No such modelling has been conducted for Algoma or Rapitan BIF-hosted iron ore systems.

# Multi source fluid models for BIF-hosted iron ore systems

The recognition that multiple fluid sources and metasomatic processes are involved during time in the upgrade of BIF to iron ore resulted in deposit-scale fluid flow models (see summary by Thorne et al., 2008) for a variety of deposits and districts.

Dalstra and Guedes (2004) provided the first attempt to relate silicate-carbonate-oxide assemblages in high-grade iron ore of various iron districts to temperatures and crustal depth at the time of ore formation. Their continuum model was further modified by Angerer et al. (2014), based on the well-studied Hamersley province and Yilgarn craton deposits in Western Australia. There are several issues with such a model (cf., Hagemann et al., 2008): (1) timing of mineralization: it is clear from the analyses of high-grade iron ore deposits that the upgrade process is also a function of time, specifically that the supergene enrichment processes may act only millions of years after the hypogene upgrade; ideally only a 4-D model can adequately explain the different stages of mineralization through time; (2) change of temperatures and relationship to depth levels: in many of the large iron ore districts there is a substantial temperature gradient between early and advanced alteration and mineralization (e.g., at Carajás, Paraburdoo); however, there is no evidence for large pressure/depth changes, i.e., there is a lack of alteration minerals or fluid inclusion geobarometric data that provide evidence for a change in crustal depth in a given deposit.

As an alternative to a unifying continuum model, two discrete end-member models for hypogene high-grade BIF hosted iron ore are proposed: (1) granite-greenstone belt hosted, strike-slip fault zone controlled, early magmatic (±metamorphic) fluids and late meteoric water controlled, and (2) rift basin, normal fault zone controlled early basinal (±evaporitic) brines and late meteoric water controlled. A variation of the latter is the metamorphosed rift zone model where BIF, deposited early in a basinal environment, is later metamorphosed forming unique structural fabrics in the oxides. It is during the orogenic event(s) that the upgrade of itabirite to highgrade hypogene iron is proposed. Another variation of the rift basin model is the Rapitantype model where early BIF mineralization in a reduced, glacier-controlled environment and subsequent very low-grade metamorphism is responsible for the bulk of the iron mineralization. Importantly, all of these hypogene iron ore models propose a second stage of iron enrichment during substantial weathering in Recent times within the upper portions of the crust. This led to significant supergene enrichment including an upgrade of the Fe content.

The supergene enriched iron ore model, with no evidence for deep hypogene roots, comprises: (1) goethite-rich iron ore deposits resulting from Cenozoic supergene enrichment processes, e.g., the Mining Area C in the Hamersley province (Angerer et al., 2014) or Capanema in Brazil (Ramanaidou, 2009), and (2) ancient karstic supergene iron ore (e.g., at the Sishen, Sishen South, and Beeshoek deposits; cf. Beukes et al., 2002) where blocks of BIF slumped into underlying carbonate units and subsequently experienced deep lateritic weathering (Van Schalkwyk and Beukes, 1986; Gutzmer and Beukes, 1998).

#### Acknowledgements

The data and interpretation presented in this abstract are a direct outcome of research conducted by the CET-UFMG iron ore research group members Thomas Angerer, Paul Duuring, Ana Hensler, Warren Thorne, Lydia Lobato, Rosalina Figueiredo e Silva, Carlos Rosiére, Yoram Teitler and published in "BIF-hosted iron mineral system: A review" in press, Ore Geology Reviews.

#### References

Angerer, T., Duuring, P., Hagemann, S. G., Thorne, W., & McCuaig, T. C. (2014) A mineral system approach to iron ore in Archaean and Palaeoproterozoic BIF of Western Australia: Geological Society, London, Special Publications, 393.

Beukes, N. J., Gutzmer, J., & Mukhopadhyay, J. (2002) The Geology and Genesis of High-Grade Hematite Iron Ore Deposits, Iron Ore 2002: Perth, 23-29.

Dalstra, H., & Guedes, S. T. (2004) Giant hydrothermal hematite deposits with Mg-Fe metasomatism: A comparison of the Carajás, Hamersley, and other iron ores: Economic Geology, 99, 1793-1800.

Evans, K. A., McCuaig, T. C., Leach, D., Angerer, T., & Hagemann, S. G. (2013) Banded iron formation to iron ore: A record of the evolution of Earth environments?: Geology, 41, 99-102.

Figueiredo e Silva, R. C., Lobato, L. M., & Rosiere, C. A. (2008) A Hydrothermal Origin for the Jaspilite-Hosted Giant Sierra Norte Deposits in the Cajajas Mineral Province, Para State, Brazil: Reviews in Economic Geology, 15, 255-290.

Figueiredo e Silva, R. C., Lobato, L. M., Hagemann, S., & Danyushevsky, L. (2009) Laserablation ICP-MS analyses on oxides of hypogene iron ore from the giant Serra Norte jaspilitehosted iron ore deposits, Carajás Mineral Province, Brazil, in Williams, P. J., ed., Proceedings of the 10th Biennial SGA Meeting of The Society for Geology Applied to Mineral Deposits Townsville Australia 17th - 20th August 2009: Townsville, 570-572.

Gutzmer, J., & Beukes, N. J. (1998) Earliest laterites and possible evidence for terrestrial vegetation in the Early Proterozoic: Geology, 26, 263-266.

Hagemann, S. G., Barley, M. E., Folkert, S. L., Yardley, B. B. W., & Banks, D. A. (1999) A hydrothermal origin for the giant BIF-hosted Tom Price iron ore deposit, in Stanley, C. J., ed., Mineral Deposits – Process to Processing: Rotterdam, Balkema, 41–44.

Hagemann, S., Rosiere, C. A., Gutzmer, J., & Beukes, N. J. (2008) Glossary of terms Banded Iron Formation-related high-grade iron ore: Banded Iron Formation-Related High-Grade Iron Ore, 15, 411-414. Hensler, A.-S., Hagemann, S. G., Brown, P. E., & Rosière, C. A. (2014) Using oxygen isotope chemistry to track hydrothermal processes and fluid sources in itabirite-hosted iron ore deposits in the Quadrilátero Ferrífero, Minas Gerais, Brazil: Mineralium Deposita, 49, 293-311.

McLellan, J. G., Oliver, N. H. S., & Schaubs, P. M. (2004) Fluid flow in extensional environments; numerical modelling with an application to Hamersley iron ores: Journal of Structural Geology, 26, 1157-1171.

McLellan, J. G., & Oliver, N. H. S. (2008) Application of numerical modelling to extension, heat, and fluid flow in the genesis of giant banded iron formation-hosted hematite ore deposits: Reviews in Economic Geology, 15, 185–196.

Oliver, N. H. S., Cleverley, J. S., Dipple, G. M., & Broadbent, G. C. (2007) Giant BIF hosted hematite ores: Geochemical and isotopic modeling of meteoric and basinal fluid-rock reactions: 9th Biennal SGA Meeting, Dublin, 2007, 1219-1222.

Ramanaidou, E. R., and Morris, R. C., 2009, Comparison of Supergene Mimetic and Supergene Lateritic Iron Ore Deposits, in AusIMM, ed., Proceedings Iron Ore Conference 2009, 27-29 July 2009, Perth, Western Australia, 243-246.

Rosière, C. A., and Rios, F. J., 2004, The origin of hematite in high-grade iron ores based on

infrared microscopy and fluid inclusion studies: the example of the Conceição mine, Quadrilátero Ferrífero, Brazil: Economic Geology, v. 99, p. 611-624.

Taylor, D., Dalstra, H. J., Harding, A. E., Broadbent, G. C., & Barley, M. E. (2001) Genesis of high-grade hematite orebodies of the Hamersley province, Western Australia: Economic Geology, 96, 837-873.

Thorne, W. S., Hagemann, S. G., & Barley, M. (2004) Petrographic and geochemical evidence for hydrothermal evolution of the North Deposit, Mt Tom Price, Western Australia: Mineralium Deposita, 39, 766-783.

Thorne, W., Hagemann, S., Webb, A., & Clout, J. (2008) Banded Iron Formation-Related Iron Ore Deposits of the Hamersley Province, Western Australia: Banded Iron Formation-Related High-Grade Iron Ore, Reviews in Economic Geology, 15, 197-221.

Thorne, W. S., Hagemann, S. G., Sepe, D., Dalstra, H. J., & Banks, D. A. (2014) Structural Control, Hydrothermal Alteration Zonation, and Fluid Chemistry of the Concealed, High-Grade 4EE Iron Orebody at the Paraburdoo 4E Deposit, Hamersley Province, Western Australia: Economic Geology, 109, 1529-1562.

Van Schalkwyk, J., & Beukes, N. (1986) The Sishen iron ore deposit, griqualand West: Mineral Deposits of Southern Africa, 2, 931-956.

# Recent Advances in the Analysis of Volatiles and Fluid-Mobile Elements in Melt Inclusions by Secondary Ion Mass Spectrometry (SIMS)

Jan C. M. De Hoog, R. W. Hinton & EIMF

Edinburgh Ion Microprobe Facility, School of GeoSciences, University of Edinburgh, ceesjan.dehoog@ed.ac.uk

#### Introduction

Melt inclusions are micrometre-sized pockets of melt trapped in crystals while they crystallise from magma. The crystal host acts as a robust container, shielding the melt inclusion from late stage volcanic processes such as eruption, crystallisation and degassing. Hence, melt inclusions may provide a wealth of information about pre-eruptive conditions of the magma, in particular the volatile species  $H_2O$ ,  $CO_2$ , S, Cl and F, which are often lost from the magma during its evolution and eruption.

Several analytical techniques are capable of determining volatile concentrations in melt inclusions at the high spatial resolution needed (20-500 micrometre), but few are as versatile as Secondary Ion Mass Spectrometry (SIMS or ionprobe). This technique is capable not only of determining elemental concentrations of most volatiles down to ppm level, but also isotopic ratios of these species. In addition, can many elements be analysed simultaneously with volatiles, including fluidmobile elements such as lithium and boron.

The SIMS technique works by sputtering small amounts of material of the sample surface using a high-energy focused ion beam, typically composed of  ${}^{16}O^{-}$  or  ${}^{133}Cs^{+}$ . This sputtered material is accelerated into a mass spectrometer and ion intensities are counted using an electron multiplier or Faraday cup. Multi-collector detection is also possible. The analysis pit is typically ca. 10-15 µm wide and several µm deep (Fig. 1). Sample requirements are modest, most importantly a flat surface and compatibility with high vacuum (10<sup>-9</sup> mbar).

As every analytical technique, SIMS has its limitations, the most critical one being the need of well-characterised and matrix-matched calibration standards. The following sections will briefly discuss the analytical details of different volatile and fluid-mobile elements as currently employed by the Edinburgh Ion Microprobe Facility (*EIMF*). This NERCsupported facility hosts two ion microprobes each with their own strengths, a small geometry Cameca IMS 4f and a large geometry, high-resolution Cameca IMS 1270.



**Figure 1.** Secondary electron image showing the pits created by the two stages of SIMS analysis conducted on a zircon-hosted melt inclusion. The largest oval represents the pit generated by the boron isotope analysis, the smaller oval is the pit generated by the trace element analysis. DM = daughter mineral (magnetite).

## $H_2O$

Water is typically the most abundant volatile in melt inclusions and provides key information about pre-eruptive volatile contents, magma storage depths, volcanic gas emissions and water content of the magma source [e.g., 1]. It can be measured in silicate glasses as <sup>1</sup>H or <sup>16</sup>O<sup>1</sup>H. Of all volatiles, good vacuum conditions are most critical for water analyses (<10<sup>-9</sup> mbar). Therefore, where possible samples are mounted in indium, which has superior outgassing properties compared to more commonly used epoxy resins.

At *EIMF*, H<sub>2</sub>O is generally measured using the Cameca IMS 4f using a <sup>16</sup>O- primary beam and collecting H<sup>+</sup> ions. This allows it to be measured at the same time as light volatile elements and trace elements up to z = 50-70. The Cameca IMS 4f is preferred due to its fast peak switching capability and excellent

vacuum control, including an eight-sample air lock and a cryogenic pump.

During analysis of silicate glasses, ion intensities are commonly counted relative to that of <sup>30</sup>Si and corrected for the amount of  $SiO_2$  in the sample (determined independently by, e.g., electron microprobe, EPMA). Working curves are calculated by measuring several standard reference materials and plotting known  $H_2O/SiO_2$  vs measured  ${}^{1}H/{}^{30}Si$ . Doing that, a strong matrix-induced bias is observed between basalts (SiO<sub>2</sub> ca. 50 wt%) and rhyolites (SiO<sub>2</sub> ca. 70 wt%). This effect, rather fortuitously, scales with the amount of  $SiO_2$  in the sample. Omitting the  $SiO_2$ correction for H<sub>2</sub>O analyses results in working curves that are very similar for basalts and rhyolites (Fig. 2), and can therefore be used for intermediate melt inclusion compositions  $(SiO_2 = 55-65 \text{ wt.}\%).$ 

Our analytical protocol and extensive collection of glasses with known  $H_2O$  contents allows water concentrations in nearly all natural silicate glasses with  $H_2O$  contents from 0.01-4 wt%  $H_2O$  to be determined with an accuracy of ca. 10%.



**Figure 2.** Typical working curves for water in basalt and rhyolite glasses as measured in positive ion mode using the Cameca IMS 4f. Note on the x-axis is plotted  ${}^{1}H/{}^{20}Si$  to correct for matrix-induced fractionation; without this correction the equation would have been  ${}^{1}H/{}^{20}Si \times SiO_{2}$  (wt.%).

## $CO_2$

 $CO_2$  is for volcanologist a volatile species as important as  $H_2O$  and usually measured in conjunction. At *EIMF* C is generally measured in positive ion mode like other trace elements and H<sub>2</sub>O, using either the Cameca IMS 4f or the 1270. Due to potential interference of  $^{24}Mg^{2+}$  on the  $^{12}C^+$  signal this species needs to be measured at high mass resolution of ca. 1200 to allow interference-free measurement. This is particularly important for basaltic and intermediate melt compositions. Only in rhyolitic and granitic systems where MgO<0.5 wt.% can the measurements be done using low mass resolution, but still requires peak stripping of  $^{24}Mg^{2+}$  signals based on measured  $^{25}Mg^{2+}$  signals.



**Figure 3.** Typical mass spectrum for basaltic glass in the <sup>12</sup>C mass region. Note that even though  ${}^{24}Mg^{2+}$  and  ${}^{12}C$  are not fully resolved at  $M/\Delta M=1200$ , the Mg signal is negligible at the centre of the  ${}^{12}C$  peak at mass 12.00. Using a higher resolution would lead to unnecessary loss of C sensitivity. The <sup>11</sup>BH peak is fully resolved.

In contrast to  $H_2O$ , most carbon contamination does not come from the vacuum but from the sample surface. Therefore a stringent precleaning routine by rastering the ionbeam for several minutes prior to data collection is vital. Adopting this approach we routinely achieve ~1 cps <sup>12</sup>C backgrounds even on Mg-rich materials, equivalent to ca. 10 ppm CO<sub>2</sub>. Several well-characterised sets of calibration standards obtained by *EIMF* over the last few years have shown that little matrix effect exist between basaltic and rhyolitic glasses (Fig. 4), allowing measurement of nearly all natural silicate glasses with 20 ppm - 1 wt.% CO<sub>2</sub> with an accuracy of ca. 10%.

#### Halogens (F, Cl)

Halogens are preferably measured in negative ion mode but can be measured in positive ion

mode, which allows simultaneous analysis with  $H_2O$  and light fluid-mobile elements (Li,  $B \pm CO_2$ ). Detection limits are at the low ppm level.



**Figure 4.** Working curves for  $CO_2$  in basalt and rhyolite glasses. Matrix-induced bias is negligible. Note that the highest concentration rhyolite  $CO_2$  standard (1.03 wt.%) is not shown but has been included in the calibration.

The main issue is the availability of reliable standards, particularly for F, as for many glass standards values in the literature vary by up to a factor two. A considerable matrix effect is apparent between basaltic and rhyolitic glasses but quantification of this awaits better characterised standards, and is less of an issue in negative ion mode due to much higher ionisation yields. In positive ion mode, the estimated difference in relative ion yield for F and Cl (relative to Si) between basalts and rhyolites is about a factor 2, which limits the accuracy to no better than about 25%.

#### Sulfur

Sulfur is an important volatile as it produces sulfate aerosols in the stratosphere following large volcanic eruptions, which induces significant, but short-lived, climatic effects [2]. In melt inclusions it is often present in high enough concentrations that it can be measured by EPMA and therefore demand at *EIMF* has not been high. Due to interference of  $O_2$ molecular species it can only be measured at high mass resolution, preferably in negative ion mode using a <sup>133</sup>Cs<sup>+</sup> primary beam on the Cameca IMS 1270. It is therefore not routinely measured with the other volatiles, which are predominantly measured in positive ion mode using the Cameca IMS 4f. However, it can be measured simultaneously with C and halogens in negative ion mode.

#### Stable isotopes

SIMS is particularly well-suited for measuring isotope ratios due to its production of very stable ion beams over long time periods. The rewards of developing the stable isotope systems for H, C and S will be high, as these may provide detailed information about volatile sources and degassing processes that are difficult to obtain otherwise [e.g., 3].

However, progress for the measurement of these stable isotope system has been hampered by difficulties in obtaining calibration standards with a large enough compositional range to cover that of natural samples. Therefore, matrix-induced isotope fractionation effects have not been fully assessed. Synthesising standards, as has been successfully done for volatile concentrations, has been less successful as it has proven difficult to obtain isotopically homogenous glasses in large enough quantities to allow analysis by independent techniques. Natural glasses may be better suited, but sourcing samples with sufficiently high volatile concentrations has so far been largely unsuccessful. Preliminary results in the literature suggested limited matrix-induced fractionation for sulfur isotopes [4], but this awaits further verification by other labs.

## Boron

One of the more successful stable isotope systems is that of boron. Boron occurs in nature as two isotopes, <sup>10</sup>B and <sup>11</sup>B in a ratio of about 1:4. Boron isotopes are strongly fractionated at the Earth's surface and therefore provide an excellent tracer of recycling of crustal material in subduction zones and the Earth's mantle, as well as hydrothermal processes [e.g., 5].

At *EIMF* are measured preferably using the Cameca IMS 1270 in positive ion mode. Due to the Cameca IMS 1270's large geometry, even at its lowest resolution all potentially interfering species (such as  ${}^{10}B^{1}H$  and  ${}^{9}Be^{1}H$ ) are fully resolved. Boron isotope ratios can be measured on materials with as little as 1 ppm B to a precision of ca. 1 permil (1 $\sigma$ ) in 30

minutes using mono-collection mode and an electron multiplier detector. For concentrations of 10 ppm or higher we can achieve <0.5‰ precision in 15 minutes.

As isotope ratios measured by SIMS typically show significant instrumental mass fractionation, particularly for light elements, measured isotope ratios are corrected using measurements of reference glasses with known isotopic composition (Fig. 5). Many stable isotope systems show significant matrixdependent isotope fractionation but for boron isotopes it is negligible, as a diverse range of glass standards with SiO<sub>2</sub> ranging from 45-74 wt% fall within 1.5 permil of the certified values. The largest source of uncertainty is the apparent heterogeneity of some of the reference materials.



**Figure 5.** Typical working curve for boron isotopes in silicate glasses with B contents ranging from 4-190 ppm and with  $SiO_2$  contents between 45-74 wt%. Error bars represent 2s uncertainties. Instrumental mass fractionation in this example is 31.8‰.

## Lithium

Lithium occurs in nature as two isotopes. <sup>6</sup>Li and <sup>7</sup>Li in a ratio of about 1:12. Geochemically, it provides much the same information as boron, but is more prone to kinetic fractionation [6]. Analytical conditions are virtually identical to those of boron isotopes described above. However, SIMS analysis of lithium isotopes suffers from significant matrix-dependent isotope fractionation even within single mineral species [7]. This is in part mitigated by the availability of a diverse suite of glass standards with SiO<sub>2</sub> ranging from 45-74 wt%. Lithium ionises more efficiently than B, so precision is about two times better at equal concentration, but accuracy is somewhat less due to uncertainty associated with matrixinduced fractionation.

# Summary

The analysis at *EIMF* of  $H_2O$  and  $CO_2$ concentrations in melt inclusions is now routine with good sets of calibration standards and well-tested analytical protocols. The same can be said about boron and lithium isotope ratios. Halogen concentrations are still somewhat challenging, but recently more standard material has become available and these are now being tested as well as crosscalibrated with other materials. Stable isotope analysis of H, C and S still awaits reliable standard material, which is actively being worked on. Work in other labs suggest that matrix-induced fractionation is limited for S isotopes, so this is probably the most promising application in the short term.

# Web site

See the Edinburgh Ion Microprobe Facility web site at for more information, instrument access, sample preparation, etc.

www.geos.ed.ac.uk/facilities/ionprobe/

## References

 Wallace P.J. "Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data," J Volcanol Geotherm Res 140, pp. 217-240, 2005.
Pollack et al. "Volcanic explosions and climate change: a theoretical assessment," J Geophys Res 81, pp. 1071-1083, 1976.

[3] Shaw A. et al. "Hydrogen isotopes in Mariana arc melt inclusions: Implications for subduction dehydration and the deep-Earth water cycle," Earth Planet Sci Lett 275, pp. 138-145, 2008.

[4] Mandeville C. et al. "Sulfur isotope variation in basaltic melt inclusions from Krakatau revealed by a newly developed secondary ion mass spectrometry technique for silicate glasses," AGU Fall Meeting, abstract #V13F-07, 2008.

[5] Jones R. et al. "Temporal variations in the influence of the subducting slab on Central Andean arc magmas related to flat-slab subduction: evidence from boron isotopes," Earth Planet Sci Lett 408, pp. 390-401, 2014. [6] Marschall H.R. et al. "The lithium isotopic composition of orogenic eclogites and deep subducted slabs," Earth Planet Sci Lett 262, pp. 563-580, 2007. [7] Bell et al. "Lithium isotope analysis of olivine by SIMS: Calibration of a matrix effect and application to magmatic phenocrysts," Chem Geol 258, pp. 5-16, 2009.

# Fluid Inclusion Gold Concentrations: From Analysis to Implications for Hydrothermal Ore Formation

# Thomas Pettke & Larryn W. Diamond

University of Bern, Institute of Geological Sciences, CH-2012 Bern, Switzterland. pettke@geo.unibe.ch

Hydrothermal vein gold deposits have been exploited for millennia but the processes that lead to wt%-concentrations of native gold in such veins (Fig. 1) have remained unresolved. A prerequisite for their understanding are reliable estimates of gold concentrations in the ore-bearing fluids via fluid inclusion analyses, e.g. by Laser Ablation - Inductively Coupled Mass Spectrometry, LA-ICP-MS (Günther et al., 1997; Heinrich et al., 2003; Allan et al., 2005; Pettke et al., 2012). However, many published analyses often show remarkable, unexplained scatter, and the highest values are likely to be unrealistic according to current knowledge of solubility constants (e.g., Pokrovski et al., 2014).

This presentation addresses key requirements of successful fluid inclusion analysis with emphasis on (i) how to optimize the measurement strategy to obtain reproducible gold (or any other metal) concentrations in the sub- $\mu$ g g<sup>-1</sup> range, such that the values represent those of the fluid at the time of inclusion entrapment, and (ii) how to evaluate the fluid inclusion measurements obtained. In this way, fluid inclusion assemblages containing, e.g., 0.07  $\mu$ g g<sup>-1</sup>  $\pm$  20% (1 SD) gold, can be quantified (e.g., Pettke et al., 2012).



*Figure 1:* Gold overgrowing hydrothermal quartz from the Monte Rosa Gold District, Western Alps.

High scatter in LA-ICP-MS analyses of gold (and some other metals) is reported even within individual assemblages of homogeneously trapped inclusions. This contradicts the fundamental principle that each fluid inclusion in a homogeneously entrapped assemblage has an identical chemical composition and density. Indeed, some workers have used the evidence of high scatter in trace metal contents as an argument that such inclusion assemblages cannot have been trapped homogeneously.



**Figure 2:** LA-ICP-MS signal for a 30 µm equant brine inclusion (45 wt% NaCl<sub>equiv</sub>) from Bingham Canyon, Utah. Numbers in bold denote beam sizes used for laser ablation. Straight ablation mode for the fluid inclusion following stepwise beam size increase minimized breakout of host quartz crystal, and avoids uncontrolled inclusion ablation. Modified after Pettke et al. (2012).

We place the blame for this contradiction on the quality of LA-ICP-MS data, not on the traditional criteria used to identify the phasestate of fluid inclusion entrapment. There are several critical issues in analysing metals in fluid inclusions by LA-ICP-MS: (i) how well inclusion ablation can be controlled, (ii) how the measurement of fast transient analyte signals can be rendered representative when using a sequential mass spectrometer, (iii) how well the element used as the internal standard (commonly Na) can be measured, and last but not least (iv) how appropriate the host mineral correction is for obtaining the element concentrations in the pristine fluid inclusion. Issues (i) and (ii) have been elaborated upon in the literature (e.g., Pettke et al., 2012) and are tractable (Fig. 2). Issue (iii) is generally not serious. Sodium commonly provides the highest signal/background intensity ratios and also homogeneous signals; hence. uncertainties on the external reproducibility of Na for a series of fluid inclusion analyses within an assemblage can be as good as 3% 1 SD (unless the bulk salinity is very low). Consequently, issue (iv), the host-mineral correction, now typically sets the limit on analytical quality for high-quality fluid inclusion LA-ICP-MS analyses.



**Figure 3:** Schematic vertical section of an LA-ICP-MS analysis of a pseudosecondary fluid inclusion in quartz. Regular growth zoning of Qtz-1 is cut by dark fracture-filling Qtz-2 that encloses the fluid inclusion. Different LA-ICP-MS signal sections are colour coded (yellow = Qtz-1; orange = Qtz-1 - Qtz-2 mixture; green = host quartz ablated together with the fluid inclusion, consisting predominantly of Qtz-2).

The standard approach to determining the host-mineral background has been to measure its signal sections before or after the fluid inclusion ablation (Fig. 2), but this may well be problematic. First, such signal intervals may not derive from quartz of the same formation age as that which hosts the target inclusion. Therefore, its signal intensity may not be a valid basis to unmix the combined inclusion+host signals to obtain the element concentrations solely within the inclusion (Fig. 3). Second, in hydrothermal gold deposits, native gold is often present in hydrothermal quartz as irregularly distributed particles in the sub-µm size range. This is demonstrated by LA-ICP-MS analyses of clear vein quartz that show fluctuating gold contents as a function of

ablation depth, even though no opaque minerals and no fluid inclusions are visible in normal transmitted light microscopy (Fig. 4).



**Figure 4:** LA-ICP-MS signal of quartz from the Monte Rosa Gold District (Brusson, NW Italy) analyzed with an 80  $\mu$ m beam size. The smooth Si and Al signals contrast with the highly irregular Au signal, the apparent concentration for which is clearly significant and equals 1.08  $\mu$ g g<sup>-1</sup>. This quartz could well correspond to Qtz-2 of Fig. 3. Note the elevated signals for Au and Al at the beginning of ablation, documenting the presence of surface contamination in the amorphous layer of material produced during polishing.

The combination of these two effects is that an older or younger generation of gold-free quartz may be inadvertently used to correct the mixed host+inclusion signal to obtain the seemingly pure inclusion element concentrations (yellow and orange signal intervals in Fig. 3). It follows that the particulate gold in Qtz-2 immediately surrounding the inclusion cannot be corrected for by host quartz subtraction; hence, an apparently high gold concentration in the inclusion results. Because such particulate gold is irregularly distributed throughout the inclusion-bearing Qtz-2, fluid inclusions from one assemblage yield apparent gold concentrations upon LA-ICP-MS analysis that vary well beyond typical external reproducibilities obtained for elements of similar concentration in this assemblage.

How can the problem be overcome? Here we propose an approach which we suggest should be adopted as a minimum requirement for valid metal analyses in fluid inclusions. In a first step the target fluid inclusion assemblage must be characterized by standard petrographic, microthermometric and perhaps other non-destructive methods to establish the phase-state of the fluid(s) at the time of entrapment, and to establish or rule out any post-entrapment modifications of the inclusions. We emphasize that the result of this interpretation (e.g. "homogeneous entrapment") is to be treated thereafter as an immutable fact, since it is based on the properties of major chemical components (e.g.,  $H_2O$ , NaCl,  $CO_2$ ) in the fluid inclusions. That is to say, it is not logically permissible to later modify this initial interpretation of the phasestate of entrapment based on the results of trace element analyses obtained by destructive LA-ICP-MS analysis.

In a second step, the host quartz crystal must be analysed at 2 or 3 spots between visible fluid inclusions in the target assemblage by ablating to a level somewhat deeper than the fluid inclusions themselves. The resulting depth profiles reveal the distribution of particulate gold through the host quartz. If fluctuating gold contents are detected in these signals, then the planned analysis of the fluid inclusion assemblage should be abandoned, as useful results are logically precluded. In assemblages with closely spaced inclusions it may be wise to reverse the order and analyse the inclusions first to avoid breaching any valuable inclusions during the quartz ablations. However, the principle is the same.

Numerous fluid inclusions need to be analysed in the target assemblage such that at least 4 or 5 good LA-ICP-MS signals remain (e.g., Fig. 2), following initial quality filtering, for further data reduction. Rigorous error propagation for each inclusion would be desirable; however, this cannot be done mathematically because essential uncertainties cannot be quantified. These include the quality of inclusion ablation and its completeness (did the inclusion explode upon laser drilling or was part of the inclusion missed?) and the issues of representative recording of the shortlived transient signal that arises when analysing daughter crystals within Au inclusions. Minimum uncertainties can be estimated based on counting statistics uncertainties; however, how minimal these values are remains unconstrained.

Consequently, the only option remaining to assess analytical quality is to examine the variation of element/Na mass ratios within the assemblage. The uncertainty of alkalielement/Na ratios like K/Na provide the measured analytical uncertainty on the external reproducibility of the data set for the given assemblage. For cases where other metal signals are not limited by counting statistics uncertainties, the variance of metal/Na ratios should be comparable to that obtained for K/Na, i.e., analytical uncertainty dominates the data set. Variance beyond the analytical uncertainty determined on alkali-element/Na ratios points to additional analytical problems or sample problems. The former is basically dictated by controlled ablation of an individual inclusion and the representative recording of the analyte signals. Sample problems can include the presence of accidentally trapped Au particles in the inclusion and/or in the quartz immediately surrounding it.

One could imagine excluding one or two very high gold values from the dataset, thereby leaving 4 or more Au/Na ratios with the same values within error. However, if no systematic pattern between the values is apparent then the entire dataset must be discarded, because a basis to interpret the concentration of gold that was trapped in the fluid is lacking.

With currently available LA-ICP-MS technology, which limits the practical diameter of laser ablation craters to smaller than ~ 50 µm (because larger inclusions tend to explode during laser drilling), many natural fluid inclusion assemblages will not satisfy the minimum criteria that we have proposed above for validity of gold analyses. Many samples have too many closely spaced fluid inclusions or only very small fluid inclusions, or assemblages in which only one or two adequately sized inclusions for LA-ICP-MS analysis can be found per assemblage at appropriate depths for analysis. The latter can, of course, be mitigated somewhat by repolishing the quartz chip after analysis so that deeper inclusions can be brought to a good depth for a subsequent analytical session.

Applying the above reasoning and data evaluation to two Na-K-Ca-Fe chloride fluid inclusion assemblages from a porphyry-Au deposit (assemblage B1 = 52.6 wt% NaCl<sub>equiv</sub>,

n = 6; assemblage B2 = 43.6 wt% NaCl<sub>equiv</sub>, n= 4) returns the following results. The 1 SD on K/Na uncertainties ratios of the assemblages are 21% and 9%, respectively, and the corresponding ones for Au/Na ratios are 41% and 11%. The average gold concentration for B1 is 0.18  $\pm 0.08$  (47%) µg g<sup>-1</sup>, with two concentrations at 0.26 and 0.29, respectively; excess scatter in the Au analyses is thus indicated. Assemblage B2 contains 0.47  $\pm 0.05$  (10%) µg g<sup>-1</sup>. No excess scatter is revealed by this data set; consequently, these gold measurements are deemed reliable.

Literature data on concentrations of dissolved gold in natural samples are scarce to date. For magmatic-hydrothermal ore deposits, most values range from tens to hundreds of ng g<sup>-1</sup> (e.g., Ulrich et al., 1999; Pettke, 2008; Seo et al., 2009; Su et al., 2009; Pettke et al., 2012), while concentrations above 1  $\mu$ g g<sup>-1</sup> are rarer. For metamorphic fluids, there is one report by Rauchenstein-Martinek et al. (2014) who determined up to 0.3  $\mu g g^{-1}$  for late Alpine fissure mineralization not related to gold deposits, while Garofalo et al. (2014) report gold concentrations between 0.5 and 5  $\mu$ g g<sup>-1</sup> for an orogenic gold deposit. In view of these ranges we suspect that rigorous data evaluation would identify many of the high gold and perhaps other metal contents to be problematic. Our findings suggest that fluids with surprisingly low Au contents (i.e.,  $< 1 \mu g$ g<sup>-1</sup>) may be responsible for forming even giant porphyry deposits, and possibly even bonanzatype orogenic vein deposits.

We recognize that there will always be an understandable desire to analyse sub-optimal fluid inclusions for their metal contents, but it is our opinion that the inevitably sub-optimal numbers that result will cause more confusion than enlightenment in the scientific literature.

## References

Allan M. M. et al. 2005. Validation of LA-ICP-MS fluid inclusion analysis with synthetic fluid inclusions. Am. Mineral. 90, 1767-1775.

Garofalo, P. S. et al. 2014. Physical-chemical properties and metal budget of Au-transporting hydrothermal fluids in orogenic deposits, in: Gold-Transporting Hydrothermal Fluids in the Earth's Crust (Garofalo, P. S. & Ridley, J. R., eds). Geol. Soc. London, Spec. Pub. 402, 71-102

Gunther D., Frischknecht R., Heinrich C. A. & Kahlert, H. J., 1997. Capabilities of an Argon Fluoride 193 nm excimer laser for laser ablation inductively coupled plasma mass spectrometry microanalysis of geological materials. J. Anal. Atom. Spectrom. 12, 939-944.

Heinrich C. A. et al. 2003. Quantitative multielement analysis of minerals, fluid and melt inclusions by laser-ablation inductively-coupledplasma mass- spectrometry. Geochim. Cosmochim. Acta 67, 3473-3497.

Pettke T., 2008. Analytical protocols for element concentration and isotope ratio measurements in fluid inclusions by LA-(MC)-ICP-MS. In: Laser ablation ICP-MS in the Earth Sciences: Current practices and outstanding issues (Sylvester, P., ed). Mineral. Assoc. Can. Short Course Series 40, 189-218.

Pettke T. et al. 2012. Recent developments in element concentration and isotope ratio analysis of individual fluid inclusions by laser ablation single and multiple collector ICP-MS. Ore Geol. Rev. 44, 10-38.

Pokrovski G. S. et al. (2014) Gold speciation and transport in geological fluids: insights from experiments and physical-chemical modelling, in: Gold-Transporting Hydrothermal Fluids in the Earth's Crust (Garofalo, P. S. & Ridley, J. R., eds). Geol. Soc. London, Spec. Pub. 402, 9–70.

Rauchenstein-Martinek K., Wagner T., Waelle M. & Heinrich C. A., 2014. Gold concentrations in metamorphic fluids: A LA-ICPMS study of fluid inclusions from the Alpine orogenic belt. Chem. Geol. 385, 70-83.

Seo J. H., Guillong M. & Heinrich C. A., 2009. The role of sulfur in the formation of magmatichydrothermal copper-gold deposits. Earth Planet. Sci. Lett. 282, 323-328.

Su W. C. et al. 2009. Sediment-Hosted Gold Deposits in Guizhou, China: Products of Wall-Rock Sulfidation by Deep Crustal Fluids. Econ. Geol. 104, 73-93.

Ulrich, T., Gunther, D., and Heinrich, C. A., 1999. Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits. Nature 399, 676-679.

# Hydrocarbon inclusions, an efficient proxy for basin modeling through time and space

# **Jacques PIRONON**

Université de Lorraine, CNRS, CREGU, GeoRessources Lab, Nancy, France. <u>jacques.pironon@univ-lorraine.fr</u>,

Fluid inclusions. located inside diagenetic minerals, are the precious witnesses of paleofluids when they are unchanged in volume and composition with time. They can be used to reconstruct the history of fluid migration inside petroleum basins. Oil inclusions are frequently observed in petroleum reservoirs, and may be one-phase (liquid or vapour), twophase (vapour bubble in a liquid phase) or three-phase (vapour, liquid and solid phases) at room conditions. Their composition and phase equilibrium are related to the PVTX conditions at the time of trapping. Oil inclusions are also frequently described in Mississippi Valley Type deposits. The presence of organic gases is detected in metamorphic environments. Fluids in petroleum reservoirs are mixtures of nonmiscible phases as binary (brine + oil) or ternary systems (brine + liquid oil + gases).

This work is based on the characterization and modelling of fluid inclusions from samples containing transparent minerals such as quartz, feldspars, carbonates, fluorite, anhydrite, salts, ... It is based on the coupling of aqueous and petroleum fluid systems. Paleo-fluid reconstruction can help us to determine the time of petroleum migration, the pressure and/or overpressure fluid regime and the composition of the original fluid. These results should be integrated in a complete regional study in order to determine possible sourcerocks and drain connections. Comparisons can be made between the oil in the reservoir and the oil in the inclusions in order to determine the bio-and/or thermal-degradation of the oil between the time of trapping and the present.

Fluid inclusions are the only direct markers of pressure and temperature in diagenetic environments. Non-direct markers are conventionally used as geothermometers: the maturity index of organic matter, recorded through the vitrinite reflectance (Philippi, 1965, Hunt, 1995, Fedor and Hamor-Vido, 2003) or through Rock-Eval parameters (Espitalié et al., 1977, Sykes and Snowdon, 2002), is interpreted as equivalent temperature and used for basin modelling. In favourable cases, fission track lengths and densities are related to maximum thermal peaks and can lead to date the fluid migration episodes (Green, 1980, Bertagnolli et al., 1981).

Previous works have shown specific studies of petroleum inclusions by unique individual or bulk techniques. UV fluorescence has been developed to approximate the fluid density (Bodnar, 1990), GC-MS to acquire bulk composition (Horsfield and Mc Limans, 1984, George et al., 1997) and FT-IR to determine the presence of gases (Pironon et al., 2001). Associated aqueous inclusions are arbitrary considered as methane saturated or methanefree. However, recent works have shown that dissolved aqueous methane can be routinely detected by Raman (Guillaume et al., 2003, Caumon et al., 2014). The objective of this paper is to combine different analytical and modelling approaches to estimate a rigorous P-T couple of fluid trapping conditions, to approximate the composition of the fluids and to date fluid migration.

In a sample, petroleum inclusions are located together with aqueous fluid inclusions indicating that, in first approximation, these palaeofluids were trapped at the same time. Therefore, the petroleum and aqueous fluid inclusions are interpreted as the two nonmiscible fluids at equilibrium. The bulk homogenization of fluid inclusions representative of the two end-members should be the same and representative of the temperature of trapping. However, petroleum inclusions, containing a small quantity of liquid water, show a first homogenization of the hydrocarbon phase before the bulk homogenization that it cannot be accurately measured (Pironon et al, 2000). Generally the first homogenization of the petroleum inclusions occurs before the homogenization of the aqueous inclusions. This is due to the slope of the isochores that is more important

for aqueous fluids than for hydrocarbon fluids. Vapour filling of petroleum inclusions (Fv) constrains the location of the bubble point curve of the petroleum system. On another hand, the methane molar content of the aqueous inclusions constrains the location of the bubble point curve of the aqueous inclusions.

A good approximation of the P-T conditions of trapping of the two fluids is the intersection of the petroleum inclusion isochore with the isochore of the methane-bearing aqueous inclusion (Figure 1). Three main scenarios of intersection can be described:

-1) the aqueous and petroleum fluids are gasundersaturated (Figure 1a). The P-T conditions of trapping are located at the intersect of the two isochores; they are higher than the homogenization P-T conditions of the aqueous and petroleum inclusions. The bubble point curve of the aqueous system can be above or below the bubble point curve of petroleum.

-2) the aqueous and petroleum fluids are gassaturated (Figure 1b). The P-T conditions of trapping are located at the intersection of the two isopleths or bubble point curves; they correspond to the  $P_h$  and  $T_h$  of the aqueous and petroleum inclusions. This scenario implies that a very weak water quantity is present in petroleum inclusion.

-3) the aqueous fluid is gas-saturated, the petroleum fluid is gas-undersaturated (Figure 1c). The P-T conditions of trapping are located at the intersection of the two isochores, on the bubble point curve of the aqueous system. They are higher than the homogenization P-T conditions of the petroleum inclusions, and equivalent to the homogenization P-T conditions of the aqueous inclusions.

Scenarios 2 and 3 correspond to gas-rich systems such as wet or dry gas, gas condensate and volatile oils, whereas scenario 1 is essentially applicable to gas-depleted black oils. These scenarios show how it is important to know gas content into the aqueous fluid. It can help us to fix the pressure and temperature of trapping.

In order to validate this approach synthetic hydrocarbon and aqueous inclusions have been created in the laboratory batch reactors in order to mimic inclusion formation or reequilibration in deeply buried reservoirs (Pironon and Bourdet, 2008). Inclusions were synthesized in quartz and calcite using pure water and dead oil, or n-tetradecane ( $C_{14}H_{30}$ ), at a temperature and pressure of 150 °C and 1 kbar. Homogenization temperatures were recorded and the maxima of Th plotted on histograms are in good agreement with expected Th in a range of 6 °C. The histogram broadening is due to the fragility of the fluid inclusions that were created by re-filling of pre-existing microcavities. Such Th histograms are similar to Th histograms

Pressure (bar)



**Figure 1:** Three main scenarios of isochore intersection for aqueous (grey) and hydrocarbon (black) inclusions (from Pironon 2004)

recorded on natural samples from deeply buried carbonate or siliciclastic reservoirs. The results confirm the ability of fluid inclusions containing two immiscible fluids to lead to PT reconstructions, even in overpressured environments.

The timing of the fluid migration and the estimate of overpressure can be determined mixing PVT data from inclusion analysis and 1D basin modelling. The procedure is summarized in three steps (Figure 2): A) Pressure and temperature of fluid trapping in inclusions are determined using the technique of the isochore intersection applied to fluid inclusions (red dot). B) The lithostatic and hydrostatic gradients are reconstructed from 1D basin modelling and projected in a P vs. T diagram. The timing of geodynamic events can be indicated on the gradient curves (ages in Ma). C) The red dot is placed onto the PT diagram figuring the lithostatic and hydrostatic

A. PVTX Reconstruction from fluid inclusion data



**Figure 2:** Estimation of the age and overpressure from fluid inclusion analysis and basin modelling.

gradients. Therefore the age of fluid inclusion creation can be estimated and the pressure differential from hydrostatic gradient can lead to the overpressure estimate.

In the study of past climates, known as paleoclimatology, climate proxies are preserved physical characteristics of the past that stand in for direct measurements, to enable scientists to reconstruct the climatic conditions that prevailed during much of the Earth's history. In the study of basin history, known as paleothermobarometry, PVTXt proxies (i.e. fluid inclusions) are preserved physical/chemical characteristics of the past that stand in for direct measurements, to enable scientists to reconstruct the PVT conditions that prevailed during much of the Earth's history.

By analogy to paleoclimate proxies hydrocarbon inclusions can be considered as efficient proxies for basin modelling through time and space.

# Acknowledgements

This work has been supported by CNRS, PEMEX and Total.

## References

BERTAGNOLLI E., MARK E., BERTEL E., PAHL M. & MARK T.D. (1981) Determination of paleotemperatures of apatite with the fission track method. Nuclear tracks, 5, 175-180.

BODNAR, R.J. (1990) Petroleum migration in the Miocene Monterey Formation, California, U.S.A. Constraints from fluid-inclusion studies. Mineralogical Magazine, 54, 295-304.

CAUMON M.C., ROBERT P., LAVERRET E., TARANTOLA A., RANDI A., PIRONON J., DUBESSY J., GIRARD J.P. (2014) Determination of methane content in NaCl-H2O fluid inclusions by Raman spectroscopy. Calibration and application to the external part of the Central Alps (Switzerland) Chemical Geology, 378-379, 52-61.

ESPITALIE J., LAPORTE J.L., MADEC M., MARQUIS F., LEPLAT P., PAULET J. & BOUTEFEU A. (1977) Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. Revue de l'Institut Français du Pétrole 32, 23–42. FEDOR F. & HAMOR-VIDO M. (2003) Statistical analysis of vitrinite reflectance data – a new approach. International Journal of Coal Geology, 56, 277-294

GEORGE, S.C., KRIEGER, F.W., EADINGTON, P.J., QUEZADA, R.A., GREENWOOD, P.F., EISENBERG, L.I., HAMILTON, P.J. & WILSON, M.A. (1997) Geochemical comparison of oil-bearing fluid inclusions and produced oil from the Toro sandstone, Papua New Guinea. Organic Geochemistry, 26, 155-173.

GREEN P.F. (1980) On the cause of the shortening of spontaneous fission tracks in certain minerals. Nuclear Tracks, 4, 91-100.

GUILLAUME D., TEINTURIER S., DUBESSY J. & PIRONON J. (2003) Calibration of the Raman analysis of methane in H2O-NaCl-CH4 fluid inclusions. Validation using natural hydrocarbon and aqueous fluid inclusions. Chemical Geology, 194, 21-49.

HORSFIELD, B. & MC LIMANS, R.K. (1984) Geothermometry and geochemistry of aqueous and oil-bearing fluid inclusions from Fateh Field, Dubai. Organic Geochemistry, 6, 733-740.

HUNT J.M. (1995) Petroleum Geochemistry and Geology, 2nd ed., Freeman, New York.

J. PIRONON (2004) Fluid inclusions in petroleum environments: analytical procedure for PTX reconstruction. Acta Petrologica Sinica, 20(6): 1333-1342.

J. PIRONON, J. BOURDET (2008) Petroleum and aqueous inclusions from deeply buried reservoirs: Experimental simulations and consequences for overpressure estimates. Geochimica et Cosmochimica Acta, 72, 4916-4928.

PHILIPPI G. T. (1965) On the depth, time, and mechanism of petroleum generation. Geochimica et Cosmochimica Acta, 29, 1021-1049.

PIRONON J., THIERY R., AYT OUGOUGDAL M., BEAUDOIN G. & WALGENWITZ F. (2001) FT-IR measurements of petroleum fluid inclusions: methane, n-alkanes and carbon dioxide quantitative analysis. Geofluids, 1, 2-10.

PIRONON J., THIERY R., TEINTURIER S. & WALGENWITZ F. (2000) Water in petroleum inclusions. Evidence from Raman and FT-IR measurements, PVT consequences. Journal of Geochemical Exploration, 69-70, 663-668. SYKES R. & SNOWDON L.R. (2002) Guidelines for assessing the petroleum potential of coaly source rocks using Rock-Eval pyrolysis. Organic Geochemistry, 33, 1441-1455.
# **Oral Presentations**

## H<sub>2</sub>O-NaCl fluid inclusions in wonderland

#### **Ronald J. Bakker**

Resource Mineralogy, Department of Applied Geosciences and Geophysics, Montanuniversity Leoben, Leoben, Austria. <u>bakker@unileoben.ac.at</u>

The fluid system  $H_2O$ -NaCl has been subject of investigation for many years in chemistry and physics, and is of special interest to fluid inclusion studies. Both components occur in the majority of fluid inclusions known to geologists. The properties of this fluid system are of major importance to interpret trapping conditions of fluid inclusions in many types of rock.

The principle objective of the present study investigate experimental was to reequilibration behaviour of synthetic H<sub>2</sub>O-NaCl-rich fluid inclusions. The study was orientated towards detecting diffusion brittle deformation processes, processes (micro-cracking), and fluid inclusion wall recrystallization in and around synthetic fluid inclusions with well-defined composition and density under well-defined temperaturepressure-fugacity conditions. In due course of the project, a number of additional objectives were defined due to unexpected results: 1. Do synthetic H<sub>2</sub>O-NaCl fluid inclusions have densities that corresponds to the experimental T-P conditions?; and 2. How can I change fluid inclusion compositions against the applied gradients in fugacity compared to an external fluid?

The synthesis of pure H<sub>2</sub>O and H<sub>2</sub>O-NaCl fluid inclusions was performed according to the descriptions of Doppler [1,2]. Fluid inclusions were synthesized at 600 °C and 337 MPa, within the  $\alpha$ -quartz stability field. These experimental conditions were monitored accurately with an internal thermocouple. A pure H<sub>2</sub>O fluid has a molar volume of  $25.02 \pm$  $0.02 \text{ cm}^3 \cdot \text{mol}^{-1}$  at these conditions (calculated with program Loner HGK. http://fluids.unileoben.ac.at), which correspond to homogenization temperatures  $(T_{\rm h})$  at 296.3  $\pm$  0.2 °C. However the contraction of quartz from experimental homogenization conditions conditions to results in a correction of these values to 292.7  $\pm$  0.2 °C. The measured T<sub>h</sub>'s correspond exactly to these numbers. This example

illustrates that excellent theoretical predictions can be outlined from accurate equations of state and careful experimental work.

A similar calculation procedure can be performed with the synthesis of H<sub>2</sub>O-NaCl fluid inclusions. The theoretical  $T_{\rm h}$ 's of 10.0, 16.3, and 19.8 mass% NaCl aqueous fluid inclusions should be  $309.8 \pm 0.2$  °C,  $319.3 \pm$ 0.2 °C, and 324.3  $\pm$  0.2 °C, respectively (calculated with programs Loner AP and AqSo http://fluids.unileoben.ac.at). DH. The measured  $T_{\rm h}$ 's deviate significantly from these 313.9. 328.5. and 329.7 values: °C. respectively (mean values). Moreover, the spread in  $T_{\rm h}$  values is relative large (Fig. 1)



**Figure 1:** Distribution (histogram) of  $T_h$ 's from 19.8 mass% NaCl fluid inclusions.

This discrepancy remained unnoticed in many previous experimental studies on the synthesis of  $H_2O$ -NaCl fluid inclusions, due to the absence of accurate equations of state or insufficiently defined experimental conditions (e.g. external thermocouple), although the large spread in  $T_h$ 's have been reported.

Preliminary results of re-equilibration experiments with these fluid inclusions have been already presented in previous conferences [e.g. 3]. The experiments were designed at constant temperature (600 °C) and constant pressure (337 MPa) and specific fugacity gradients. The fluids involved in the experiments are illustrated in this table:

experiment	synthesis	re-equilibration
1	$H_2O$	$H_2O$
2	$H_2O$	H <sub>2</sub> O-NaCl
3	H <sub>2</sub> O-NaCl	$H_2O$

The so-called *blank* experiment 1 illustrates that multiple loading and unloading does not affect the fluid properties of the original synthesized inclusions. Inclusions from experiment 2 modified their density according to expected diffusion processes  $(H_2O)$ , whereas NaCl remains immobile.  $T_{\rm h}$ 's were modified to higher values. The modifications of H<sub>2</sub>O-NaCl inclusion from experiment 3 are significant, both  $T_{\rm m}$ 's and  $T_{\rm h}$ 's are strongly affected (Fig. 2). The intensity of modification is directly related to experimental run time, which may imply diffusion processes.



**Figure 2:** Dissolution temperature of ice  $(T_m)$  versus modification of  $T_h$  of three experiments with 19.8 mass% NaCl aqueous inclusions.

These results are accurate, clear and definite, however, close examination of the outcome of these experiments reveals a number of enigmas. First, fugacity gradients must result in diffusion of H<sub>2</sub>O into the inclusions resulting in a relative decrease of salinity, that correspond to higher  $T_m$ 's. Second,  $T_m$ 's decrease to values below the eutectic temperature of the binary H<sub>2</sub>O-NaCl system. Third, freezing experiments illustrate different nucleation behaviour after re-equilibration. Fourth, short term experiments have a reversed modification of  $T_h$  compared to long term experiments. Fifth, theoretical modelling of  $H_2O$  diffusion out of the inclusions (calculated with the programs *AqSo DH* and *ReqDif*, <u>http://fluids.unileoben.ac.at</u>) result in a completely different trend of paired  $T_h$  and  $T_m$  modifications.

Consideration of unexpected parameters in the experimental setup cannot account for all these enigmas. For example, fluid inclusions may be contaminated with an unknown substance after re-equilibration. Diffusion is the only process to add this substance to inclusions, however salt appeared to be immobile. Other components than H<sub>2</sub>O and NaCl were not detected within the inclusions. Due to the heterogeneity of the original assemblage (Fig.1) an unexpected minor pressure gradient must have been present during re-equilibration experiments, which may only account for minor modifications of density.

observed modifications The in microthermometrical data can only be obtained by preferential H<sub>2</sub>O loss. However, bulk H<sub>2</sub>O diffusion alone cannot account for these modifications, but a paired process of H<sub>2</sub>O loss and SiO<sub>2</sub> gain may result in observed trend of  $T_{\rm h}$  and  $T_{\rm m}$ . This process is not driven by H<sub>2</sub>O-fugacity gradients and only occurs with H<sub>2</sub>O-NaCl bearing fluid inclusions. Quartz is not a passive membrane, but involved in the modifications of fluid inclusions.

#### Acknowledgements

This work is supported by the FWF, project P224460-N21, as part of the PhD thesis of Doppler.

#### References

[1] Doppler G., Bakker R.J. & Baumgartner M. (2013) Fluid inclusion modification by H<sub>2</sub>O and D<sub>2</sub>O diffusion, Contrib. Mineral. Petrol., 165, 1259-1274.

[2] Doppler G. & Bakker R.J. (2014) The influence of the  $\alpha$ - $\beta$  phase transition of quartz on fluid inclusions during re-equilibration experiments, Lithos, 198-199, 14-23.

[3] Doppler G., Bakker R.J. & Baumgartner M. (2013) NaCl-enrichment in re-equilibrated synthetic H<sub>2</sub>O-NaCl bearing fluid inclusions in quartz, ECROFI XXII Abstract Book (eds. N. Hanilci & G. Bozkaya), 10-11.

## Comparison of fluid inclusion studies in cordierite-andalusite-rich leucogranite dykes and tourmaline-bearing aplite-pegmatite dykes (Elba, Italy)

Ronald J. Bakker, & Sebastian E. Schilli

Resource Mineralogy, Department of Applied Geosciences and Geophysics, Montanuniversity Leoben, Leoben, Austria. <u>bakker@unileoben.ac.at</u>

The late magmatic-hydrothermal stage of the Monte Capanne pluton (Elba, Italy) is associated with abundant fluid sources, of which the remnants are present in numerous fluid inclusion assemblages in associated leucogranite dykes, and aplite-pegmatite dykes and veins [1]. They are mainly located in the pluton and its thermometamorphic aureole close to the pluton's contact. The studied dykes were sampled in serpentinitic host rock. The leucogranite dyke contains abundant andalusite and cordierite (peraluminous). The pegmatite vein is mainly composed of coarsequartz, grained plagioclase and foitic tourmaline.



Figure 1: Fluid inclusion types in leucogranite

A variety of fluid inclusion assemblages were observed in andalusite-plagioclase-quartz

(leucogranite, Fig. 1) and tourmaline-quartz (aplite-pegmatite, Fig. 2).



*Figure 2: Fluid inclusion types in aplite- pegmatite.* 

The contents of fluid inclusions were detected microthermometry and with Raman spectroscopy. Complex gas mixtures of CO<sub>2</sub>,  $CH_4$ ,  $H_2$ ,  $N_2$ , and locally  $H_2S$  and alkanes were detected in the vapour phase of all types of inclusions (Fig. 3). Anhydrous inclusions in andalusite contain a low density CO<sub>2</sub>-rich gasmixture and abundant accidentally trapped mica's. Some inclusions contain diaspore and quartz, which are reaction products of H<sub>2</sub>O (completely consumed) and host mineral. Inclusions in plagioclase contain a H<sub>2</sub>-CH<sub>4</sub>rich vapour phase. Type 1 inclusions in quartz contain a mixture of H<sub>2</sub>O and H<sub>2</sub>, and usually an accidentally trapped mica, which can only be detected by Raman. Type 2 inclusions have a CO<sub>2</sub>-CH<sub>4</sub>-rich vapour phase with up to 16 mole% H<sub>2</sub> and N<sub>2</sub>. Some minor amounts of dissolved sassolite ( $H_3BO_1 < 2.5 \text{ mass}\%$ ) and NaCl are detected in the liquid phase. The bulk fluid properties of this assemblage reveal a H<sub>2</sub>O-rich composition (93 mole%) and a molar volume of 30.43 to 31.70  $\text{cm}^3 \cdot \text{mol}^{-1}$ . Type 3 inclusions have also a H<sub>2</sub>-CH<sub>4</sub>-rich vapour phase, but the bulk composition is nearly pure H<sub>2</sub>O with a molar volume varying between 20.01 and 22.75 cm<sup>3</sup>·mol<sup>-1</sup>.

Tourmaline from the aplite-pegmatite contains exceptional large fluid inclusions. The liquid phase contains higher concentrations of sassolite (4 to 6 mass%), which nucleate to crystals by Raman laser irradiation at room temperatures. Arsenolite and arsenic was observed in some inclusions. The vapour phase is a gas-mixture of CO<sub>2</sub> and CH<sub>4</sub>, with locally minor amounts of H<sub>2</sub>S, N<sub>2</sub> and H<sub>2</sub>. The bulk fluid properties are similar to Type 2 from quartz in the leucogranite. Also the fluid inclusions in quartz from the aplite-pegmatite contain traces of sassolite (< 2.5 mass%), and the vapour phase is CO<sub>2</sub>-rich, with minor amounts of CH<sub>4</sub>. Other gases were not detected in these inclusions.

Both types of rock (leucogranite and aplitepegmatite) reveal similar fluids in inclusions, which may imply a similar origin.  $H_2O$  is the most important component of all fluid inclusion assemblage. The absence of melt inclusions in both rock types emphasizes their hydrothermal origin. Details about accessory components such as NaCl,  $H_3BO_3$  and gascompositions in different fluid inclusion assemblages illustrate the development of rock-forming conditions. Whereas the CO<sub>2</sub>-rich fluids in andalusite suggest a magmatic source, a highly reduced fluid ( $H_2$  and  $CH_4$ ) that is found in early assemblages in quartz and plagioclase illustrates the strong influence of fluid properties from the surrounding host rock (serpentinites). Mixing of these fluid sources is documented in younger fluid inclusion assemblage in quartz and tourmaline. The presence of Boron and the similarity of Type 2 fluid inclusions in quartz from the leucogranite and the inclusion assemblages in tourmaline from the aplite-pegmatite suggest similar fluid sources that were trapped at similar conditions. The concentration of Boron in the leucogranite did not reach saturation values of tourmaline growth. The fluid sources of both rock types are poor in NaCl.

The solvus boundary of a Boron- $H_2O$  rich granitic melt, the presence of andalusite, and the specific molar volume of homogeneous fluid inclusion assemblage restrict formation conditions of both leucogranite and aplite-pegmatite to a narrow T-P window at about 600 °C and 300 MPa.

*Figure 3:* Gas compositions of fluid inclusion assemblages in leucogranite and aplite-pegmatite



## Role of dissolved gases in the formation of liquid inclusions

Emilie Bobo, Valérie Dupray, Samuel Petit & Gérard Coquerel

Normandie Université, Université de Rouen, Unité de Cristallogenèse EA 3233 SMS, Mont Saint Aignan, France, emilie.bobo1@univ-rouen.fr

Fluid inclusions have intensely been studied by mineralogists in order to understand the major climatic and environmental events that appeared on earth. Indeed, the pockets of liquid trapped in minerals contain a lot of information about the prevailing conditions during crystal growth. If many minerals contain inclusions, crystals produced in industry have also more than often fluid inclusions. We found a striking analogy between the displacement of inclusions in olivine in a temperature gradient at circa  $1800^{\circ}\text{C} - 1750^{\circ}\text{C}$  [1], and the displacement of fluid inclusions in *ɛ*-caprolactam crystallized in acetone and put in a temperature gradient near room temperature.

This study is about the inorganic compound Ammonium Perchlorate (AP) used as propellant for Ariane V boosters for example. Unfortunately AP crystals obtained in aqueous solution contain many inclusions [2] which reduce the efficiency of the propellant. To reduce the occurrence of inclusions in crystals grown in solution, manufacturing parameters such as temperature, seeding, stirring rate, cooling rate, effects of additives, etc can be adjusted [3]; but the mechanism still remains unclear and is a fundamental question for the access to pure AP.

Since fluid inclusions are known to contain a gas bubble (with or without thermal treatment applied on the crystal), the role of the dissolved gases have been investigated. Waldschmidt et al. have proposed a mechanism of formation of inclusions where nano-bubbles are attached to the crystal surface and being involved in the crystal growth inhibition [4].

AP crystals were obtained under  $CO_2$  atmosphere (1 bar) to ensure high concentration in  $CO_2$  in the solution during the crystallization. In presence of water,  $CO_2$  is known to form the clathrate  $CO_2$ , 5.75H<sub>2</sub>O at - 56°C under ambient pressure [5]. The crystals

containing inclusions were frozen in order to trigger the formation of clathrate and then prove the importance of dissolved gases in the solution in the formation of fluid inclusions.

The formation of clathrate was monitored by cold stage microscopy (in Figure 1). Fluid inclusions were cooled down to -41°C and a concomitant shrinkage of the bubble was observed. Then by decreasing the temperature -45°C, new phase to a (possibly  $CO_2$ , 5.75H<sub>2</sub>O) grew exactly where the gas bubble was. This phenomenon appeared far from the eutectic of the mix AP/water which crystallized at -2.7°C. The relatively high temperature formation of the clathrate suggests that the pressure inside the inclusion is at circa 2 to 3 bar [5].





All fluid inclusions studied do not necessary reveals the formation of clathrate at low temperature, and suppose that solvent bubbles can also exist (for the bubbles obtained thermally). Moreover, crystallization under  $O_2$ and  $N_2$  have been performed but the temperature of formation of clathrate is too low to be reached.

#### Acknowledgements

This work was supported the French Ministry of Research to Emilie Bobo via the E.D. n°351 (SPMII).

#### References

[1] Schiano P., Provost A., Clocchiatti R. & Faure F. (2006) Transcrystalline melt migration and Earth's mantle, Science, 314(5801), 970–974.

[2] Bobo E., Petit S. & Coquerel G. (2015) Growth rate dispersion at single crystal level, Chem. Eng. Technol. Accepted Paper.

[3] Hiquily N., Laguerie C. & Couderc J. (1985) Analyse Expérimentale de la Formation d'Inclusions au Cours de la Cristallisation du Perchlorate d'Ammonium en Solution Aqueuse, Chem. Eng. J., 30, 1-9.

[4] Waldschmidt A., Couvrat N., Berton B., Dupray V., Morin S., Petit S. & Coquerel G. (2011), Impact of Gas Composition in the Mother Liquor on the Formation of Macroscopic Inclusions and Crystal Growth Rates. Case Study with Ciclopirox Crystals, Cryst. Growth Des., 11, 2463-2470.

[5] Longhi J. (2006) Phase equilibrium in the system CO2-H2O: Application to Mars, J. Geophys. Res., vol. 111, E06011.

## Sulfur forms in the hydrothermal fluids and their role in ore formation

Alexandr S. Borisenko<sup>1,2</sup>, Andrey A. Borovikov<sup>1</sup>, Ivan D. Borisenko<sup>1,2</sup>, Nikolay S. Bortnikov<sup>3</sup>, Vsevolod Yu. Prokofiev<sup>3</sup>, Olga V. Vikent'eva<sup>3</sup>, Gennady N. Gamyanin<sup>3</sup>, Ivan V. Gaskov<sup>1</sup>,

<sup>1</sup>Sobolev V.S. Institute of Geology and Mineralogy SB RAS; Novosibirsk, Russia; <sup>2</sup> Novosibirsk State University Novosibirsk, Russia; <sup>3</sup> Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow, Russia;

Results of fluid inclusion study in minerals of different type deposits (TR-carbonatite, Cu-Mo and Au-Cu porphyry, Sn-W and Mo-W greisen, Au-quartz) show that mineral-forming fluids with different salt and gaseous composition, Eh and pH, contain high sulfur contents. Hydrothermal fluids depending on the redox-potential and pH of aqueous solutions contain sulfur in sulfate or sulfide forms. Native sulfur was detected in the fluid halite inclusions in of contactly metamorphosed evaporates in the Lena-Tunguska province [1], in quartz and fluorite of the Pb-Zn-F deposits in Spain [2], in ruby from metamorphic rocks of Vietnam [3], and in orthopyroxene from dunite in Italy [4].

We identified native sulfur using Raman spectroscopy by characteristic 471.8 cm<sup>-1</sup> line of spectrum in the fluid inclusions in quartz from ore veins of different types.

1. W-Sn месторождения. Sn-W greisen veins of the Alyaskitovoe deposit (Yakutia, Russia) linked with Li-F granite bear cassiterite-wolframite, sulfide (Fe, Sn, Pb, Ag, Zn) and Au mineralization. Native sulfur was found in two-phase and gaseous fluid inclusions in smoky quartz from cassiteritewolframite-arsenopyrite association (Fig.1 a,b). Two-phase inclusions contain chloride solution (6.4-5 mas.% NaCl-eq.), gas phase and small native sulfur phase (2-3  $\mu$ m) which dissolves at the temperature 210-190°C. Homogenization of inclusion occurred at the T 280-270°C. Gaseous inclusions with native sulfur show homogenization temperatures of 135 to 150°C. Gas phase is represented by CO<sub>2</sub> (79.8), N<sub>2</sub> (13.5), H<sub>2</sub>S (2.1) and CH<sub>4</sub> (4.7) (mol.%).

2. Mo-W deposits. Fluid inclusions containing native sulfur as solid phase were found in quartz phenocrysts of granite porphyry and in quartz of chalcopyrite-molybdenite veins (Fig. 1, I, f) from the Kalgutinskoe Mo-W(Be) greisen deposit

(Gorny Altai, Russia). Gaseous phase of these inclusions is represented by  $CO_2$  (96.8-86.9 mol.%) and  $H_2S$  (13.1-3.2 mol.%). Inclusion solutions contain dissolved  $CO_2$ ,  $H_2S$  and  $HS^-$ . Heating of  $CO_2$  dominant fluid inclusions with



**Figure 1**: Fluid inclusions with native sulfur (shown by arrow). Two-phase fluid inclusion in quartz of ore veins from the Alyaskitovoe deposit (a). The same inclusion (a): bright patch of reflected laser light on the native sulfur guarantees a successful record of its Raman-spectrum (b). Fluid inclusion with liquid CO<sub>2</sub>, Samolazovskoe deposit (c). Multiphase fluid inclusion containing halite crystal and syngenite plate (d). Carbon dioxide rich inclusion, Svetlinskoe deposit (e). Multiphase inclusion (f). CO<sub>2</sub> –rich fluid inclusion , Kalgutinskoe Mo-W(Be) deposit (I). Multiphase inclusion (j).

native sulfur led to the homogenization of solution into gas phase at the temperature 285-270°C and sublimation of liquid sulfur at 482-489°C.

**3.** Au-sulfide deposits. Native sulfur occurs in sulfate multiphase fluid inclusions in fluorite and in two-phase fluid inclusions in quartz at the Samolazovskoe deposit (Central Aldan), formation of which was linked with alkaline magmatism. Native sulfur associates with liquid CO<sub>2</sub> phase in the inclusions. Solid phases of inclusions are represented by sulfates (thenardite, gypsum, syngenite), and carbonates (nakholite). The following ions are detected in the inclusion solutions using Raman spectroscopy:  $SO_4^{2-}$ , HS  $HSO_4^{-}$ , and  $HCO_3^{-}$ . Gaseous phase contains CO<sub>2</sub> (100-91.4), N<sub>2</sub> (8.6-0) and H<sub>2</sub>S (0.1-0 mol.%).

4. Au(Te)-quartz-sulfide deposits. The Svetlinskoe (Southern Ural) is the large goldtelluride deposit with veinlet-disseminated ores located within the volcano-sedimentary rocks metamorphosed up to amphibolitic facies (amphibolite, biotite-bearing schist, etc.). The gold-sulfide-telluride-quartz veins and veinlets are superimposed on the disseminated pyrite-pyrrhotite mineralization. Spherical phase of native sulfur was detected in aqueous-vapor CO2-H2S bearing fluid inclusions in early quartz veins from the marble of the eastern flank of the Svetlinskoe deposit. Gas phase of these inclusions contains  $CO_2$  (85.8),  $N_2$  (1.2) and  $H_2S$  (13 mol.%). Multiphase fluid inclusions contain halite and solid phases of complex composition (Chalcoalumite Group) (Fig. 1, e, f). Native sulfur in gaseous inclusion sublimates at 150-135°C, homogenization occurs at 260-250°C. Solid phases in the multiphase inclusions dissolve at the temperature of 120-110°C, dissolves 205-210°C, sulfur phase at homogenization of inclusion occurred at the temperature range 280-270°C.

These data demonstrate native sulfur as usual component of fluid inclusions with dense gaseous phase (CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>) that shows connection of sulfur with high density gaseous fluids and supposes idea of effective sulfur transport in the gas flow.

High contents of sulfur (up to 15 mas.%) were found in the composition of oxidized highly concentrated carbonate-chloride-sulfate fluids of Cu-Mo and Au-Cu porphyry deposits and TR-carbonatite deposits linked with

alkaline magmatism. According to the preliminary estimations, reduced fluids of the Sn-W and Mo-W greisen deposits also could contain native sulfur. We have found different sulfur forms  $(SO_4^{2-}, HSO_4^{-}, HS^{-}, H_2S \text{ and } S^0)$  in fluid inclusions. Detection of wide range of sulfur forms indicates the possibility of other compounds presence including thiosulfates and sulfates. The Raman spectra of fluid inclusions rich in native sulfur from the Kalgutinskoe deposit contain weak lines (cm <sup>1</sup>): 433, 444, 628, 675, 1017, 1161, which are characteristic for crystal thiosulfates and  $(S_2O_3)^{2-}$  ion in aqueous solution [5, 6]. These facts point out to the thiosulfate presence in the natural endogenous systems. Detection of thiosulfates in the ore-forming fluids is important fact for conclusions about effective forms of transport of ore elements (including hydrothermal environment. gold) in Thiosulfate complexes of gold are highly soluble that is the basement for recent industrial technology of Au leaching from the ores.

## Acknowledgements

The work was supported by the RFBR grants № 12-05-00618-a and №14-05-00893, Russian Science Foundation - Project 14-17-00693

## References

[1] Grishina S.N., Dubessi J. 1989. Native sulphur in carbon dioxide inclusions. Geokhimia. N 4. P. 525-531.

[2] Bény C., Guihaumou N., Touray J.-C. 1982. Native sulphur-bearing fluid inclusions in the CO<sub>2</sub>-H<sub>2</sub>S-H<sub>2</sub>O-S system. Microtermometry and Raman microprobe (MOLE) analysis. Thermochemical interpretations. Chemical Geology. V 37. Is. 102. P.113-127.

[3] Guiliania G., Dubessy J., Banks D., Hoang Quang Vinhd, Lhommeb Th., Pirononb J., Garniere V., Phan Trong Trinhd, Pham Van Longf, Ohnenstettere D., Schwartzg D. 2003. CO<sub>2</sub>. H<sub>2</sub>S-COS-S8-AlO(OH)-bearing fluid inclusions in ruby from marble-hosted deposits in LucYen area, North Vietnam. Chemical Geology. 194. P. 167-185.

[4] Frezotti M.L., Tecce F., Casagli A. 2012. Raman spectroscopy for fluid inclusion analysis. Journal of Geochemical Exploration. 112. P. 1-20. [5] Y. Barona, J. Mirzaa, E.A. Nicola, S.R. Smitha, J.J. Leitcha, Y. Choib, J. Lipkowskia. SERS and electrochemical studies of the gold– electrolyte interfaceunder thiosulfate based leaching conditionsJ // Electrochimica Acta 111 (2013) 390–399.

[6] Y. S. Yamamoto, K. Hasegawa, Y. Hasegawa, N. Takahashi, S. Fukuoka, N. Murase, Y. Baba, Y. Ozaki, and T. Itoh. Direct Conversion of Silver Complexes to Nanoscale Hexagonal Columns on Copper Alloy for Plasmonic Applications // Electronic Supplementary Material (ESI) for Physical Chemistry. Chemical Physics This journal is © The Owner Societies 2013.

## Explosive brecciation and base-metal-Au mineralization at Koru, NW Turkey. P-T-x of the hydrothermal fluids.

Gülcan Bozkaya<sup>1</sup> & David A. Banks<sup>2</sup>

<sup>1</sup>*Pamukkale University, Dept. of Geological Engineering,20070, Denizli-TURKEY gbozkaya@pau.edu.tr* <sup>3</sup>*School of Earth and Environment, University of Leeds, Leeds, UK. <u>d.a.banks@leeds.ac.uk</u>* 

The northwest of Turkey is a particularly prospective area for epithermal and porphyry mineralization. However in some instances studies on individual mineralized locations may, in fact, be all part of the same hydrothermal fluid system. In this study we present details of the mineralization and Koru which is spatially close to other mineralized locations such as Tesbihdere, Azitepe, Basmakci, Sahinli. The majority of the deposits, in northwest Turkey, are low to intermediate sulphidation Au + Ag deposits but there are a smaller number that are exploited for Pb and Zn as galena and sphalerite, Koru being one of these. A common theme amongst all these deposits is the presence of a hydrothermal fluid of ~2 wt% salinity and a temperature of  $\sim 300^{\circ}$ C. however some have fluid inclusions of greater salinity ~10 wt.% salinity at comparable temperatures and these are generally associated with base-metal-Au deposits.

The volcanogenic rocks hosting Pb-Zn deposits consist of agglomerate, lapillistone and tuff with andesite intercalations at the lower parts, silicified rhyolitic breccia at middle parts and silicified rhyolitic tuffs in the upper parts (Figure 1). All rock types, to variable, degrees are affected by hydrothermal alteration mainly to zeolites and chlorites from interaction of volcanic glass and sea water. Silicification increases at the middle and upper parts, in which the main components with pyroclastic breccias and tuffs formed from intensely silicified precursor minerals. Stockwork veinlets become dominant in the silicified-tuffs in the upper parts, whereas massive and/or horizontal veins (WNW-ESE direction) are found in the lower parts.

However, the vein-type mineralization in deeper parts and the stockwork-type mineralization in upper parts of both the Tahtalikuyu and Eskikisla sectors (Figure 2) of the Koru deposit exhibit similar depositional styles to those of volcanic-hosted massive sulfide deposits. But several data, (1) cutting of ore-filled fault zone stockwork zone and overlying tuffs levels up to the uppermost levels, (2) filling the stockwork-type ores into spaces amongst the pebbles of agglomerates rather than internal-pressure related fissures, (3) the absence of stratiform ore as lenses and layers on the stockwork zone, indicate that the Koru base metal mineralizations are epigenetic after deposition of volcanosedimentary sediments (Figure 3).



*Figure 1.* Entrance to mining area showing stockwork zone and silicified rhyolite breccia above the entrance.

In the Pb-Zn ore veins, sphalerite, galena, pyrite, chalcopyrite, quartz, barite and calcite are the main minerals and they are accompanied by small amounts of fahlore (tennantite), marcasite, covellite and bornite. Barite and scarce quartz minerals are the main gangue minerals in Koru deposit. Galena and sphalerite show generally anhedral and rarely subhedral crystals. These minerals were formed in at least two episodes as early- and late-stage. Early-stage of sphalerite crystals were cracked and disaggregated and have a by late-stage galena crystals. Chalcopyrite was generally formed as later than sphalerite and galena, and most of chalcopyrite occurrences contain galena and sphalerite inclusions.



**Figure 2.** Section through the ore-zones showing the relation of the mineralized veins with the overlying stockwork and silicified breccias.



*Figure 3.* Vein style early galena-quartz mineralized veins which are cut by later quartz and barite.

In Qz1 Th<sub>liq</sub> values are between  $249^{\circ}C$  and  $354^{\circ}C$ , in Qz2 between  $166^{\circ}C$  and  $251^{\circ}C$  and could not be observed due to the darkness of inclusions makes us treat these values with caution as the majority of the inclusions in baryte are L-only. Tm<sub>ice</sub> values for L-V inclusions in Qz 1 are from -0.9°C to -5.1°C (1.6 to 8 equiv wt% NaCl), Qz2 Th<sub>vap</sub> homogenization for vapour-rich inclusions associated with Qz1 are between  $315^{\circ}C$  and  $354^{\circ}C$ . In Sph1 Th<sub>liq</sub> values are between the sphalerite. In Sph2 Th<sub>liq</sub> was between  $134^{\circ}C$ 

and 228°C. Th<sub>liq</sub> values for baryte inclusions were between  $70^{\circ}$ C and  $217^{\circ}$ C, but the large range and the petrography of the L-V 248°C and 341°C, although there were some V-rich inclusions homogenization between -0.6°C and -5.6°C (1.1 to 8.7 equiv. wt% NaCl) but could not be observed in V-rich inclusions. In Sph1 Tm<sub>ice</sub> are between -1.8°C and -5.5°C (3.1 to 8.7 equiv. wt% NaCl) and in Sph2 between  $-0.1^{\circ}$ C and  $-7.5^{\circ}$ C (0.2 to 11.1 equiv. wt% NaCl). In baryte Tmice are between - $0.3^{\circ}C$  and  $-3.4^{\circ}C$  (0.5 to 5.5 equiv. wt%) NaCl). The salinities of the inclusions in the different minerals essentially covers the same range, however the highest salinities are in sphalerite hosted inclusions (Figure 4).



*Figure 4. Th-salinity of inclusions from the vein and stockwork zones.* 

The structural and fluid inclusion evidence suggests variable pressures during mineralization, sometimes of a rapid and vigorous nature. This produced the brecciation and stockwork zones at higher levels with the majority of mineralization in the deeper veins. The early mineralization is cut by lower temperature fluids that have a similar salinity range to those responsible for the main mineralization. However, these veins are dominated by barite, quartz and calcite with little sulphides. The explosive nature of the early fluids also affected the overlying rhyolites which are extensively brecciated and silicified.

## The role of illites in determination of age and origin of hydrothermal fluids, Biga Peninsula, NW Turkey

Gülcan Bozkaya<sup>1</sup>, Ömer Bozkaya<sup>1</sup>, I. Tonguç Uysal<sup>2</sup>, David A. Banks<sup>3</sup>

<sup>1</sup>Pamukkale University, Dept. of Geological Engineering,20070, Denizli-TURKEY gbozkaya@pau.edu.tr <sup>2</sup>Hacettepe University, Dept. of Geological Engineering,20070, Ankara-TURKEY t.uysal@uq.edu.au <sup>3</sup>School of Earth and Environment, University of Leeds, Leeds, UK. <u>d.a.banks@leeds.ac.uk</u>

In hydrothermal systems, some factors controlling clay formation processes, such as fluid composition, fluid/rock ratio become significant from those of burial more diagenetic environments. If clay minerals precipitated in equilibrium with the fluid (without any kinetic isotope fractionation) Hand O- isotope composition of the clays can be used to infer the fluid isotope composition (if the fluid temperature is known) or temperature (if the fluid isotopic composition is known). Radiometric dating of illitic clays provides information on the timing of the hydrothermal activity. The advantage of using illite is its higher stability in relatively high temperature environments compared to the other clay minerals, such as chlorite, kaolinite and mixed-layer illite-smectite. In this study, we aimed to understand the role of hydrothermal illites on various features (i.e., origin of fluids, temperature conditions, age of hydrothermal activity etc.) for three Pb-Zn-Cu deposits in which fluid inclusion studies were already made. Hydrothermal illites in the altered tuffs from argillic and phyllic zones from three deposits are investigated bv detailed "crystalliniy", mineralogical (illite  $d_{060}$ , polytype) and geochemical (major, trace, O-H and Rb/Sr isotope) methods.

The three Pb-Zn-Cu deposits studied (Koru, Tesbihdere-Sahinli and Kumarlar) are aligned NW-SE, and located in the Lapseki and Çan districts of the Biga Peninsula, NW Turkey. They are comparable to low to intermediate sulphidation volcanic-hosted epithermal basemetal-Au deposits. The deposits are similar in terms of host-rocks (Oligocene pyroclastics), ore and gangue minerals (Galena-sphaleritechalcopyrite, quartz, barite) and style of mineralization (veins depth at and disseminations and stockworks in the upper parts). The Tesbihdere and Kumarlar areas are more representative of deeper parts, whereas those of the Koru area are more representative of the upper parts of the volcanic-volcanogenic

succession. Argillic, sericitic (illites) and chloritic alteration was developed within the volcanic mass and pores of the pumice as neoformed minerals. Hydrothermal alteration resulted in silica (quartz, chalcedony) clay (kaolinite, illite, I-S and smectite), sulphate (barite, alunite) and iron oxi-hydroxide (limonite) occurrences. Pure illite-bearing samples have intense illitization (sericitization) as fine-grained scaly micaceous occurrences within the volcanogenic matrix

The alteration products of the volcanic and pyroclastic rocks are quartz, illite, kaolinite, mixed-layer illite-smectite (I-S), chlorite-smectite (C-S) and smectite. The Kübler Index (KI,  $\Delta^{\circ}2\theta$ ) values of illites change from 0.28 to 0.97  $\Delta^{\circ}2\theta$  indicating high-grade diagenesis (Koru deposit) and anchizone conditions (Tesbihdere and Kumarlar deposits, Figure1).



**Figure 1:** The distributions KI vs  $d_{060}$  data of illites. (Temperature values from Th of fluid inclusions in sphalerite and quartz).

The percentages of swelling layers (smectite components, 2-7 %) and crystallite sizes (N, 15- 50 nm) of illites change with grades. The  $d_{060}$  values of illites (1.5003-1.5033 Å) indicate dioctahedral composition with low octahedral Fe+Mg (0.19-0.53 atoms). Illite

polytypes are represented by  $2M_1$ , 1M and  $1M_{\rm d}$ , but  $1M_{\rm d}$  polytype is dominant for all illites, except for Kumarlar deposit. The shape and size of illites show some differences with respect to the grades. Illites or R3 I-S (90% I, 10% S) in low-grade parts (sample TK-64 from Koru) exhibit fine-grained,  $\geq 2 \mu m$ , curved flakes and extremely fine-grained fiber-like, < 2 µm plumy flakes. Euhedral kaolinites and alunites with hydrothermal origin associate to illite and I-S. Euhedral to subhedral platy illites were developed as extremely coarse-grains, up to 20 µm, in highgrade parts, from Tesbihdere and Kumarlar. Euhedral dickites, loosely as stacked aggregates or booklets, indicate in situ formation from the hydrothermal fluids.

The trace and rare-earth element (*REE*) concentrations of illites show similar for deposits, but small differences in metals (Cu, Pb, Zn, Cd). Illites are enriched in *REE* compared to chondrite. The chondrite normalized *REE* patterns and abundances of illites of Tesbihdere and Kumarlar deposits have negative europium anomalies and have a pattern of H*REE* enrichment compared to the samples from Koru.

The oxygen and hydrogen isotope compositions of illites ( $\delta^{18}O_{SMOW}$ =3.1 to 7.6‰,  $\delta D_{\text{SMOW}} = -88.8$  to -89.1%) indicate hypogen condition (Figure 2). Illite of Koru deposit represents argillic zone (Th=147°C), whereas illite of Kumarlar deposit typifies phyllic zone (Th=278°C). For the calculation of the fractionation factors of illites. these temperature values were used. The calculated water compositions are located an area between local geothermal (or meteoric) water and magmatic water composition, that are similar to water compositions of fluidinclusions in quartz and barite. Fluids in barites reflect meteoric or local geothermal water origin, whereas fluids in quartz indicate magmatic water origin.

The Rb–Sr isotope data for the different sized illite fractions ( $<1\mu$ m,  $<0.5\mu$ m) of samples from three deposits are plotted on a Rb–Sr isochron diagram (Figure 3). The slope of the linear relationship between  ${}^{87}$ Sr/ ${}^{86}$ Sr and  ${}^{87}$ Rb/ ${}^{86}$ Sr ratios for the whole data set corresponds to an age of 22.4±2.3 Ma.



**Figure 2:** Distribution of oxygen and hydrogen isotope values of illites. Fluid compositional areas, obtained from fluids trapped in hydrothermal quartz and barite crystals from Koru, Balcilar and Tesbihdere-Şahinli are shown for comparison.



**Figure 3:** Rb-Sr isochron diagram of illites from Koru (TK), Kumarlar (KU) and Tesbihdere (TD) deposits.

The different methods applied to illites provide an alternative and confirmatory approach for understanding of various features (i.e., origin of fluids, temperature conditions and age) of hydrothermal conditions. These illites are similar to hydrothermal illites from many deposits worldwide. KI values are compatible with the temperature conditions, obtained from fluid inclusions, stable isotope data plot between the magmatic water box and meteoric water line (local geothermal water) comparable with the composition of fluid inclusions within the barite and quartz. The latest Oligocene and lowest Miocene Rb/Sr age is consistent with the plutonic intrusions. Thus, it is possible to determine the age source and temperature of the alteration associated with mineralization from a single source.

## Progress in 3D multiphoton microscopy of fluid inclusions

## **Robert C. Burruss<sup>1</sup>**

<sup>1</sup>Eastern Energy Resources Science Center, U.S. Geological Survey, Reston, VA, USA. burruss@usgs.gov,

Since the publication of our initial results [1] we have continued to explore the potential of multiphoton methods to image fluid inclusions 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 microscopes used in biomedical research can routinely image samples with two simultaneous modes, second harmonic generation (SHG) and two-photon excitation fluorescence (TPEF). Systems capable of imaging with Raman scattering, either coherent anti-Stokes Raman scattering (CARS) or stimulated Raman scattering (SRS), can create images in all three modes simultaneously.

Multiphoton microscopy is a type of laser scanning confocal microscopy (LSCM) but it has distinct advantages over fluorescence LSCM. Unlike LSCM, multiphoton responses are generated only in the focal volume of the objective, yielding high contrast images without confocal pinholes. SHG can image non-fluorescent aqueous inclusions at the same time that TPEF creates images of fluorescent hydrocarbon inclusions whereas LSCM can only image hydrocarbon inclusions. CARS and SRS can create chemically specific images based on the C-H stretch of hydrocarbons or the O-H stretch of water. Although this is possible with scanning confocal Raman systems, the multiphoton methods are orders of magnitude faster.

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 FIGI (ref) identifies 37 inclusions ranging in volume from 0.5 to 7232  $\mu\text{m3}$  with log-normal size distribution.



**Figure 1:** 3D image volume, 170 x 170 x 110 µm. 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 [2].

In some SHG images of quartz the field of view (FOV) 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. Polarization resolved SHG may provide a method to differentiate the response from twinning from the response at the inclusion wall.



Figure 2: SHG image of epithermal quartz showing multiple Brazil twins with holes where 2phase aqueous inclusions occur. 170 x 170 x 150 µm volume, Olympus FemtoCARS FV1000 microscope 25x, 1.05 N.A. water immersion objective. Image processing with ImageJ [2].

TPEF images of hydrocarbon inclusions should be similar to 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.



**Figure 3:** 3D distribution of oil inclusions (TPEF, green) and aqueous inclusions (SHG, red) in fracture filling quartz. 250 x 250 x 74 µm volume. USGS built microscope, 20x 0.7 N.A. objective,

ScanImage acquisition software [3], image processing with ImageJ [2].

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]. We are currently testing a new microscope for imaging with stimulated Raman scattering (SRS) over a wider spectral region 900 to 3600 cm<sup>-1</sup> so that we can image some host minerals (carbonates, sulfates, phosphates) as well as inclusion fluids.

#### Acknowledgements

This work is supported by the U.S. Geological Survey (USGS) Energy Resources Program and the USGS Innovation Center for Earth Sciences. The work would not have been possible without the support and encouragement from Albert Stolow, PI of CARSLab, NRC-Canada. Staff, post-docs, and graduate students at CARLab, Andrew Ridsdale, Aaron Slepkov, Adrian Pegoraro, and Marie-Andrée Houle, have all been essential for moving this work forward. Use of commercial or tradenames is for information purposes only and does not constitute endorsement by the U.S. Geological Survey or the U.S. Government.

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

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

## The Smaller the Harder: Theorization of a Threshold Size below which Fluid Inclusions do not Decrepitate

Marcello Campione, Nadia Malaspina, Eduardo Oglialoro, & Maria Luce Frezzotti

Department of Earth and Environmental Sciences, Università degli Studi di Milano Bicocca, I-20126 Milano, Italy. <u>marcello.campione@unimib.it</u>

Fluid inclusions are known to be formed at pressures reaching some tens of kilobars. The solid matrix encompassing the fluid filled cavity experiences decompression as a consequence of uplift processes such as eruptions. This event may prompt the mechanical failure of the host-mineral matrix through either stretch or decrepitation, depending on a ductile or brittle mechanism of matrix failure, respectively [1-3].

Laboratory experiments performed on synthetic inclusions show that the decrepitation temperature is strongly size dependent, with smaller cavities observed to decrepitate at higher temperatures [4]. On the other hand, natural inclusions which undergo migration through a pressure gradient are always found intact below a critical size [5].

In this paper, we model fluid inclusions as spherical cavities in a continuous elastic medium. Under these conditions, the tangential stress applied in the matrix has a cubic dependence on 1/r (Figure 1a). This means that the maximum tensile stress concentrates at the cavity/matrix interface, and, as can be demonstrated [6], this stress is independent on cavity size. This means that if a fracture criterion based on the maximum stress concentration is adopted, there is no way for accounting for the size dependence of fracturing.



Figure 1: a) Stress state within an elastic matrix at 1 bar confining pressure hosting a spherical fluid inclusion of diameter D at pressure p'. At the cavity/matrix interface the tensile stress reaches its maximum value  $\sigma_m$ . The average stress over a distance 2d from the interface is  $\sigma_d$ . b) Decrepitation internal pressure as a function of D for  $H_2O$  inclusions in quartz (after Bodnar et al. [4]; the graph reports 88 estimates over 132). The blue curve is our model calculation by taking  $T_0 =$ 0.45 kbar and  $d = 0.25 \ \mu m$ . The dotted curves are calculated with the same function by taking d =0.10  $\mu m$  (lower) and  $d = 0.50 \mu m$  (upper). The curve has one abscissa asymptote  $D_{th}$  and one ordinate asymptote  $2T_0$ , being the threshold size for decrepitation and twice the matrix tensile strength.

Here, we address this problem by adopting a non-local stress approach to fracturing. Our mechanical model is based on two parameters: *d*, a characteristic distance which is materialdependent and accounts for the *brittleness* of the matrix [7], and  $T_0$ , the uniaxial tensile strength of the matrix.

We show that the model calculation well approximates experimental datasets relating internal pressure to cavity size (Figure 1b) and we demonstrate the fundamental prediction that the decrepitation phenomenon is characterized by a threshold size,  $D_{th}$ , and a threshold internal pressure of the cavity, below which decrepitation would not be allowed.

The order of magnitude of the decrepitation threshold size is 1  $\mu$ m for the analysed datasets of quartz and olivine inclusions. This means that *unperturbed* inclusions are likely to be observed, even though the submicrometric and nanometric ones would preserve, if accessible with non-destructive methods, the real world of Earth interior.

#### Acknowledgements

The Scottish Whiskey Industry is undoubtedly acknowledged for its kind support to stimulating discussion among strongly heterogeneous experts. Some other valuable inputs from more Mediterranean specialties such as Vin Santo and Marsala must be mentioned for their useful contribution.

#### References

[1] Bodnar, R. J., and P. M. Bethke (1984), Systematics of stretching of fluid inclusions; I, Fluorite and sphalerite at 1 atmosphere confining pressure, Econ. Geol., 79(1), 141–161.

[2] Vityk, M. O., and R. J. Bodnar (1995), Do fluid inclusions in high-grade metamorphic terranes preserve peak metamorphic density during retrograde decompression?, Am. Mineral., 80(5), 641–644.

[3] Bodnar, R. J. (2003), Re-equilibration of fluid inclusions, in Fluid inclusions: Analysis and interpretation, vol. 32, pp. 213–230, I. Samson, A. Anderson, and D. Marshall.

[4] Bodnar, R. J., P. R. Binns, and D. L. Hall (1989), Synthetic fluid inclusions - VI. Quantitative evaluation of the decrepitation behaviour of fluid inclusions in quartz at one atmosphere confining pressure, J. Metamorph. Geol., 7(2), 229–242.

[5] Roedder, E. (1984), Fluid inclusions, Reviews in Mineralogy, Paul H. Ribbe.

[6] Timoshenko, S., and J. N. Goodier (1951), Theory of elasticity, McGraw-Hill, New York.

[7] Lajtai, E. Z. (1972), Effect of tensile stress gradient on brittle fracture initiation, Int. J. Rock Mech. Min. Sci. Geomech. Abstr., 9(5), 569–578.

## Insights into Pre-Campanian Ignimbrite volcanism in the Campanian Plain (Southern Italy): a Melt Inclusions Approach

**Claudia Cannatelli**<sup>1</sup>, Angela L. Doherty<sup>1</sup>, Paola Petrosino<sup>1</sup>, Harvey E. Belkin<sup>2</sup>, Giuseppe Rolandi<sup>1</sup>, Annamaria Lima<sup>1</sup>, Stefano Albanese<sup>1</sup>, & Benedetto De Vivo<sup>1</sup>

<sup>1</sup>Department of Earth, Environmental and Resources Sciences, University of Naples Federico II, Italy <u>claudia.cannatelli@unina.it</u>

<sup>2</sup>U.S. Geological Survey, Mail Stop 956, 12201 Sunrise Valley Drive, Reston, VA 20192, USA

The Campanian Volcanic Zone (CVZ) is an area of approximately 2000 km<sup>2</sup>, located in Southern Italy between the Tyrrhenian Sea and the Apennine Chain. Explosive volcanism started at least 300 ka with the emplacement of several ignimbrites [1], associated with magma up-rise along mainly NE-SW directed fault lineaments [1, 2]. Presently, the active volcanic sources in the CVZ are represented by the Campi Flegrei area, the Somma-Vesuvius Volcano and the Island of Ischia, all in a quiescent state, but expected to resume explosive activity in the future.

While at Ischia Island the eruptive record of on-land cropping products, starting from 150 ka B.P. is quite complete, at Campi Flegrei and Somma-Vesuvius we have full evidence for only the last 39 ka, corresponding to the age of the Campanian Ignimbrite (CI) eruption. The few scattered pre-CI ignimbrite outcrops left, experienced intense alteration, which complicates stratigraphic correlations among different sequences located quite far from each other.

In order to better constrain the pre-CI volcanic activity in the CVZ, we collected samples from the Taurano Ignimbrite succession (AFIS, 205.6-183.8 ka), Moschiano Ignimbrite (MS - 184.7 ka) and Durazzano Ignimbrite (DR - 116 ka) (Fig.1). Selected glass and melt inclusions have been investigated for all the sampled products, with the aim of determining the geochemical features of the CVZ ancient ignimbrites (i.e. magma source composition and evolution, volatile content, differentiation patterns, etc..).

All samples show two types of melt inclusions (MIs): crystallized and glassy ( $\pm$  bubbles). While pyroxenes trapped both types of MIs, feldspars trapped mainly glassy MIs.



**Figure 1** Schematic stratigraphic column of the Taurano-Acqua Freconia (AFSI), Durazzano (DR) and Moschiano (MS) sections showing the older ignimbrite below the basal pumice and Campanian Ignimbrite (CI, Unit-1).

Although bulk rock compositions are not available, due to intense alteration of the units, they can be approximated by the composition of the glass shards, which in general have similar geochemistry to the most evolved feldspar hosted MIs. Petrographically, more primitive MIs appear crystallized, while more evolved MIs are glassy ( $\pm$  bubbles). Crystallized MIs have been reheated in the Linkam TXY1400 in order to obtain a homogeneous glass ( $\pm$  bubbles). Crystals have been mounted on single epoxy rods and polished in order to bring MIs to the surface and analyze them by EMP and SIMS.

The youngest unit (DR1) displays two types of pyroxenes, both in the diopside field, trapping MIs with different composition. Crystallized (re-heated) MIs lie in the field of basaltic composition, while glassy MIs have been trapped in more evolved pyroxene and display the same composition of feldspar-hosted MIs (trachyte). MIs of intermediate composition are not present, either in pyroxenes or feldspars. Overall, the composition of MIs trapped in pyroxene and feldspars and the glass shards lie on the theoretic line of perfect fractional crystallization.

One of the oldest units, MS1, shows the most evolved MIs of the entire succession, all hosted in feldspars. Pyroxenes from this sample are all melt inclusions free. The main difference between MIs from DR1 and MS1, is the greater alkali content for the MS1 samples.

Units AFYI 12-13 display very strongly zoned pyroxenes, which have trapped MIs at different times during their crystallization, representing two possible types of melt. Bulk rocks are represented by the glass shards composition, which falls on the phonolitetrachyte boundary. AFYI 12 reaches the most phonolitic stage of magmatic evolution, with alkali content of about 15%, but overall AFYI 13 displays greater alkali enrichment.

Units AFYI 7-9 are the oldest of the succession and contain pyroxenes of slightly different composition, which have trapped portions of melt during the magmatic evolution. Pyroxenes hosted MIs have a composition that span between intermediate (tephri-phonolite/trachy-andesite) and primitive (trachy-basalt) compositions. Feldspars on the other hand, host very evolved MIs (trachyte) possibly representing the final stage of the magmatic evolution.

Compared to CI (39ka, [3]), reheated pyroxene hosted MIs [4] overlap most consistently with

both glassy and reheated MIs of this study. A similar bimodal distribution can be observed in pyroxenes hosted MIs from the CI, which also reached trachytic compositions. Because the pre-CI primitive MIs composition overlap with primitive composition MIs from CI, one may theorize a possible common source of magma. The differences seen in the more evolved compositions of the MIs in the pre-CI (present study) respect to the CI, can be the result of subsequent differences in the evolutionary path of the magma (i.e. oxygen fugacity, interaction with country rocks, residence time, etc).

#### Acknowledgements

This work was supported by the Italian Ministry of University and Research, PRIN Project (PRIN2010PMKZX7).

#### References

[1] Rolandi G., Bellucci F., Heizler M.T., Belkin H.E., De Vivo B. (2003) Tectonic controls on the genesis of ignimbrites from the Campanian Volcanic Zone, southern Italy. Mineralogy and Petrology 79, 3-31.

[2] Milia A., Torrente M.M. (2011) The possible role of extensional faults in localizing magmatic activity: a crustal model for the Campanian Volcanic Zone (eastern Tyrrhenian Sea, Italy). Journal of the Geological Society 168, 471-484.

[3] De Vivo B., Rolandi G., Gans P.B., Calvert A., Bohrson W.A., Spera F.J., Belkin H.E. (2001) New constraints on the pyroclastic eruptive history of Campanian volcanic Plain (Italy). Mineralogy and Petrology 73, 47–65.

[4] Webster J. D., Raia F., Tappen C., De Vivo B. (2003) Pre-eruptive geochemistry of the ignimbrite-forming magmas of the Campanian Volcanic Zone, Southern Italy, determined from silicate melt inclusions. Mineralogy and Petrology 79, 99-125.

## Unlocking the Evolution of the Grey Porri Tuffs of Monte dei Porri, Salina, Southern Italy: a Complete Picture Using Melt Inclusion Geochemistry and Volatile Contents.

**Angela L. Doherty<sup>1</sup>**, Claudia Cannatelli<sup>1</sup>, Harvey E. Belkin<sup>2</sup>, Robert J. Bodnar<sup>3</sup>, & Benedetto De Vivo<sup>1</sup>

<sup>1</sup>Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, University of Naples Federico II, Naples, Italy. ilovevolcanoes@gmail.com

<sup>2</sup>United States Geological Survey (retired), 11142 Forest Edge Dr, Reston, VA 20190 USA

<sup>3</sup> Fluids Research Laboratory, Department of Geosciences, Virginia Tech, Blacksburg, VA 24060, USA

The island of Salina lies in the central Aeolian Island Arc, in the south Tyrrhenian Sea, southern Italy. Salina lies at the intersection of the arcuate chain of submarine seamounts and islands and the terminus of the Tindari-Lettojani-Malta tectonic line. Its location and range in erupted products (from basalt to rhyolite) make it an important study area in order to understand regional geochemical and tectonic variations in the Aeolian Arc.

The Grey Porri Tuffs (GPT) were produced by a very explosive series of eruptions that ended the ~60ka of quiescence after the coneforming eruptions of Fossa delle Felci, and began the period that would build the twin peak of Monte dei Porri. These eruptions produced an interbedded series of air-fall pumice and scoria units found in outcrops all over Salina, and also across many of the other Aeolian Islands[1]. Both the pumice and scoria units of the GPT were sampled for this study, and were split into sub-levels based on *insitu* petrographic characteristics.

Evidence suggests that the Grey Porri Tuff deposits are the result of a mixing of at least 2 magmatic compositions[2]. One is represented by melt inclusions (MI) hosted in feldspar and pyroxene crystals of the pumice units of the GPT. The composition of these MI plot in the dacitic-trachydacitic field and appear largely degassed, containing 497-616ppm S, 233-576ppm  $CO_2$ , 1.7-2.8% H<sub>2</sub>O but was enriched in Cl compared to other units, with 0.5-0.7 wt% Cl.

A second magma is represented by olivinehosted MI in the pumice units. This magma is more primitive, plotting in the basalt-basaltic andesite field and is enriched in volatiles compared to the MI of the evolved mineral hosts of the same unit. This second magma was particularly enriched in  $H_2O$  and S with 4.1-5.1 wt%  $H_2O$  and 3227-4032ppm S, but contained less Cl, 0.3-0.4 wt%.

The whole rock concentration of the pumice unit, falls in the high-silica andesite field, that is, between the two MI compositions.

Geochemistry and minimum entrapment pressure modelling using  $H_2O/CO_2$  data from selected MI suggest that the more evolved magma was most probably resident in a shallow magma chamber, and was intruded by the second, primitive, volatile-rich magma. This primitive magma contains olivine- and pyroxene-hosted MI which were entrapped at a much greater pressure and depth than the MI entrapped in feldspar and pyroxene. The more recent sub-level of the pumice unit outcrop (11b in this study) contains also pyroxene- and feldspar- hosted MI which have entrapped a magma of intermediate, basaltic-andesite composition suggesting these magmas may have begun to mix.

The scoria unit of the GPT is most likely a continuation of the mixing of these two magmas, with olivine, pyroxene and feldspar all crystallising at the same time, entrapping a magma of the same intermediate composition. The magma is also partially degassed, containing 2.4-3.3 wt% H<sub>2</sub>O, 1638-2245ppm S and lower Cl concentrations similar to those found in the olivine-hosted MI of the pumice unit. In outcrop, this unit was split into 3 sublevels as the middle unit (4b in this study) exhibited much finer clast size and other petrographic differences. This difference is noted in the geochemistry of this level which also contains more primitive olivine and pyroxenes containing the volatile-rich MI of the pumice-hosted olivine crystals. It is possible during this phase of the eruption, a pocket of the volatile-rich magma was tapped or another small pulse of primitive magma was introduced into the system.

#### References

[1] Lucchi, F., Gertisser, R., Keller, J., Forni, F., De Astis, G. & Tranne, C.A. (2014) Eruptive history and magmatic evolution of the island of Salina (central Aeolian archipelago), Geological Society, London, Memoirs, 37 155-211.

[2] Doherty, A.L., Bodnar, R.J., De Vivo, B., Bohrson, W.A., Belkin, H.E. & Messina, A. (2012) Bulk rock composition and geochemistry of olivine-hosted melt inclusions in the Grey Porri Tuff and selected lavas of Monte dei Porri Volcano, Salina, Aeolian Islands, southern Italy, Central European Journal of Geosciences, 4(2)338-355.

## Constraining the source of Archean fluids involved in the formation of BIF-hosted hypogene iron ores in the Yilgarn Craton of Western Australia

**Paul Duuring**<sup>1</sup>, Steffen G. Hagemann<sup>1</sup>, David A. Banks<sup>2</sup>, Christian Schindler<sup>1</sup>, & Thomas Angerer<sup>1</sup>

<sup>1</sup>Centre for Exploration Targeting, University of Western Australia, Australia. paul.duuring@uwa.edu.au, <sup>2</sup>School of Earth and Environment, University of Leeds, Leeds, UK.

The Yilgarn Craton is endowed with large resources of primary low-grade (~25-45 wt % Fe), magnetite-rich iron orebodies hosted by Archean banded iron formation (BIF), as well as higher-grade (>55 wt. % Fe) but smaller resources of magnetite-, specular hematite-, and hematite-goethite- enriched BIF. Critical parameters in the genetic model for highergrade iron orebodies include: (i) the presence of a thick Fe-rich BIF, (ii) modification of the BIF by abundant Si-dissolving (undersaturated) fluids, (iii) widespread fluid/BIF reactions controlled by structurallyenhanced permeability, (iv) exhumation and surficial modification of the BIF, and (v) preservation of the ore body from complete erosion. A present weakness of current Mineral System models for BIF-hosted iron ore deposits in the Yilgarn craton is that the physicochemical properties and source of fluids responsible for the formation of magnetite- or specular hematite-rich orebodies are poorly constrained. This abstract presents preliminary results of microthermometry and in situ laser ablation inductive coupled mass spectrometry (LA-ICP-MS) analyses of fluid inclusions from two hypogene iron ore types.

Samples of magnetite- and specular hematiterich ores (Figs. 1A and 1B, respectively) were collected from locations distributed throughout the Yilgarn Craton, including the Beebyn, Madoonga, Windarling, and Koolyanobbing iron camps. In all studied camps, Archean magnetite-dolomite alteration assemblages are locally overprinted by Archean specular hematite-quartz assemblages. Representative samples were collected below the present weathering horizon and are unaffected by near-surface supergene fluid alteration. Microthermometry was performed at the University of Western Australia on magnetitedolomite and specular hematite-quartz samples.



Figure 1: (A) Primary silica-rich bands in BIF are replaced by ferroan dolomite and disseminated hypogene magnetite at the Beebyn camp. Later dissolution of dolomite results in the concentration of magnetite to form high-grade ore. (B) Specular hematite-quartz veins hosted by brittle fault zones at the Madoonga camp.

Dolomite from magnetite-rich ores hosts 5 to 20 µm-diameter, three-phase aqueous (liquid + vapour + halite) primary fluid inclusions. Locally, these fluid inclusion assemblages define crystal growth zones in dolomite grains. Dolomite from the Beebyn camp host fluid inclusion assemblages with eutectic temperatures ( $T_e$ ) of -50° to -60°C, whereas equivalent fluid inclusion assemblages from the Koolyanobbing camp display a T<sub>e</sub> range of -33° to -44°C. The Te estimates suggest the presence of cations such as  $Ca^{2+}$ ,  $Mg^{2+}$ , in addition to Na<sup>+</sup> and K<sup>+</sup>. Final ice-melting temperatures (T<sub>m ice</sub>) for all measured fluid inclusion assemblages range from -8° to -15°C. The three-phase fluid inclusions from the Beebyn and Koolyanobbing camps have a homogenisation temperature  $(T_h)$  range (to the

liquid phase) from 120° to 165°C and total homogenisation temperatures  $(T_{h(total)})$  by halite dissolution that range from 238° to 336°C. Calculated salinities range from 37 to 40 equiv. wt.% NaCl.

Quartz from specular hematite-quartz veins located at the Madoonga, Koolyanobbing, and Windarling camps host 3 to 25  $\mu$ m-diameter primary and pseudo-secondary fluid inclusions that define clusters and trails that terminate at quartz grain boundaries (Fig. 3).



**Figure 3:** Quartz bordered by specular hematite secondary trail comprises multiple two-phase (L-V) fluid inclusions that define an assemblage.

Two-phase aqueous (liquid + vapour) fluid inclusion assemblages are present in Koolyanobbing and Windarling samples, whereas two-phase or three-phase aqueous (liquid + vapour + halite) fluid inclusions are locally hosted by quartz in Madoonga samples. The T<sub>e</sub> estimates range from -51° to -74°C for Koolyanobbing, -27° to -75°C for Windarling, and -22° to -60°C for Madoonga samples. The Te estimates indicate the likely presence of  $Ca^{2+},\ Mg^{2+},\ Na^{+},\ and\ K^{+}.$  The  $T_{m\ ice}$  for twophase fluid inclusion assemblages from Madoonga, Koolyanobbing, and Windarling range from -3° to -22°C, -12° to -40°C, and -5° to -34°C, respectively. These temperatures correspond to a wide range of calculated salinities for the two-phase fluid inclusions of 3.4 to 20.0 equiv. wt.% CaCl<sub>2</sub> for Madoonga, 14.3 to 36.0 equiv. wt.% CaCl<sub>2</sub> for Koolyanobbing, and 5.4 to 32.6 equiv. wt.% CaCl<sub>2</sub> for Windarling. Three-phase fluid inclusions from Madoonga samples display T<sub>e</sub> and T<sub>m ice</sub> estimate ranges of -35° to -60°C and -23° to -49° C, respectively. Preliminary T<sub>h</sub>

measurements for two-phase fluid inclusions from Windarling range from 113° to 162°C. Three-phase fluid inclusions from Madoonga display a  $T_h$  range (to the liquid phase) from 87° to 123°C and a  $T_{h(total)}$  by halite dissolution range from 132° to 146°C. Calculated salinities range from 24 to 29 equiv. wt.% CaCl<sub>2</sub>.

LA-ICP-MS analyses were performed on fluid inclusions hosted by quartz in specular hematite-quartz samples from the Madoonga, Koolyanobbing, and Windarling camps. The fluid inclusions are rich in Fe, Ca, Mg, and Na, with moderate enrichments in K, Mn, Zn, Cu, Ba, and Sr, with very low concentrations of Pb, Sn, Co, and Bi. Element/Ca ratios for the analysed fluids from the different camps are remarkably similar, despite the Madoonga camp being located 400 km away from the Koolyanobbing and Windarling camps.

Microthermometry data for magnetitedolomite iron ores suggest that the parent BIF reacted with a hypersaline (Na, Ca, Fe, Mgbearing) fluid at temperatures ranging from 238° to 336°C. Fluid interaction resulted in the pervasive replacement of primary silica-rich bv hydrothermal dolomite bands and magnetite. Dissolution of the dolomite resulted high-grade magnetite-rich in ores. Microthermometry and LA-ICP-MS data for specular hematite-quartz iron ores suggest the interaction between BIF and ancient, saline to hypersaline (Fe, Ca, Mg, Na-rich), lowertemperature (113° to 162°C) fluids. The fluids circulated within subvertical brittle faults that cut folded BIF macrobands. Archean seawater is a possible source for these fluids based on the salinity and temperature ranges of measured fluid inclusion assemblages, the presence of Ca as a dominant cation in the fluids, and the > 400 km recorded distribution of these fluids. Further work will include acquiring LA-ICP-MS data for magnetitedolomite ores, as well as leachate analyses for both ore types.

#### Acknowledgements

This study was funded by the Geological Survey of Western Australia's Exploration Incentive Scheme (a Royalties for Regions initiative). Stephane Roudaut assisted with the collection of microthermometry data.

## Dauphiné Twin Planes in Quartz Trap Fluid Inclusions and Indicate Paleostress in Deeply Buried Sandstones

András Fall<sup>1</sup>, Estibalitz Ukar<sup>1</sup>, Randall Marrett<sup>2</sup>, & Stephen E. Laubach<sup>1</sup>

<sup>1</sup>Bureau of Economic Geology, Jackson School of Geosciences, The University of Texas at Austin, U.S.A. andras.fall@beg.utexas.edu

<sup>2</sup>Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, U.S.A.

Establishing the stress state history of hydrocarbon reservoirs for exploration and production purposes is essential because dynamic mechanisms governed by the existing stress state drive hydrocarbon migration and accumulation. Therefore, paleostress history, rather than the present-day stress state, is responsible for most natural structures in a reservoir. Our current research on quartz deposits in fractures in tight-gas sandstone reservoirs reveals an opportunity to explore and potentially validate the use of Dauphiné twins in quartz as paleostress history indicators.

Recent advancements in electron backscattered diffraction techniques (EBSD) show that Dauphiné twins are widespread in quartz fracture cements that show synkinematic textures. In these cements, the relative sequence of deformation events is recorded in a spatial pattern of crack-seal textures and Dauphiné twins that can be mapped using SEM-based technology. By reconstructing the fracture opening history through SEM-CL mapping of quartz cement bridges with crackseal texture that span the fracture, and by relating the temperatures obtained from fluid inclusion assemblages trapped in crack-seal cement increments to the known burial history of the formation, the duration of fracture opening can be estimated. Recent reconstructions of partially cemented natural fractures from tight-gas sandstone reservoirs suggest that fractures widen in aperture over tens of millions of years [1, 2, 3]. [1, 2, 3] also mention the presence of fluid inclusion trails that are perpendicular to the fluid inclusion trails that are trapped in crack-seal increments and these trails are therefore normal to the fracture walls and cannot be simple byproducts of the crack-seal process. Although these inclusions trap a fluid population within the fracture cement, they have hitherto been omitted from fracture interpretations due to

ambiguous petrographic evidence of their origin in the cement bridges.

Correlating transmitted light images with SEM-CL- and EBSD-based images reveals that the trails of fluid inclusions normal to the fracture walls were trapped along Dauphiné twin planes (Figure 1). Both (coexisting) aqueous and hydrocarbon gas inclusions were trapped along these planes. Fracture wall-parallel crack-seal increments contain similar inclusions. Homogenization temperatures of the aqueous inclusions thus represent true trapping temperatures [4]. Inclusions normal to the fracture wall are larger and more irregularly shaped than those in crack-seal trails, but both show similar liquid-to-vapor ratios.



**Figure 1:** A. Transmitted light image of quartz cement bridge showing numerous trails of fluid inclusions. Inclusions in crack-seal increments that are parallel to fracture wall (colored boxes) show temperatures increasing from ~130s°C to 150s°C in subsequent crack-seal increments. Inclusions in trails that are perpendicular to fracture wall (green lines) show temperatures in the 150s°C.

**B**. Panchromatic SEM-CL image of the quartz cement bridge used to establish relative timing of crack-seal increments.

C. EBSD image of bridge, showing Dauphiné twin planes perpendicular to fracture walls and crack-

seal increments. Dauphine twin planes coincide with wall-perpendicular fluid inclusion trails.

Dauphiné twins can either be growth or mechanical twins. Growth twins mimic previously twinned quartz crystallography, while mechanical twins would form as a response to compressional stress. Detailed fluid inclusion microthermometry of quartz cement bridges allowed us to determine that Dauphiné twins in the studied sandstone reservoirs are mechanical. If twinning happened in the early stages of cement bridge growth, and the crack-seal increments grow on a twinned substrate, temperatures obtained from fluid inclusions in the crack-seal and trails perpendicular to them would be identical within the corresponding cement increment. in our samples, However, measured temperatures of fluid inclusion trails normal to the fracture wall are different from those in fracture wall-parallel crack-seal increments. Moreover, wall-normal trails correspond to the highest (and latest) temperatures measured in these quartz bridges. Such temperature trends point to a mechanical origin of Dauphiné twinning in quartz bridges that postdates crack-seal growth.

Dauphiné twinning represents a rotation of 180° (or 60°) about the c-axis of one part with respect to another of the quartz lattice (electrical or orientational twinning), with no breakage of lattice bonds along the twinning plane. This precludes contact between a free fluid phase and the twinning plane surface, preventing trapping of fluid inclusions. Thus, inclusions trapped along twin planes are probably inclusions trapped earlier in the crack-seal increments that were reequilibrated during twinning to later P-T trapping conditions.

Mechanical Dauphiné twins in quartz cement bridges in tight-gas sandstones probably formed due to contraction due to fracture strain relaxation after the natural fracture opening ceased, or as a partial collapse of the fracture in the latest stages of fracture opening. Contraction directions recorded by Dauphiné twins were estimated using the kinematic method of [5], and the orientation of maximum compression was estimated using a graphical P-dihedra method [6]. Contraction/compression orientations normal to the fracture wall estimated in this manner are compatible with the tectonic history of the area. These results demonstrate the potential for Dauphiné twinning to be a robust paleopiezometer for sedimentary rocks, in low temperature and pressure environments, during fracture opening and hydrocarbon charge.

#### Acknowledgements

This work was supported by grant DE-FG 02-03ER15430 from the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, and industrial sponsors of the Fracture Research and Application Consortium. Additional support was provided by The GDL Foundation.

#### References

[1] Becker, S.P., Eichhubl, P., Laubach, S.E., Reed, R.M., Lander, R.H., and Bodnar, R.J. "A 48 m.y. history of fracture opening, Cretaceous Travis Peak Formation, East Texas", GSA Bulletin, v. 122, p. 1081-1093, July/August 2010.

[2] Fall, A., Eichhubl, P., Cumella, S.P., Bodnar, R.J., Laubach, S.E., and Becker, S.P. "Testing the basin-centered gas accumulation model using fluid inclusion observations: southern Piceance Basin, Colorado", AAPG Bulletin, v. 96, p. 2297-2318, December 2012.

[3] Fall, A, Eichhubl, P., Bodnar, R.J., Laubach, S.E., Davis, J.S. "Natural hydraulic fracturing of tight-gas sandstone reservoirs, Piceance Basin, Colorado", GSA Bulletin, v. 127; no. 1/2; p. 61– 75, January/February 2015.

[4] Goldstein, R.H., and Reynolds, T.J. "Systematics of fluid inclusions in diagenetic minerals", Society for Sedimentary Geology Short Course, v. 31, SEPM (Society for Sedimentary Geology), Tulsa, Oklahoma, 199 p, 1994.

[5] Marrett, R. A., and Allmendinger, R. W. "Kinematic analysis of fault-slip data", Journal of Structural Geology, v. 12, p. 973-986, 1990.

[6] Angelier, J., and Mechler, P. "Sur une methode graphique de recherche des contraintes principales egalment utilisable en tectonique et en seismologie: La methode des diedres droits", Bulletin de Societie Geologique de France, v. 19, p. 1309-1318, 1977.

## Fluid Inclusion and Pb Isotope Evidence for the Origin of Mississippi Valley-type Mineralization in the North American Mid-Continent: Insights from Trace Occurrences of Mineralization

Joshua D. Field<sup>1</sup>, Martin S. Appold<sup>1</sup>, & Raymond M. Coveney, Jr.<sup>2</sup>

<sup>1</sup>Dept. of Geological Sciences, University of Missouri, Columbia, Missouri, USA. jdfc6f@mail.missouri.edu,

<sup>2</sup>Department of Geosciences, University of Missouri-Kansas City, Kansas City, Missouri, USA.

Mississippi Valley-type (MVT) mineralization is widely distributed in Paleozoic carbonate rocks of the North American mid-continent. Most of this mineralization consists of no more than traces of sphalerite and, in rare cases, galena, but in a few locations mineralization has accumulated into large ore deposits that have been subjects of intensive geological research for decades. Fluid inclusion research has made many fundamental contributions to the present understanding of these large midcontinent MVT ore deposits. Early research showed that the deposits were precipitated from sedimentary basinal brines dominated by Na, Cl, and Ca at temperatures between 80 to 150° C. More recent fluid inclusion research has further characterized these brines as having low, dolomitizing Ca/Mg ratios, high K/Na ratios, and high methane contents. A subset of fluid inclusions in each MVT ore district studied thus far contains apparent high Pb concentrations (hundreds to a few thousand ppm) that correlate with elevated Ca/Na ratios, suggesting that the ore deposits formed as a result of mixing between a Pb-rich fluid and a Pb-poor fluid, inferred to have been enriched in sulfide.

The great contrast in scale of MVT mineralization in the North American midcontinent raises the question of what factors controlled deposit growth. Why was the MVT mineralizing process at most locations arrested after the deposition of no more than a few grams of Zn or Pb, whereas in a few locations like the Southeast Missouri and Tri-State districts, millions of tons of Zn and Pb were deposited? The present study is seeking answers to this question by analyzing the homogenization temperature and composition of fluid inclusions in trace MVT occurrences to see if they are systematically different in any way from fluid inclusions in MVT ore deposits.

obtained thus far show subtle Results differences between fluid inclusions hosted by trace MVT occurrences and MVT ore deposits. Relative to fluid inclusions in the Ozark and Illinois-Kentucky districts, fluid inclusions in the trace MVT occurrences tend to have slightly lower homogenization temperatures, Ba/Na and K/Na ratios, no detectible methane, and similar Ca/Na ratios. The Mg/Na and Sr/Na ratios of fluid inclusions in the trace MVT occurrences are similar to those of fluid inclusions in the Ozark MVT districts, but the Mg/Na ratios are significantly higher than those of fluid inclusions in the Illinois-Kentucky district, while the Sr/Na ratios are significantly lower than those of fluid inclusions in the Illinois-Kentucky district. Lead was detected in sphalerite-hosted fluid inclusions in trace MVT occurrences, but less frequently than in sphalerite-hosted fluid inclusions in the Ozark MVT districts. However, apparent maximum Pb concentrations in fluid inclusions in trace occurrences and ore deposits are similar, reaching a few thousand 1000 ppm. Thus, the fluids that formed trace MVT occurrences in the North American mid-continent are broadly similar to but nonetheless distinguishable from the fluids that formed MVT ore deposits. This indicates that the trace MVT occurrences formed from typical MVT brines, but not necessarily the same brines that formed the MVT ore deposits.

The absence of methane in fluid inclusions in the trace MVT occurrences may have genetic significance in that it may indicate redox conditions that were oxidizing enough to favor sulfate over sulfide in the brines and thus limited sulfide mineral precipitation. The apparent high Pb concentrations in some fluid inclusions hosted by trace MVT mineralization may also have genetic significance. If metalrich fluids with Pb concentrations as high as 1000's of ppm participated in the formation of trace MVT mineralization, then sulfide mineral precipitation may have been limited by the absence of abundant local H<sub>2</sub>S.

Lead isotope compositions were determined in the present study for sphalerite and galena from several trace MVT occurrences. Lead in the trace MVT occurrences is distinctly less radiogenic than Pb in the Ozark MVT ore deposits, which is highly radiogenic and was probably derived from Proterozoic igneous basement rocks. Thus, trace MVT occurrences may have been precipitated from fluids that did not circulate deeply enough to reach the granitic basement, in contrast to the fluids that formed the Ozark MVT ore deposits, but instead derived their Pb from shallower and perhaps more local sources.

#### Acknowledgments

Funding for this research was provided by National Science Foundation grant, EAR-1322018



*Figure 1:* Map of the central U.S. in the North American mid-continent showing the locations of trace MVT occurrences (black dots) targeted in the present study, major MVT ore districts (red), and major geologic features pertinent to MVT mineralization.

## Fluid Inclusion LA-ICPMS Analysis of Ore Fluids from Orogenic Gold Deposits of the Late Archean Hattu Schist Belt, Eastern Finland

**Tobias Fusswinkel<sup>1</sup>**, Thomas Wagner<sup>1</sup>, Grigorius Sakellaris<sup>2</sup>

<sup>1</sup>Department of Geosciences and Geography, University of Helsinki, Finland. <u>tobias.fusswinkel@helsinki.fi</u> <sup>2</sup>Endomines Oy, Hatuntie 450, FI-82967 Ilomantsi, Finland

The late Archean Hattu schist belt, Eastern Finland, is part of the 300 km long Ilomantsi-

Kostamuksha greenstone belt and it represents one of the best preserved Archean supracrustal sequences in Finland. It is composed primarily of metamorphosed (upper greenschist to lower amphibolite facies) epiclastic and felsic volcanic rocks, which are intruded by typical Archean TTG series tonalites and granodiorites. The schist belt hosts a large number of structurally controlled orogenictype gold deposits of differing mineralization styles, including gold bearing quartz and quartz-tourmaline veins as well as gold disseminations in various host rocks. The sample suite comprises the active Pampalo and Rämepuro mines, as well as the Hosko, Korvilansuo, and Kuittila prospects. The mineralization at Pampalo is characterized by disseminations in an intermediate pyroclastic rock unit as well as gold bearing and barren recording auartz veins a protracted deformation history. Detailed structural and petrographic analysis of different quartz generations provided the paragenetic framework for establishing clear cut time

relations of compositionally different fluid types. In addition to conventional microthermometry, we used quantitative Raman spectroscopy as well as in-situ laserablation ICPMS of individual fluid inclusions to fully characterize the fluid compositions. This yielded one of the most complete multielement datasets on fluid compositions from orogenic gold deposits. The LA-ICPMS data show quantifiable concentrations for alkaline and earth-alkaline metals, As and Au. Systematic correlations between fluid trace element compositions and fluid inclusion types elucidate the fluid evolution history of the Pampalo orogenic gold forming hydrothermal system. The fluid composition data will be combined with thermodynamic modelling of fluid-mineral equilibria to firmly constrain the key factors that resulted in gold deposition in the Ilomantsi greenstone belt.

#### Acknowledgements

This work was supported by the Academy of Finland, grant number 266180, and Endomines Oy.

## **Evolution of Carbonic Fluids in Crack-sealed Quartz veins**

Laura González-Acebrón<sup>1</sup>, MaialenLópez-Elorza<sup>1</sup>, José Ramón Mas<sup>1</sup>, José Arribas<sup>2</sup>, Robert H. Goldstein<sup>3</sup>

 Dpto. Estratigrafía, Facultad de Ciencias Geológicas (UCM)- Instituto de Geociencias (CSIC), Madrid, Spain. lgcebron@geo.ucm.es
Dpto. Petrología y Geoquímica, Facultad de Ciencias Geológicas (UCM)- Instituto de Geociencias (CSIC), Madrid, Spain.
Department of Geology, University of Kansas, Kansas, USA.

Fracture opening timing and temperatures and their subsequent sealing by mineral precipitation has been scarcely studied although they can provide transient fluid migration pathways in sedimentary basins, including oil and gas. Here we present an example of crack-seal quartz veins related to a Cretaceous hydrothermal process in the Cameros Basin, North Spain.

The basin infill is composed of a thick sedimentary sequence (up to 6500 m), generated under an extensional regime characterized by high rates of subsidence, from the Tithonian to the early Albian. This research is focussed on fluid inclusions in quartz veins (fig. 1) and quartz syntaxial ovegrowths both hosted in Valaginian to Barremian quartzites of the Urbión Gr [1], deposited in the eastern sector of the Cameros Basin. The quartz veins are mostly perpendicular to the stratification (fig. 1). The hydrothermal process occurred from Albian to Coniacian [2].



*Figure 1: Quartz veins hosted in quartzites of the Urbión Gr.* 

Nine samples were collected systematically from 7 quartz veins and 3 quartzite host rocks in the stratigraphic section, in three different positions of this section (I, II, III from bottom to top). Position I is separated by a total of 860 m of sediments from position III. Two of the samples show the contact between the host rock and the vein. All these samples have been studied though microthermometry in order to understand the origin of the hydrothermal fluids and the influence of these fluids in the sandstone host rock.

Primary fluid inclusions in quartz syntaxial overgrowths (fig. 2) usually present inconsistent Fluid Inclusion Assemblages (FIA) with variable liquid : vapor ratios (L:V from 80:20 to 95:5), in the system (H<sub>2</sub>O+NaCl) + CO<sub>2</sub> gas. Modal values of homogeneization temperatures ( $T_h$ ) in position I are 230°C, in position II around 140°C and in position III around 190°C.



**Figure 2:** Quartz syntaxial overgrowth in the quartzites of the Urbión Gr. Fluid inclusions are encircled.

On the other hand, quartz veins present primary fluid inclusions in the system  $(H_2O+NaCl) + CO_2$  liquid + CO\_2 gas (fig. 3A) with ratios around 95:3:2. They usually display very irregular morphologies, showing reentrants of the host quartz, which sometimes can be confused with daughter minerals if they are on the bottom or on the top of the fluid inclusion (fig. 3B and C). Quartz veins present crack and sealing texture detected under SEM-CL (fig. 4). Based on these criteria, reequilibration with the host quartz has been deduced.



**Figure 3:** Fluid inclusions in quartz vein. A.  $(H_2O+NaCl) + CO_2 liquid + CO_2 gas FIA B. Fluid inclusion with irregular morphology showing reentrants (arrow). C. Fluid inclusion with apparent daughter mineral. Scale bar is <math>10 \mu m$ .



Figure 4: Quartz vein under parallel light and SEM-CL (30 kV and 16 mm of working distance). Notice that quartz stage marked as 1 is rich in fluid inclusions and clearer under CL. Crack and sealing generates quartz 2, which is poorer in fluid inclusions and darker under CL. Quartz 2 penetrates in quartz 1 as fractures (arrows). Scale bars 0.2 mm in both.

Homogenization of CO2 liquid and CO2 gas (ThCO<sub>2</sub>) occur between 22.7-31.4°C, with the lowest values (highest densities) in the deepest samples and viceversa. Clathrates final melting temperatures usually range from 8 to 9.6°C, pointing to low salinity fluids, and no difference in this temperature have been recorded among all samples. Fluid inclusions usually homogenize to the liquid in a range between 110 °C and 276°C. More specifically, Th lower than 145°C were only recorded in position I, and minimum Th values are higher to the top of the section (from I to III, fig. 5). In addition, modal values in positions I and II are around 160°C, with maximum values of 259°C and 276°C, respectively. Position III histogram is narrower than the previous ones, with modal Th around 200°C, and maximum values of 224°C (fig. 5). In addition, consistent

FIAs are more common in positions II and III, in comparison to position I which present more inconsistent FIAs.



Figure 5: Th histogram for quartz veins. Blue for position I, red for position II, green for position III.

Based on the variations in the CO<sub>2</sub> density, we consider the hydrothermal fluids came from bottom to top. Reequilibration textures can be related to pressure drops during crack and sealing process. Further, the quartz syntaxial overgrowths were affected by the hydrothermal event, especially in the bottom part of the record. The apparent inconsistency of FIAs in quartz syntaxial overgrowths is probably due to a mixture of diagenetic and hydrothermal fluid inclusions.

#### Acknowledgements

This work was supported by the CGL2011-22709 Spanish project. We thank Ronald Bakker for his petrographic help.

#### References

[1] Mas R, García A, Salas R, Meléndez A, Alonso A, Aurell M, Bádenas B, Benito MI, Carenas B, García-Hidalgo JF, Gil J, Segura M (2004) 5.3.3. Segunda fase de rifting: Jurásico Superior-Cretácico Inferior. In: Geología de España (J. Vera Ed.), SocGeolEsp – IGME, 503-509.

[2] Casquet C, Galindo C, González-Casado JM, Alonso A, Mas R, Rodas M, García E, Barrenechea JF (1992) El metamorfismo en la Cuenca de Los Cameros. Geocronología e implicaciones tectónicas. Geogaceta 11:22-25.

## Identification of CaCl<sub>2</sub>-bearing daughter minerals in natural inclusions

Svetlana Grishina<sup>1</sup>, Jean Dubessy<sup>2</sup>, Lucas Uriarte M.<sup>2,3</sup>, Sergey Goryanov<sup>1</sup>, Igor Yakovlev<sup>4</sup>

<sup>1</sup>Institute of Geology and Mineralogy, Novosibirsk, Russia, <u>grishina@igm.nsc.ru</u>

<sup>3</sup>MALTA-Consolider Team, Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad

Complutense de Madrid, 28040-Madrid, Spain

<sup>4</sup>Novosibirsk State University, Russia

Calcium chloride hydrates in a system with (Ca>Na) have been described in natural [1] and synthetic inclusions [2] and in synthesized solids in capillary [3]. Here we present data of hydrate and non-hydrate daughter minerals in highly saline inclusions with (Ca>K>Na and Cl). The H<sub>2</sub>O-NaCl-KCl-CaCl<sub>2</sub> system is representative of the chemistry of several geological fluids. According to the phase diagram of this system, the expected solid phases salt are numerous: hydrate 2KCl·CaCl<sub>2</sub>·H<sub>2</sub>O, non-hydrated salts KCaCl<sub>3</sub> and CaCl<sub>2</sub>, along with calcium chloride hydrates CaCl<sub>2</sub>·nH<sub>2</sub>O [4]. KCaCl<sub>3</sub> is a rare mineral named as chlorocalcite, reported at Vesuvius volcano. Until now there is no Raman spectra reference of chlorocalcite in databases. Actually Raman spectra of chlorocalcite was published but on another name - as CaCl<sub>2</sub>·KCl solid inclusion [5].

For the assignment of Raman spectrum to  $CaCl_2$ ·KCl microanalysis of the brine, produced by dissolution of giant (till 800 µm) inclusions in doubly-distilled water have been done by the method of Petrichenko [6]. EDS spectra confirmed presence of Ca, K and Cl. The absence of water in these solids was demonstrated by the absence of bands in the Raman spectrum region corresponding to symmetric and antisymmetric H<sub>2</sub>O stretching (2700-4000 cm<sup>-1</sup>). The bands at low wavenumbers below 200 cm<sup>-1</sup> have been publised [5].

In this work we present identification of the same phase, (we named chlorocalcite), in halite from several endogenic deposits of Large Igneous Province at Siberian Platform. They were documented as rounded or euhedral individual crystals or as daughter minerals in brine inclusions. Bands at 140 and 195 cm<sup>-1</sup> are remarkably constant and match reported Raman spectra at low frequency region with shift  $\pm 1$  cm<sup>-1</sup> (Fig.1). Additional band at 149 cm<sup>-1</sup> is frequent.



**Figure 1:** Raman spectra of chlorocalcite: 1 individual euhedral crystal inclusion; 2- rounded chlorocalcite in polyphase inclusion; 3 – chlorocalcite daughter mineral inside brine inclusion; 4 – in CO2 inclusion; 5 – spectra of references [5].

Chlorocalcite inclusions have been identified in more than 30 samples using Raman spectroscopy. Another anhydrous solid inclusions was tentatively determined as hydrophilite (CaCl<sub>2</sub>) only in two samples. Hydrophilite was discredited , because it transforms to hydrates [Burke, 2007]. However the advantage of hydrophilite sealed

<sup>&</sup>lt;sup>2</sup> Université de Lorraine, CNRS, GéoRessources, Vandoeuvre-lès-Nancy, France

as inclusion is possibility to retain anhydrous, as it does not contact with water from air. In cavities of fresh broken inclusions a visible rim of liquid can be observed at optical microscope. EDS spectrum show presence of Ca and Cl in hydrates crystals that are formed by precipitation from the fluid as it escapes from the inclusion. The Raman spectrum of natural inclusion confirms the only presence of anhydrous phase, due to the absence of bands in the water stretching region (2700-4000 cm<sup>-1</sup>). The spectrum in the low wavenumber region is rather different from those reported for synthesized CaCl<sub>2</sub> [3].

In the studied inclusions several chloride hydrates coexist with anhydrous chlorocalcite solids. Micro-Raman analyses both at room temperatures and at -150 and -170°C were carried out at the CREGU-Nancy on a X-Y Dilor microspectrometer, equipped with an ionized Ar laser. Raman spectra only at room temperatures were acquired by confocal laser Micro-Raman spectrometer, T64000 Horiba Jobin Yvon (at Novosibirsk), using a 514.5 nm line of Ar laser at 30 mW, a laser spot size of 0.8 µm.

The comparison of Raman spectra, collected for hydrates (CaCl<sub>2</sub>·nH<sub>2</sub>O) from natural inclusions with reference Raman spectra [3] of synthesized solids revealed quite similar values in the stretching and bending regions of structural H<sub>2</sub>O both at room temperature and at -172 °C. The difference in Raman shift between the stretching and bending modes of water is less than 7 cm<sup>-1</sup>.

Identification of CaCl<sub>2</sub>-bearing solid phases is challenging in opening inclusions because of the deliquescence properties of chloride salts. BSE images of small inclusions usually reveal empty cavities instead of precipitated CaCl<sub>2</sub> hydrates or solely KCl crystals after incongruent melting of KCaCl<sub>3</sub> (Fig.3).



**Figure 3.** (a) Liquid-absent inclusion in plane-polarized light containing  $KCaCl_3$  and  $CaCl_2 \cdot 6H_2O$ ; (b): BSE image of the same open inclusion containing solely KCl crystals. Chloride xenoliths from kimberlites of Udachnaya East pipe, Siberia.

#### Conclusions

Raman spectroscopy is the preferential method for identification of CaCl<sub>2</sub>-bearing daughter minerals, because of their fragility and short life after opening. Sinjarite (CaCl<sub>2</sub>·2H<sub>2</sub>O), CaCl<sub>2</sub>·4H<sub>2</sub>O and antarcticite have been identified in natural inclusions according to reference Raman spectra [3]. CaCl<sub>2</sub>·0H<sub>2</sub>O have been determined tentatively. Raman spectra of chlorocalcite inclusions from the different localities display constant bands at 140, 150, 149 cm<sup>-1</sup> with only  $\pm 1$  cm<sup>-1</sup> shift.

#### Acknowledgements

This work was supported by grant RFBR # 15-05-09345.

#### References

[1] Schiffries C.M. (1990) C.M. [2] Baumgartner M. and Bakker R. (2009.) [3] Uriarte L. M., et al. (2014 and in review). [4] Assarsson (1950). [5] Grishina S. et al.(1992). [6] Petrichenko O.(2005). [7] Burke, E.A.J. (2007).

## **Porphyry and Epithermal deposits of the Urals: P-T-x-parameters**

**E.O. Groznova<sup>1,2</sup>**, O.Yu. Plotinskaya<sup>1</sup>, S.S. Abramov<sup>1</sup>, A.A. Borovikov<sup>3</sup>, S. Milovska<sup>4</sup>, J. Luptakova<sup>4</sup>, R. Seltmann<sup>5</sup>

<sup>1</sup> Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry RAS, 35, Staromonetny per., 119017, Moscow, Russia, grozelena@yandex.ru

<sup>2</sup> Institute of Experimental Mineralogy Chernogolovka, Moscow region, Russia

<sup>3</sup> Institute of geology and mineralogy SB RAS, Novosibirsk,

<sup>4</sup> Geological Institute, Slovak Academy of Sciences, B. Bystrica

<sup>5</sup> Center for Russian and Central EurAsian Mineral Studies (CERCAMS), Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, UK

Data concerning P-T conditions of formation of porphyry and porphyry-related deposits of the Urals are limited [1, 2 and references therein]. In the present paper we report fluid inclusion data for the Talitsa Mo-porphyry (Middle Urals), the Mikheevskoe Cuporphyry, the Kalinovskoe Cu-porphyry, the Bereznyakovskoe Au-Ag epithermal and the Biksizak base-metal carbonate replacement deposit.

#### **General geology**

The Talitsa Mo-porphyry deposit lies on the western margin of the East Uralian terrane. It is located within Carboniferous intrusives of granodiorite to quartz monzonite composition with minor monzodiorite cut by granodiorite to quartz monzonite and granite porphyry stocks and dykes. The country rocks are Devonian rhyolites and basalts and serpentinite. Zones of potassic alteration (mainly K-feldspar) are confined to porphyry stocks and dykes. Phyllic (sericite and quartz-sericite) alteration is developed throughout the central zone of the Talitsa intrusion whereas propylitic alteration occurs typically on its margins. Mineralization (0.04- 0.34% Mo, 0.09-0.47% Cu, 0.1-0.4 ppm Au, Cu/Mo=0.5 to 3) occurs as disseminations and as stockwork zones [3].

The Mikheevskoe Cu-porphyry deposit is hosted by Late Devonian-Early Carboniferous sandstones, tuffstone and basaltic andesites, overlain by Early Carboniferous basaltic lavas, tuffs, sandstones. Intrusives of Carboniferous age are quartz diorite stocks and numerous diorite and granodiorite porphyry dykes [4]. Volcanic-sedimentary rocks rather than dykes host the ore (373.5 Mt ore @ 0.38% Cu, http://www.allmetals.ru/index.php?id=2091). Other deposits occur within the Birgilda-Tomino ore cluster situated in the East Uralian volcanic megazone. The Ordovician aphyric basaltic lavas and tuffs form the base of the visible section and host the Kalinovskoe, Tomino and Birgil'da porphyry Cu-porphyry deposits with total inferred resources of about 2.8 Mt Cu. The Cu porphyry mineralization is confined to an irregularly shaped diorite stock, approximately 2-3 km in size. Quartz-sericite alteration with chalcopyrite, (phyllic) molybdenite and minor bornite forms the central part of the deposit. Marginal zones are composed of propylitic (chlorite, epidote, carbonate) alteration with pyrite-chalcopyrite mineralization. Bismuth-gold-base metal mineralization forms an epithermal overprint on the earlier stages. The basalts are overlain by a Middle Ordovician-Lower Silurian marble hosting the Biksizak skarn-related carbonate replacement Zn deposit (inferred resources 1.7 Mt Zn). The Bereznyakovskoe Au-Ag-Te epithermal field (inferred resources 36 t Au) is hosted by Upper Devonian – Lower andesitic-dacitic Carboniferous volcanosedimentary rocks. All deposits are associated with quartz diorite and andesite porphyry intrusions of the K-Na calc-alkaline series (Birgil'da-Tomino igneous complex) formed in a subduction-related volcanic arc [1].

#### Fluid inclusion data

Fluid inclusions in quartz, carbonate, barite and sphalerite from all assemblages of the aforementioned deposits were studied. Raman spectroscopy of vapor and solid phases was carried out using the Ramanor U-1000 (Institute of Geology and Mineralogy. Novosibirsk, Russia) and LabRAM-HR (Geological Institute, Banska Bystrica, Slovakia). The results are summarized in fig.1 and table 1.

T <sub>hom</sub> .,°C	P, bar	C, wt.%- eq.NaCl	Composition of					
			liquid/ vapor /solid					
			phase					
Bereznyakovskoe (enargite, tennantite, Au native,								
Au, A	Au, Ag, Pb tellurides, galena, sphalerite)							
150-250	80-60	4-15	Na-Cl/ H <sub>2</sub> O, CO <sub>2</sub> / -					
<b>Biksizak</b> (pyrite, sphalerite, galena, tetrahedrite)								
150-270	~300	1-10	Na-Cl/ H <sub>2</sub> O, CO <sub>2</sub> / -					
Kalinovskoe, porphyry stage (chalcopyrite,								
bornite, molybdenite)								
	450–1100	15–30	Ca(Mg,Na)-Cl,					
250–540			Mg,Na-Cl/CO <sub>2</sub> , N <sub>2</sub> ,					
			$H_2S/calcite,$					
			hematite, magnetite					
Kalino	o <b>vskoe</b> , suł	o-epither	mal stage (pyrite,					
chalcopyrite, Bi sulfosalts, native Au)								
150-250	190-350	3-12	Na-Cl/ CO <sub>2</sub> / –					
Mikheevskoe, porphyry stage, propylites (pyrite,								
chalcopyrite)								
			Ca(Mg,Na)-Cl, Mg,					
150–350	100-650	10–35	Na-Cl, Na-Cl/ CO <sub>2</sub> ,					
			N <sub>2</sub> / calcite, halite					
Talitsa, potassic alteration (molybdenite-pyrite								
stage)								
			Mg,Na-Cl, Na-Cl/					
320-510	900-1700	25-35	CO <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> /					
			nahcolite, halite					
Talitsa, phyllic alteration (pyrite, chalcopyrite,								
tetrahedrite, sphalerite, galena)								
200–450	400–1300	5–15	Na-Cl/ CO <sub>2</sub> , CH <sub>4</sub> ,					
			N <sub>2</sub> /Silicate?					

Table 1.	P- $T$ - $x$	parameters	of porphyry	and
epitherma	ıl depos	sits of the Ur	als (– not deter	cted)

Porphyry-style mineralization was deposited from highly saline (up to 35 wt.% NaCl eq.) Mg- and Ca-chloride-rich fluids at high temperatures (up to 550°C) and pressures 400 to 1700 bar. Vapor phases are characterised by  $CO_2$  and minor admixture of  $N_2$  and  $H_2S$  at Kalinovskoe and Mikheevskoe Cu-porphyry deposits while at the Talitsa Mo-porphyry deposit  $CH_4$  is present together with  $CO_2$ . Mineralization of epithermal style (Bereznyakovskoe) and sub-epithermal style (Kalinovskoe) was deposited from low to moderately saline (1 to 10 wt.% NaCl eq.) Nachloride fluids at low temperatures (up to 270°C) and pressures less than 300 bar.

#### Acknowledgements

This is a contribution to IGCP-592 sponsored by UNESCO-IUGS. It was supported by the RFBR NN 13-05-00622 and 14-05-00725, and by NHM (via the CERCAMS fellowship program).



**Figure 1:**  $T_{hom}$  vs C (a) and  $T_{hom}$  vs P (b) diagrams for porphyry and epithermal deposits of the Urals. T - Talitsa, M - Mikheevskoe K - Kalinovskoe, BR – Bereznyakovskoe, BZ - Biksizak

#### References

[1] Plotinskaya O.Y., Grabezhev A.I., Groznova E.O. et al. (2014) The Late Paleozoic porphyryepithermal spectrum of the Birgilda–Tomino ore cluster in the South Urals, Russia, J Asian Earth Sci, 79, 910-931.

[2] Grabezhev A.I., Borovikov A.A., & Vigorova V.G. (2008) Fluid inclusions study in quartz and calcite veinlets from copper-porphyry deposits of the Urals. In: Annual – 2007 Yekaterinburg, IGG UB RAS, pp. 308–312. in Russian

[3] Azovskova O.B. & Grabezhev A.I. (2008) The Talitsa porphyry copper-molybdenum deposit, the first object of a subalkaline porphyry system in the Central Urals, Dokl Earth Sci, 418(1), 99-102.

[4] Shargorodskii, B.M., Novikov, I.M., & Aksenov, S.A. (2005) The Mikheevskoe porphyry copper deposit in the South Urals, Otech. Geol., (2), 57-61. in Russian

## Properties of Fluid Inclusions from the Potassic Alteration Zone of the Karakartal Deposit (Erzincan, Central Eastern Turkey)

**Oğuzhan Gümrük**<sup>1</sup>, Miğraç Akçay<sup>1</sup> & David A. Banks<sup>2</sup>

<sup>1</sup>Department of Geology, Karadeniz Teknik Üniversitesi, 61080 Trabzon, TR. <u>ogumruk@hotmail.com</u> <sup>2</sup>School of Earth and Environment, University of Leeds, Leeds, UK. <u>d.a.banks@leeds.ac.uk</u>

Located near the Kabataş village (Kemaliye-Erzincan) in a metallogenic zone covering Divriği (Sivas), İliç-Kemaliye (Erzincan) and Tunceli provinces within east central Anatolia, the Karakartal deposit shows typical properties of porphyry Au-Cu systems. It has a welldeveloped hydrothermal alteration pattern represented by potassic-, phyllic-, propyliticchlorite-sericite, as well as skarn and alteration. The central zone is characterised by potassic alteration that grades outwards into phyllic-and propylitic alteration towards the outermost part of the deposit. The skarn type alteration is dominant along the contacts of the intrusives with the volcano-sedimentary rocks

#### **Mineralisation and Vein Types**

The Karakartal deposit is a small and currently uneconomical property with all features of porphyry systems. Lying within intermediate to basic intrusives (varying in composition and petrography from porphyritic andesites to quartz diorites and microdiorites), as well as in the metasedimetary rocks intruded by these subvolcanic rocks, the mineralisation is in the form of disseminations and veins/veinlets. Disseminations are dominant within the core of alteration halo that also contain crosscutting quartz veins with low sulphide content. Veins are more enriched in sulphides in the country rocks especially where they are converted into hornfels.

Quartz veins in the potassic alteration zones can be classified into five main groups: a) magnetite  $\pm$  chalcopyrite  $\pm$  quartz veins, b) biotite  $\pm$  quartz veins, c) quartz + K'feldspar  $\pm$ chalcopyrite  $\pm$  pyrite veins, d) quartz + chalcopyrite  $\pm$  pyrite veins, e) quartz + chlorite + chalcopyrite  $\pm$  pyrite veins. They are crosscut by post-mineralisation veining composed of anhydrite  $\pm$  pyrite- and calcite veins. The phyllic and chlorite-sericite alteration zones are mainly associated with quartz + chalcopyrite  $\pm$  pyrite, and quartz + pyrite  $\pm$ chalcopyrite veins, respectivly. The intrusionhornfels contact zones show a different mineral paragenesis and contain quartz + molybdenite  $\pm$  pyrite, as well as quartz + specularite veins.

#### **Microthermometric Studies**

Quartz veins found in the Karakartal deposit are very complex and diverse in mineralogical composition, which is also reflected in fluid inclusion content. We only present the results of fluid inclusion studies within the veins in Ksilicate alteration zone. FI's in this zone have very complex compositions. Single phase, two-phase, multi-phase and melt inclusions, varying in size from <5 to 35 micron in size are present. Of these, multi-phase inclusions are dominant and have subtypes based on the type and number of salts and other daughter minerals.



**Figure 1:** Microphotographs of fluid inclusions from the K-silicate alteration zone showing monophase inclusions(a), vapour-rich L+V type inclusions (b), L+V+S type inclusions (c) and very complex multi-phase inclusions (d).

The two-phase L-V type inclusions have both liquid and vapour rich subtypes. The former ones have very low eutectic temperatures showing that they contain variety of salt components such as  $CaCl_2+FeCl_2+NaCl+KCl$ . They have salinities of 15-25 wt% NaCl eq.
and homogenise at  $200-350^{\circ}$ C, which are compatible with the chlorite geothermometry [1]

Multi-phase inclusions are very complex, contain salt crystals, hematite, sulphides, sulphates and biotite, have rather low liquidand variable gas contents. Some inclusions contain only halite, some halite and sylvite, some Mg-and Fe-salts in addition to others, supported by eutectic temperatures as low as -55°C. The homogenisation of gas in these inclusions takes place at 300-875°C. Salt phases homogenise at intervals of 125-425°C and 400-680°C, and opaque phases (Fe oxides and sulphides) at 850-1050°C, resulting in salinity values of up to 80 wt % NaCl eq. This, in turn, suggests strongly that salt brine is responsible for such inclusions.

#### **LA-ICP-MS** Analyses

LA-ICP-MS analyses of the fluid inclusions (carried out in Leeds University, UK) indicate that they have very complex chemical compositions with very high Na, K and Mg contents (Fig. 2). It was shown that K is the most dominant cation in the M-S type inclusions, whereas L-V and V type inclusions have rather equal amounts of Ca, Na and K. Iron is more abundant than copper and is more dominant in V type inclusions than in MS type inclusions. Manganese is more important as a cation in LV type inclusions compared to other two types. Overall, K and Fe are more abundant in all types of inclusions compared to Ca, Mg, Cu and Mn.



Figure 2: Ternary diagrams showing the composition of all types of fluid inclusions from the K-silicate alteration zone of Karakartal deposit based on LA-ICP-MS analyses.

Similar results were also obtained from ratio analyses. MS type inclusions are characterised by similar amounts of K- and Na salts, whilst K/Na ratios of LV type inclusions are <1. Ca and Mg contents are similar in all type of inclusions with Mg/Na and Ca/Na contents of <1.



**Figure 3:** Histograms showing results of the LA-ICP-MS analyses from fluid inclusions in different alteration zones at Karakartal deposits

#### Results

It was shown that K-silicate alteration zone was formed by brine solutions under magmatic temperatures, as indicated by MS type FIs with a variety of daughter phases. The brines are equally enriched in Na and Ca, and also contain minor Ca and Mg in similar quantities. Fe is more dominant than Cu.

#### Acknowledgements

This work was financially supported by the Turkish Research Fund (Tübitak Project No 110Y308).

#### References

[1] Akçay M., Gümrük O., & Aslan N. (2012) Ultra-High temperature K-silicate alteration in porphyry systems: Examples from the Çöpler (İliç) and Karakartal (Kemaliye) deposits in eastern Turkey, IESCA 2012, pp. 158.

# Importance of melt inclusions in study of carbonatites: insight into Kerimasi melt evolution

Tibor Guzmics<sup>1</sup>, Réka Káldos<sup>1</sup>, Zoltán Zajacz<sup>2</sup>, Csaba Szabó<sup>1, 4</sup>

<sup>1</sup>Lithosphere Fluid Research Lab, ELTE, Budapest, Hungary <u>tibor.guzmics@gmail.com</u> <sup>2</sup>University of Toronto, ON M5S 3B1, Canada <sup>4</sup>ELTE Faculty of Science Research and Instrument Core Facility, Budapest, Hungary

Our study demonstrate that detailed study of a statistically significant number of melt inclusions is an appropriate method describing melt evolution at Kerimasi from melilitenephelinite to natrocarbonatite through calcic carbonatite [1, 2, 3]. We shed light behavior of elements during silicate-carbonate liquid immiscibility and fractional crystallization along the liquid line of descent.

Using compositional data of melt inclusions (n=610) in three different plutonic rocks jacupirangite (afrikandite, and calciocarbonatite), we have reconstructed the geochemical evolution of the immiscible silicate and carbonate melt, and various crystalline phases in the subvolcanic reservoir of Kerimasi Volcano in the East African Rift. The results of microthermometric experiments for the melt inclusions combined with the relevant phase diagrams show a temperatureranges from 1150-1000 through 1000-900 to 900-700 °C for crystallization of the studied afrikandite. jacupirangite and calciocarbonatite. respectively. Silicatecarbonate liquid immiscibility occurred during the generation of carbonatite magmas from a CO<sub>2</sub>-rich melilite-nephelinite parent magma to natrocarbonatite through calcic carbonatite magma at pressure range from 10 to 2 kbar. All these indicate that immiscible silicate and carbonate melts separated from the afrikandite body, which was followed by the formation of jacupirangite from these separated melts. Calciocarbonatite started to crystallize from the calcic carbonate melt that was physically separated during formation of jacupirangite. The fractionating mineral phase assemblage and the element partitioning systematics upon silicate-carbonate melt immiscibility are strongly depended on the parental magma Our results indicate that composition. preferential partitioning of oxidized sulfur (as  $SO_4^{2^-}$ ), Ca and P (as  $PO_4^{3^-}$ ) into the carbonate melt may promote the partitioning of Nb, Ta,

Pb and all REE into this phase. However, changes in the partition coefficients of elements between minerals and the coexisting melts along the liquid line of descent are rather significant at Kerimasi. This is why, in addition to the REE; Nb, Ta and Zr are also enriched in Kerimasi calciocarbonatites. Volatiles (e.g. alkalis, S, F, Cl and H<sub>2</sub>O) were incorporated principally in nyerereite, shortite, burbankite, nahcolite and sulfohalite, as identified by Raman spectrometry. These extremely unstable minerals cannot be found in the bulk rocks, because of alteration by secondary processes. Based on these data, an evolutionary model is proposed for Kerimasi plutonic rocks, which contributes to our better understanding of the petrogenesis of carbonatites and associated silicate rocks.

#### Acknowledgements

This research was granted by the Hungarian Science Foundation (OTKA, PD 105364) to T. Guzmics. Part of these results has been carried out in the framework of the REG\_KM\_INFRA\_09 Gábor Baross Programme and TÁMOP project nr.4.2.1/B-10-2011-0002.

#### References

[1] Guzmics et al., (2011) Carbonatite melt inclusions in coexisting magnetite apatite and monticellite in Kerimasi calciocarbonatite Tanzania: melt evolution and petrogenesis. Contributions to Mineralogy and Petrology, 161, 177-196.

[2] Guzmics et al., (2012) Liquid immiscibility between silicate, carbonate and sulfide melts in melt inclusions hosted in co-precipitated minerals from Kerimasi volcano (Tanzania): evolution of carbonated nephelinitic magma: Contributions to Mineralogy and Petrology, 164, 101-122.

[3] Guzmics et al., (2015) The role of liquid–liquid immiscibility and crystal fractionation in the genesis of carbonatite magmas: insights from Kerimasi melt inclusions. Contributions to Mineralogy and Petrology, 169, 17.

# Preliminary microthermometric data from the Kışladağ Au deposit, Western Turkey: Porphyry / Porphyry-Epithermal transition?

Nurullah Hanilçi<sup>1</sup>, Gülcan Bozkaya<sup>2</sup>, David A. Banks<sup>3</sup>, <u>Vsevolod Prokofiev</u><sup>4</sup>, Yücel Öztaş<sup>5</sup>

<sup>1</sup>Istanbul Univeristy, Dep. of Geological Engineering, Avcilar, Istanbul, TURKEY <u>nurullah@istanbul.edu.tr</u>

<sup>2</sup>PamukkaleUniversity, Dep. of Geological Engineering,20020, Denizli-TURKEY <u>gbozkaya@pau.edu.tr</u> <sup>3</sup>School of Earth and Environment, University of Leeds, Leeds, UK. d.a.banks@leeds.ac.uk,

<sup>4</sup> Department of Geology of Ore Deposits, IGEM RAS, Moscow, Russia

<sup>5</sup>Tuprag Metal Madencilik, Ovacık Mevki Gümüşkol Köyü, Ulubey Merkez/Uşak <u>yucelo@kisladag.com</u>

The Kışladag Au deposit, the first porphyry type gold deposit discovered in Turkey, is located approximately 55 km southwest of Usak, in western Turkey. In the Usak region, the Early to Late Tertiary volcanic complexes comprises outcrops of the Elmadağ, İteciktepe and Beydağı stratovolcanoes [1] resulting from an extensional tectonic regime in western Anatolia. These stratovolcanoes occur in a NE-SW direction and are dated at between 17.29 my and 12.15 my [1].

The Kışladağ Au deposit is related to intrusive and sub-volcanic rocks of the Bevdağı volcanic complex. The main mineralized lithologies of the deposit area are quartztrachyte quartz-latite to flows and volcanoclastic rocks intruded by a series of nested subvolcanic porphyritic intrusives of alkali affinity [2]. Three different phases of intrusions have been identified from their cross-cutting relationships, alteration and mineralization. These are (i) intrusion 1 (IN1), (ii) intrusion 2 (IN2) and the altered equivalent of intrusion 2 (IN2A), (iii) intrusion-3 (IN3) as shown in Fig.1. The most productive intrusions with respect to Au are IN1 (Au>1.5 ppm) and IN2/IN2A (Au<1 ppm). These intrusions intruded into basement schists of the Paleozoic Menderes Massive, and are overlain by Miocene volcanics in the area surrounding the deposit.

Fluid inclusion studies have been carried out on primary and pseudo-secondary inclusions in quartz from the IN1, IN2 and IN3 intrusions. The fluid inclusions have been classified as LV-type (liquid-vapour), VL-type (vapour rich), V-type (vapour), LVS-type (liquid-vapour-solid), and LVMS-type (liquidvapour-multi-solid) inclusions (Fig.2).



Figure 1: Geological map of the Kışladağ Au deposit (modified after[1]).

#### **Preliminary Results:**

Ore-stage quartz in IN1 includes LV, VL, LVS, and LVMS-type inclusions, and can categorize into two groups. The first group is high temperature represented by VL-type inclusions which homogenise to the vapour vapour phase between 424 and 520°C (avrg. 486°C), and have a low salinity (avrg. 4.2% NaCl eqv.). The second group are moderate to high temperature between 322 and 483°C (avrg. 385°C) with high salinity (>35 % NaCl) inclusions that homogenize to the liquid phase.

Post-ore stage quartz in IN1 contains LV-type inclusions, with a low temperature (avrg. 285°C) and low salinity (5.2 % NaCl eqv.). These fluids which may be indicative of an epithermal system.

Ore-stage quartz in IN2 includes VL, and LVtype inclusions. The VL-type inclusions homogenised to the vapour phase between 480 and 584°C (avrg. 555°C), and have a moderate salinity (17.8 %NaCl eqv.). The LV-type inclusions homogenised to the liquid phase between 370 and 443°C (avrg. 392°C), and have a moderately high salinity (avrg.18.2 % NaCl eqv.).



**Figure 2:** Photomicrograph of different types of fluid inclusion observed in quartz veins of Kışladağ Au deposits. (a) LV-type inclusions in IN2, (b) VL-type inclusion in IN1, (c) V-type inclusions in IN3, (d) LVS-type inclusions in IN1, and (e) LVMS-type inclusion in IN1.

Fluid inclusion types in quartz of IN3, which contains uneconomical low grade Au (<0.5 ppm), are mostly LV, VL, V-type and rare LVS-type. The homogenisation of VL-type inclusions were  $>600^{\circ}$ C to the vapour phase, and have a low salinity (avrg. 4.3 %NaCl eqv.). There is clathrate formation at low temperature indicating that this type of inclusion includes  $CO_2$ . While some V-type inclusions showed no observable phase change at low temperature, some of them do contain CO<sub>2</sub> at low temperature due to formation of CO<sub>2</sub>-ice, and homogenised at low temperature (at  $-4.6^{\circ}$ C). The LV-type inclusions homogenised to the liquid phase at an average of 465°C, and have moderate to high salinity (avrg. 23.6 %NaCl eqv). Some of LV-type inclusions homogenised at lower temperature (avrg. 285°C), and have lower salinity (avrg. 9.7 %NaCl eqv.) again indicating a more epithermal character of the fluids similar to post-ore stage fluids in IN1.

The preliminary microthermometric data shows that ore forming fluids associated with the Kışladağ Au mineralisation do not have the typical characteristics of porphyry regime. While inclusions of high homogenisation temperature (>600°C), high salinity (>35 %NaCl eqv.), and vapour-rich are closely associated with the porphyry system, the moderate to low homogenisation temperature and low salinity fluid inclusions are more indicative of an epithermal regime. The general scenario is one of repeated pulses of fluids typical of porphyry systems followed by a change to lower temperature epithermal mineralization. However as the pulses of fluids progress with time the amount of gold mineralization becomes less and suggests that the source reservoir is being depleted in some critical metals. The existing of different fluid characters at the same structural levels (hotter then cooler) is supportive of the repeated injection of more magmatic fluids associated to the different intrusions.

#### Acknowledgements

The authors thanks to Tüprag Metal Mining company for supporting field study and giving permission for sampling.

#### References

[1] Karaoğlu Ö., and Helvacı, C., (2012) Growth, destruction and volcanic facies architecture of three volcanic centres in the Miocene Uşak–Güre basins: a contribution to the discussion on the development of east–west and north trending basins in western Turkey. Geological Magazine 134, 163–175.

[2] Juras, S., Miller, R., Skayman, P., (2010) Technical Report for the Kışladağ Gold Mine, Turkey, 2010.

# Fluid Inclusion Characteristics of the Giant Tertiary Kadjaran Porphyry Mo-Cu Deposit, Tethys Metallogenic Belt, Armenia, Lesser Caucasus

Hovakimyan S.<sup>1, 2</sup>, Moritz R.<sup>1</sup>, Tayan R.<sup>2</sup>, Rezeau H.<sup>1</sup>

<sup>1</sup>Earth and Environmental Sciences, University of Geneva, Switzerland <u>samvel.hovak@gmail.com</u> <sup>2</sup>Institute of Geological Sciences of the Armenian National Academy of Sciences

The giant Kadjaran Mo-Cu porphyry deposit (2244 Mt reserves, 0.18% Cu, 0.021% Mo and 0.02 g/t Au) is located in Southern Armenia, Lesser Caucasus and belongs to the central segment of the Tethyan metallogenic belt. The deposit is hosted by the Tertiary Meghri composite pluton, which is characterized by a long lasting Eocene to Pliocene magmatic, tectonic and metallogenic evolution (Fig.1).



*Figure 1:* Geology of the southernmost Lesser Caucasus and location of the Kadjaran deposit (Moritz et al. 2013).

On-going fluid inclusion studies of the Kadjaran deposit are being carried out on sections, sampled from different parts of the Kadjaran open pit, drill cores and from the Geological Museum of the Zangezur Copper-Molybdenum Combine. Fluid inclusion petrography and microthermometry combined with SEM-CL images (Scanning electron microscope - cathodoluminescence) of quartz, revealed several characteristics of the ore-forming fluids at the Kadjaran deposit.

Quartz from the different mineralization stages contains a large variety of fluid inclusions, which can be classified into five families according to their nature, bubble size, and daughter mineral content: vapor-rich, aqueous-carbonic, brine, polyphase brine and

liquid-rich inclusions (Fig. 2). The size of fluid inclusions ranges from 2µm up to 100µm. In some cases they can be larger. Vapor-rich (Fig. 2D) fluid inclusions contain a large vapor bubble at room temperature (70-90 vol %). They contain a thin crescent-shaped meniscus with a liquid phase. These inclusions have isometric, rarely irregular shapes, as well as negative crystal shapes. Their size can be up to 20µm. Aqueous-carbonic (Fig.2A) fluid inclusions are complex inclusions with three phases at room temperature, containing aqueous liquid, carbonic liquid and carbonic vapor phases. Brine fluid inclusions contain an aqueous liquid, a vapor bubble and a halite crystal at room temperature. The bubble fills ~20 to 30 vol % of the inclusion. Polyphase brine (Fig. 2B) fluid inclusions contain daughter crystals and a bubble. The volume of the vapor phase is about 10-20 vol %. Daughter crystals are halite, sylvite and hematite. Halite is present in almost all the inclusions of this type and occupies 10-20 vol %. Sylvite does not occur in all the inclusions and the volume is less than 8 vol %. Liquidrich (Fig. 2C) fluid inclusions contain a vapor bubble, which fills 20-30 vol % of the inclusions. The size of the oval and elongated inclusions does not exceed 25µm, the irregularly shaped inclusions may reach 100µm in diameter.

Cathodoluminescence (SEM-CL) images reveal four generations of quartz. Molybdenite and chalcopyrite of the Central part of the open pit are associated with two different dark luminescent quartz generations, which contain typical brine, aqueous-carbonic and vapor-rich H<sub>2</sub>O fluid inclusions, with some of them coexisting locally as boiling assemblages (Fig. 2D). Final homogenization of all brine inclusions occurs by halite dissolution. Dissolution of halite between 356<sup>0</sup>  $\pm$  8<sup>0</sup> and 422<sup>0</sup>  $\pm$  10<sup>0</sup>C in brine (B1) inclusions of quartz - molybdenite veins indicates salinities between about 42.6 to 50.7 wt % NaCl equiv. The vapor bubbles homogenized between  $278 \pm 4^{\circ}$ C and  $327 \pm 5^{\circ}$ C.



Figure 2: Different fluid inclusion types from the Kadjaran Mo-Cu porphyry deposit: A- Aqueouscarbonic fluid inclusions; B- Polyphase brine inclusions; C- Secondary liquid-rich inclusions; D-Polyphase brine inclusion coexisting with vaporrich in boiling assemblages.

In quartz of quartz-molybdenite-chalcopyrite (Q-Mo-Cp) veins, typical primary inclusions include vapor-rich, brine and aqueousfluid inclusions. Secondary carbonic inclusions are of the liquid-rich type, and of the polyphase brine type. The temperature of CO<sub>2</sub> melting of aqueous-carbonic fluid inclusions ranges from -56.9 to -56.6°C. Final clathrate melting occurs from +7.3 to  $+8.3^{\circ}$ C. Homogenization temperature of CO<sub>2</sub> could not be measured reliably, because homogenization was to the vapor, therefore phase boundaries observe. were difficult to The bulk homogenization was to the vapor phase between  $398^{\circ} \pm 10^{\circ}$  and  $427^{\circ} \pm 8^{\circ}$ C. The clathrate melting temperatures yield salinities of 3.3 to 5.2 wt % NaCl equiv.

The main copper deposition at Kadjaran is associated to quartz-chalcopyrite veins characterised by the coexistence of vapor-rich and polyphase brine inclusions (Fig. 2D). Total homogenization of polyphase brine inclusions occurs by halite dissolution between  $361^{\circ} \pm 4^{\circ}C$  and  $385^{\circ} \pm 3^{\circ}C$ . Salinities lie between 43.4 and 45.9 wt % NaCl equiv.

The richest Mo area is the 6<sup>th</sup> vein zone in the northern part of the deposit and contains eastwest-oriented quartz-molybdenite (Q-Mo) and quartz-galena-sphalerite veins. The fluid inclusion characteristics of the Q-Mo veinlets from the 6<sup>th</sup> vein zone are totally different from other Q-Mo veins of the deposit. They are mainly characterized by low-temperature liquid-rich fluid inclusions. Final ice melting of liquid-rich inclusions in the oldest light grey luminescent quartz generation is between  $-4.4^{\circ}$  and  $-5.0^{\circ}$ C, corresponding to salinities of 7.0 to 7.9 wt % NaCl equiv. Total homogenization is between  $254^{\circ} \pm 2^{\circ}$  and  $267.5^{\circ} \pm 4^{\circ}$ C.

Abrupt changes of microthermometric data of fluid inclusion between the early O-Mo, Q-Mo-Cp, Q-Cp (Th<sub>total</sub> between  $360^{\circ}$  and 425<sup>°</sup>C) and the late quartz-galena-sphalerite vein stages (Th<sub>total</sub> 300-270<sup>6</sup>C) may reflect transition from a porphyry to an epithermal environment in the Kadjaran deposit. This interpretation is supported by field observations, with late vuggy silica and advanced argillic alteration in the central and eastern parts of the deposit. The presence of enargite and tennantite-tetrahedrite in the late paragenesis also supports an intermediate - to high-sulfidation epithermal environment.

Further fluid inclusion microthermometry and modelling of hydrothermal evolution of the Kadjaran deposit is currently in progress.

#### Acknowledgements

The first author would like to thank the Swiss government for awarding the Swiss Government Excellence Postdoctoral Scholarship for the Academic Year 2014-2015.

#### References

[1] Moritz R., Mederer J., Ovtcharova M., Spikings R., Selby D., Melkonyan R., Hovakimyan S., Tayan R., Ulianov A. (2013) Jurassic to Tertiary metallogenic evolution of the southernmost Lesser Caucasus, Tethys belt. In : Erik Jonsson et al. (eds), Mineral deposit research for a high-tech world, 12th SGA Biennial Meeting, 12-15 August 2013, Sweden, Uppsala, v. 3, p. 1447-1450.

# In Situ Identification of the S<sub>3</sub><sup>-</sup> Ion in S-rich Hydrothermal Fluids from Synthetic Fluid Inclusions

Nicolas Jacquemet<sup>1</sup>, Damien Guillaume<sup>1</sup>, Antoine Zwick<sup>2</sup>, & Gleb S. Pokrovski<sup>1</sup>

<sup>1</sup>Géosciences Environnement Toulouse (GET, UMR 5563), CNRS, Université de Toulouse, IRD, France, nicolas-jacquemet@hotmail.fr, <sup>2</sup> Centre d'Elaboration de Matériaux et d'Etudes Structurales CEMES-CNRS-Université de Toulouse, France.

The chemical forms of sulfur in geological fluids control the behavior of this element and associated base and precious metals in magmatic, hydrothermal, and metamorphic environments [1, 2]. However, these forms are insufficiently known at elevated temperature (T) and pressure (P) [1, 3, 4]. In this study, sulfur speciation in model aqueous solutions of thiosulfate and sulfur (~3 wt% of total S) was examined by in situ Raman spectroscopy on synthetic fluid inclusions at T-P-pH-redox conditions typical of porphyry Cu-Au-Mo deposits. Fluid inclusions were entrapped at 2 kbar and 600 or 700 °C in quartz that served as a container for the high T-P fluid. Then, the inclusion-bearing quartz samples were reheated and examined by Raman spectroscopy as a function of T and P (up to 500 °C and ~1 kbar). At T < 200 °C, all fluid inclusions show sulfate (SO<sub>4</sub><sup>2-</sup>  $\pm$  HSO<sub>4</sub><sup>-</sup>) and sulfide (H<sub>2</sub>S  $\pm$ HS<sup>-</sup>) in the aqueous liquid phase and elemental sulfur  $(S_8)$  in the solid/molten phase; these results agree both with thermodynamic predictions of sulfur speciation and the common observation of these three S forms in natural fluid inclusions. At T > 200-300 °C, in addition to these S species, the  $S_3^-$  ion was found to appear and grow with increasing temperature to at least 500 °C. The formation of  $S_3^-$  is rapid and fully reversible; its Raman signal disappears on cooling below 200 °C, and re-appears on heating. These new data confirm the recent findings of  $S_3^-$  in similar aqueous solutions at P up to 50 kbar and T >200 °C [3, 7]; they suggest that  $S_3^-$  may account for some part of dissolved sulfur and serve as a ligand for chalcophile metals in fluids from subduction zones and related Cu-Au-Mo deposits [3, 5, 6, 7]. This work demonstrates that in situ approaches are required for determining the true sulfur speciation in crustal fluids; it should encourage future spectroscopic investigations of natural

fluid and melt inclusions at high temperatures and pressures close to their formation conditions.

#### References

[1] A. C. Simon and E. M. Ripley. The role of magmatic sulfur in the formation of ore deposits. In H. Behrens and J.D. Webster, Eds., Sulfur in Magmas and Melts: Its Importance for Natural and Technical Processes, 73, pp. 513-578. *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Chantilly, Virginia, 2011.

[2] K. Kouzmanov and G. S. Pokrovski. Hydrothermal controls on metal distribution in Cu(-Au-Mo) porphyry systems. In J.W. Hedenquist, M. Harris, and F. Camus, Eds., Geology and Genesis of Geology and Genesis of Major Copper Deposits and Districts of the World: A Tribute to Richard H. Sillitoe. *Society of Economic Geologists Special Publication*, 16, pp. 573-618, 2012.

[3] G. S. Pokrovski and L. S. Dubrovinsky. The  $S_3^-$  ion is stable in geological fluids at elevated temperatures and pressures, *Science*, 331, pp. 1052-1054, 2011.

[4] N. Jacquemet, D. Guillaume, A. Zwick and G. S. Pokrovski. In situ Raman spectroscopy identification of the  $S_3^-$  ion in S-rich hydrothermal fluids from synthetic fluid inclusions, *American Mineralogist*, 99, pp. 1109-1118, 2014.

[5] J. A. Tossell. Calculation of the properties of the S<sub>3</sub><sup>-</sup> radical anion and its complexes with Cu<sup>+</sup> in aqueous solution, *Geochimica et Cosmochimica Acta*, 95, pp. 79-92, 2012.

[6] Y. Mei, D. M. Sherman, W. Liu and J. Brugger. Complexation of gold in  $S_3$ -rich hydrothermal fluids: Evidence from ab-initio molecular dynamics simulations, *Chemical Geology*, 347, pp. 34-42, 2013.

[7] G. S. Pokrovski and J. Dubessy. Stability and abundance of the trisulfur radical ion  $S_3^-$  in hydrothermal fluids. *Earth & Planetary Science Letter*, 411, pp. 298-309, 2015.

# Analytical advances in studying melt inclusions: a HR-Raman and FIB-SEM case study of carbonate melt inclusions in jacupirangite from Kerimasi (Tanzania)

**Réka Káldos<sup>1</sup>**, Tibor Guzmics<sup>1</sup>, Tamás Váczi<sup>2</sup>, Adrienn Baris<sup>3</sup>, Márta Berkesi<sup>1</sup>,

Károly Havancsák<sup>4</sup>, Zoltán Dankházi<sup>4</sup>, Csaba Szabó<sup>1, 4</sup>

<sup>1</sup>Lithosphere Fluid Research Lab, ELTE, Budapest, Hungary <u>rekakaldos@gmail.com</u> <sup>2</sup>Department of Mineralogy, ELTE, Budapest, Hungary <sup>3</sup>Department of Materials Physics, ELTE, Budapest, Hungary <sup>4</sup>ELTE Faculty of Science Research and Instrument Core Facility, Budapest, Hungary

The goal of our study is to demonstrate that the examination of melt inclusions with coupled analytical techniques is an appropriate method discovering all existing even submicron sized daughter phases in them hence, it can contribute to a better understanding of petrogenetic processes [1].

An interesting quasi-paradox of carbonatite rocks is that the primary water-soluble minerals are missing, although their presence is unambiguously expected by experiments and natural melt inclusions [2, 3]. Due to intensive alteration (weathering) of watersoluble minerals of alkaline and associated carbonatite rocks, analyses of only the rock compositions may provide misleading results about the petrogenesis. Hence, finding all mineral phases in the melt inclusions is essential to the proper description of petrogenesis of carbonatite rocks. For this purpose, we carried out high-resolution (HR) Raman spectroscopy, including 3D Raman mapping, and focused ion beam scanning electron microscopic (FIB-SEM) analyses on unexposed diopside-hosted carbonate melt inclusions in jacupirangite from Kerimasi Volcano (East African Rift), in which melt inclusions have not been studied before and has a controversial petrogenesis. Raman spectroscopic point measurements revealed the presence of perovskite, apatite and several alkali carbonates (e.g. nyerereite, shortite, burbankite) and hydro-carbonates such as nahcolite. Confocal 3D Raman mapping was performed on a melt inclusion (Figure 1) with high spatial (step size 0.2 µm horizontally and 1.6 um vertically) and spectral resolution to reveal the distribution of mineral phases, including several alkali carbonate species. A FIB-SEM slice-and-view study was performed

previously Raman-mapped melt on the inclusion perpendicular to the surface of the host diopside. Slices were milled every 200 nm, thus the distribution of mineral phases can be observed with extremely high spatial resolution (1-4 nm) including those, which are not Raman active. FIB-SEM also allowed obtaining EDS spectra and EBSD analyses from each exposed mineral phase of the melt Combining these techniques we inclusion. could 1) create a 3D model of the melt inclusion, thereby 2) characterize the spatial distributions of minerals (even submicron sized ones) and 3) calculate their volume ratio.

Applying our results can be essential in the determination of melt and fluid properties along the liquid line of descent and post entrapment and even in the determination of the  $H_2O$  content of alkaline and carbonatite systems.



Figure 1: 3D Raman map showing the distribution of mineral phases (mostly alkali carbonates) in two confocal sections in a diopside-hosted carbonate melt inclusion.



Figure 2: NaCl crystals in an opening diopside-hosted carbonate melt inclusion. SE image was taken in the FIB-SEM apparatus.

#### Acknowledgements

Funding for this research was granted by the Hungarian Science Foundation (OTKA, PD 105364) to T. Guzmics. Part of this study has been carried out in the framework of the REG\_KM\_INFRA\_09 Gábor Baross Programme and TÁMOP project nr.4.2.1/B-10-2011-0002.

#### References

[1] Berkesi et al., (2012) The role of CO2-rich fluids in trace element transport and metasomatism in the lithospheric mantle beneath the Central Pannonian Basin, Hungary, based on fluid inclusions in mantle xenoliths. Earth and Planetary Science Letters, 331-332, 8–20.

[2] Guzmics et al., (2011) Carbonatite melt inclusions in coexisting magnetite apatite and monticellite in Kerimasi calciocarbonatite Tanzania: melt evolution and petrogenesis. Contributions to Mineralogy and Petrology, 161, 177-196.

[3] Mitchell R.H. (2009) Peralkaline nephelinitenatrocarbonatite immiscibility and carbonatite assimilation at Oldoinyo Lengai, Tanzania. Contributions to Mineralogy and Petrology, 158, 589–598.

# Fluid inclusion study of VMS-related stockwork and stratiform deposits in the Northern Apennine Ophiolites (Italy)

Gabriella B. Kiss<sup>1</sup>, Giorgio Garuti<sup>2</sup>, Federica Zaccarini<sup>2</sup>, Zsuzsanna Kapui<sup>1</sup>

<sup>1</sup>Department of Mineralogy, Eötvös Loránd University, Budapest, Hungary. <u>gabriella.b.kiss@ttk.elte.hu</u> <sup>2</sup> Department of Applied Geosciences and Geophysics, University of Leoben, Leoben, Austria

Several volcanogenic massive sulphide (VMS) deposits with Cyprus-type metallogenic signature (Cu-Fe-Zn) occur in the Tethyan Jurassic ophiolites (the Ligurides) of the Italian Northern Apennines. The geodynamic evolution of the Ligurian basin involved tectonic denudation and exposure at the ocean floor peridotite-gabbro of a mantle assemblage, prior to the extrusion of MORBtype lava and deposition of pelagic sediments. The VMS deposits are located at different stratigraphic positions in the ophiolite sequence. They occur as: i) stockwork veins within peridotite, gabbro and pillow basalts, ii) stratiform ore bodies associated with seafloor breccias derived from the breakdown of peridotite or basalt, and iii) stratabound ore bodies inside massive pillow lava flows. Recent investigations have shown that the different type of country rock (peridotite, vs. basalt and gabbro) and the different depositional setting (seafloor vs. subseafloor) have significantly influenced the ore and gangue mineral chemistry, as well as the sulphur-isotope composition of the Northern Apennine VMS deposits [1,2,3,4,5]. However, a detailed characterisation of the hydrothermal mineralising solution based on fluid inclusion investigation is not available so far. In this contribution we present the preliminary data on the composition and thermo-barometric significance of fluid inclusions in three different deposits, namely Reppia, Campegli and Boccassuolo. Reppia contains two levels of stratiform minerali-sations (one at the top of seafloor serpentinite breccia and the other at the top of basalt breccia) as well as stockwork veins in basalt. Campegli and Boccassuolo represent stockwork mineralisations cutting across massive gabbro and pillow lava flow, respectively.

The main ore minerals in the stratiform deposits (i.e. massive sulphide lens) are pyrite, pyrrhotite, chalcopyrite and sphalerite. Rare grains of detrital chromite occur in the sulphide ore associated with serpentinite breccia. This mineral assemblage is completed with a small amount of gangue minerals, e.g. quartz, chlorite, calcite and clay minerals. Primary fluid inclusions in syngenetic quartz consist of L+V(+S) with constant phase ratio (L=95-85area%, V=5-15area%), suggesting a homogenous parent fluid. A minimum formation temperature of Th(LV-L)=120-170°C was found, while the salinity was  $5.97\pm1.24$  NaCl equiv. wt% (n=48). Methane content was proven by Raman spectroscopy (0.39±0.012 mol/kg) [6].

The stockwork veins hosted in basalt and gabbro mainly consists of pyrite, pyrrhotite, chalcopyrite, sphalerite and rare galena, accompanied by calcite, sericite, chlorite, barite, epidote and clay minerals as gangue. All the stockwork veins contain various generations of quartz, suggesting a series of precipitation events. Fluid inclusions occur in the different quartz generations, as well as the late calcite. Both minerals contain L+V(+S)primary inclusions (Fig. 1.) with constant phase ratio (L=90-80area%, V=10-20area%), suggesting a homogenous parent fluid. Sericite as an accidentally trapped mineral was identified with Raman spectroscopy in several inclusions. A wide range of minimum formation temperatures was observed in the deposits associated with basalt (Th(LV-L)=370-50°C) (n=295), supporting that quartz and calcite precipitated under decreasing temperature. This is in agreement with a continuous, progressive cooling of the solution towards the most distal positions away from the centre of the main fluid flow, during the vein formation. A salinity of 8.29±2.4 -9.4±24 NaCl equiv. wt% was found, while a methane content of 0.3±0.08 mol/kg [6] was also proven by Raman spectroscopy. On the contrary, a narrower range of minimum formation temperatures was observed in the gabbro-hosted deposit (Th(LV-L)=200-90°C) (n=74). Here a salinity of 8.24±0.9 NaCl equiv. wt% was found and a methane content of 0.26±0.02 mol/kg [6] was proven with

Raman spectroscopy. The slightly higher salinities in the stockwork ore compared to the stratiform one may result from a more intense mixing with the seawater in the latter case. Calculation of the minimum formation pressures resulted 31-38 MPa for the stockwork veins in basalt, while 55-69 MPa were obtained for the stockwork veins in gabbro. The higher values in the stockwork veins of the gabbro may be caused by its original lower position in the rock series.



**Figure 1:** L+V+S fluid inclusion in the first quartz generation (Qtz1) of Boccassuolo. Methane content in the V phase and sericite as accidentally trapped mineral (S) was proven with Raman spectroscopy.

The results of chlorite geothermometry [3, and this work], based on the methods of [7] and [8], supported the following petrographical observations: the chlorite formed earlier than the quartz in the stratiform ore (at 150-215°C) and in the stockwork veins of gabbro (at 290-300°C), while in the stockwork veins of the basalt it precipitated simultaneously or between the different quartz generations (at 120-270°C). Combination of the fluid inclusion and chlorite thermometry data (in case of simultaneous precipitation), pointed out overpressure phenomenon in some cases (up to 94 MPa), which may be caused by selfsealing of the veins during the mineral precipitation.

The salinity range, as well as the methane content can be well explained by the formation of modified seawater and a possible mixing volatiles. with magmatic Petrographic observations and the estimated temperature and pressure suggest that boiling phenomenon did not occur. The obtained results contribute better understand the mineralising to hydrothermal processes responsible for the formation of the VMS deposits of the Northern Apennines ophiolites.

#### Acknowledgements

The Research Instrument Core Facility (Eötvös Loránd University) and the Eugen F. Stumpfl Electron Microprobe Laboratory (University of Leoben) are thanked. G. B. Kiss was supported by by the European Union and the State of Hungary, framework of TÁMOP 4.2.4. A/1-11-1-2012-0001 and by the Hungarian Science Foundation (OTKA, PD 112580).

#### References

[1] Garuti, G., Zaccarini, F. (2005): Minerals of Au, Ag And U in Volcanic-Rock-Associated Massive Sulfide Deposits of the Northern Apennine Ophiolite (Italy). The Canadian Mineralogist, 43, 935-950.

[2] Garuti, G., Bartoli, O., Scacchetti, M. & Zaccarini, F. (2008): Geological setting and structural styles of Volcanic Massive Sulfide deposits in the northern Apennines (Italy): evidence for seafloor and sub-seafloor hydrothermal activity in unconventional ophiolites of the Mesozoic Tethys. Boletin de la Sociedad Geologica Mexicana, 60/1, 121-145.

[3] Zaccarini, F., Garuti, G. (2008): Mineralogy and chemical composition of VMS deposits of northern Apennine ophiolites, Italy: evidence for the influence of country rock type on ore composition. Minerolgy and Petrology, 94, 61-83.

[4] Garuti, G., Alfonso, P., Zaccarini, F. & Proenza, J.A. (2009): Sulfur-isotope variations in sulfide minerals from massive sulfide deposits of the northern Apennine ophiolites: inorganic and biogenic constraints. Ofioliti, 34, 43-62.

[5] Garuti, G., Zaccarini, F., Scacchetti, M., Bartoli, O. (2011) : The Pb-rich sulfide veins in the Boccassuolo ophiolite: implications for the geochemical evolution of hydrothermal activity across the ocean-continent transition in the Ligurian Tethys (Northern-Apennine, Italy). Lithos, 124, 243-254

[6] Guillaume, D., Teinturier, S., Dubessy, J., Pironon J. (2003): Calibration of methane analysis by Raman spectroscopy in H2O–NaCl– CH4 fluid inclusions. Chemical Geology, 194, 41-49

[7] Cathelineau, M. & Izquierdo, G. (1988): Temperature — composition relationships of authigenic micaceous minerals in the Los Azufres geothermal system. Contributions to Mineralogy and Petrology, 100/4, 418-428

[8] Kranidiotis, P. & Maclean, W.H. (1987), Systematics of chlorite alteration at the Phelps Dodge massive sulphide deposit, Matagami, Quebec. Economic Geology, 82, 1898-1911

# Identification of daughter crystals in polyphase fluid inclusions: Implications for fluid chemistry at the Bingham Canyon porphyry deposit, Utah

Simon Kocher<sup>123</sup> & Jamie J. Wilkinson<sup>123</sup>

<sup>1</sup>Department of Earth Science and Engineering, Imperial College London, UK <u>s.kocher12@ic.ac.uk</u> <sup>2</sup>Department of Earth Sciences, The Natural History Museum, UK <sup>3</sup>London Centre for Ore Deposits and Exploration (LODE)

Fluids play a key role in mobilising, transporting and ultimately concentrating metals to form many types of ore deposits. To analyse these ore forming fluids, preserved as fluid inclusions in gangue and ore minerals, and to get a better understanding of the processes of ore deposition, a variety of techniques are available.

Fluid inclusion microthermometry is by far the most widely used technique and provides important information on the temperature and pressure regime during ore formation as well as a basic understanding of dissolved salt species. In saline inclusions, significantly more information on dissolved metals and anionic species can be gained by the identification and volumetric quantification of daughter crystals, precipitated during cooling from the trapping conditions to room However, temperature. the optical identification of daughter crystals can be difficult, especially for opaque phases. Proton Induced X-Ray Emission (PIXE) is one method that has been used to achieve this but it is costly and cannot quantify light elements.

As a relatively cheap alternative, Scanning Electron Microscopy has been successfully used in the past to identify daughter minerals in large fluid inclusions [1, 2]. The new generation of high resolution instruments now makes it possible to image and identify smaller phases than has previously been possible, down to a sub-micrometre scale (Figure 1). This method has therefore been used to identify daughter phases in molybdenite-rich veins from the Bingham Canyon porphyry deposit to shed light on the chemical composition of Mo-transporting fluids.

Suitable samples were ground to a thickness of 500  $\mu$ m and cut into 10 mm wide chips. To mount the samples, 5 mm deep notches were

cut into a standard 25 mm epoxy resin block. The sample chips were then vertically mounted into the notches with superglue and excess material sheared off to expose fluid inclusions on the broken surfaces. To evaporate the fluid and avoid interaction between air moisture and daughter crystals the samples were stored in a heated desiccator for 24 h prior to carbon coating. Analyses were then performed on a FEI Quanta 650 SEM at the Imaging and Analysis Centre of the Natural History Museum London using an acceleration voltage of 10 kV. Measurements were carried out both as single spot analyses and element mapping (Figure 2).



**Figure 1:** Secondary electron image of halite cube measuring to 1  $\mu$ m on edge with adhering chalcopyrite crystal in a fluid inclusion hosted in quartz from Bingham Canyon, Utah.

High salinity brine inclusions associated with molybdenite mineralisation at Bingham Canyon predominantly contain halite (NaCl) and sylvite (KCl) as transparent daughter phases. Anhydrite is another commonly found daughter and usually forms tabular or acicular crystals. Far less common and only found in a small number of inclusions are Na- and Ksulphates aphthitalite bearing such as  $((K,Na)_3Na(SO_4)_2)$ calciolangbeinite or

 $(K_2Ca_2(SO_4)_3)$ , minerals that are typically only reported from volcanic fumaroles [3]. Chalcopyrite is the most abundant opaque daughter phase, occurring in intermediate density vapour and brine inclusions. Molybdenite is rare as a daughter phase, even in molybdenite-rich veins, where it occurs as small hexagonal plates. Other phases identified include pyrite and hematite.



**Figure 2:** Element maps of Bingham Canyon fluid inclusion showing the distribution of Si, Cl, Na, Ca (left column) and O, S, K, Fe (right column). Correlations suggest the presence of halite, sylvite and anhydrite.

These results indicate that Mo-stage fluids are of a H<sub>2</sub>O-NaCl-KCl composition and carry

both reduced and oxidised sulphur species at room temperature. Interestingly, although the Mo ore zone at Bingham only contains minor Cu, the fluids responsible for transporting Mo appear to carry a significant amount of Cu in solution based on the frequency of chalcopyrite daughter crystals. Laser ablation ICP-MS analyses are planned to evaluate in more detail the composition and evolution of the Mo-mineralising fluids and to explain the lack of precipitation of Cu in the Mo-rich zones.

#### Acknowledgements

Dr Tomasz Goral and Dr Alex Ball of the Imaging and Analysis Centre at the Natural History Museum London are thanked for their support during the analysis. This Project is supported by a PhD studentship from the Department of Earth Science and Engineering and additional funding from Rio Tinto is gratefully acknowledged.

#### References

[1] Metzger F. W., Kelly, W.C., Nesbitt, B. E. & Essene, E. J. (1997). "Scanning Electron Microscopy of daughter minerals in Fluid Inclusions" Economic Geology, vol. 72, pp. 141-152.

[2] Anthony, E. Y., Reynolds, T. J., & Beane, R. E. (1984). Identification of daughter minerals in fluid inclusions using scanning electron microscopy and energy dispersive analysis. American Mineralogist, 69(11-12), 1053-1058.

[3] Pekov, I. V., Zelenski, M. E., Zubkova, N. V., Yapaskurt, V. O., Chukanov, N. V., Belakovskiy, D. I., & Pushcharovsky, D. Y. (2012). Calciolangbeinite, K2Ca2 (SO4) 3, a new mineral from the Tolbachik volcano, Kamchatka, Russia. Mineralogical Magazine, 76(3), 673-682.

# Mineral Composition of Salt Melt Inclusions of the Porphyry Gold Deposit Biely Vrch (Slovakia)

Peter Koděra<sup>1</sup>, Ágnes Takács<sup>2</sup>, Tamás Váczi<sup>2</sup>, Jarmila Luptáková<sup>3</sup> & Peter Antal<sup>4</sup>

<sup>1</sup>Dep. of Economic Geol., Fac. of Natural Sciences, Comenius Univ., Bratislava. Slovakia, kodera@fns.uniba.sk, <sup>2</sup>Eötvös Loránd Univ., Budapest, Hungary, <sup>3</sup>Geologial Institute SAS, Banská Bystrica, Slovakia, <sup>4</sup>Dep. of Inorganic Chemistry, Fac. of Natural Sciences, Comenius Univ., Bratislava. Slovakia

The porphyry gold deposit Biely Vrch in the Javorie stratovolcano in Slovakia is a typical example of a porphyry Au system with exceptionally low Cu/Au ratio and shallow emplacement depth (~ 500 m; [1]). During fluid ascent quick expansion and cooling has taken place, which resulted in the formation of a water-free salt melt with high concentrations of Fe and K, transporting several tens of ppm of gold. Anhydrous salt melts were entrapped in the form of fluid inclusions in vein quartz, where they coexist with abundant vapour-rich fluid inclusions. Salt melt inclusions were studied by in-situ LA-ICPMS microanalyses and contain about 50 wt% FeCl<sub>2</sub>, 30 wt% KCl and 20 wt% NaCl [1]. At room temperature, these salt melt inclusions contain several solid phases with different optical properties. The aim of this study was to identify these solid phases by the combination of various methods.

Heating of salt melt inclusions resulted in the melting of individual daughter minerals in the range from 270 to >570 °C. The maximum frequency of solid melting was in the 320-338 °C range, when daughter minerals of green colour and high relief melted. At the the maximum temperature of heating (~570 °C), most of the daughter minerals were dissolved, except of a single transparent crystal of halite. In the case when halite dissolution has appeared, this happened in the range from 433 to 570 °C.

Raman analyses have shown that nearly all solid phases in the inclusions are water-free, and that most peaks are predominantly located at low wavenumbers up to  $\sim 300 \text{ cm}^{-1}$ . An exception is the systematic occurrence of a greenish phase of tabular habit that has a very strong but narrow peak at about 3451 cm<sup>-1</sup> (in addition to 199 and 385 cm<sup>-1</sup> peaks), indicating the probable presence of OH groups in its structure. Large, transparent phases usually did not show any Raman signal, most likely they represent halite or sylvite. Salt hydrates were

determined just rarely, while their peak position corresponded to  $FeCl_2.2H_2O$  (small at 1620 cm<sup>-1</sup>, broad at ~3409 cm<sup>-1</sup>). Sporadically, the presence of peaks tentatively ascribed to magnetite, K-feldspar, pyroxene, scheelite and chalcopyrite have also been determined. However, several other peaks could not be assigned to any known minerals or phases.

The most common daughter minerals are green phases with high relief that produce a distinct signal with main peaks at 120 and 135 cm<sup>-1</sup> and with other peaks at ~ 67, 109, 162, 184, 236, 281 and 298 cm<sup>-1</sup>. These phases always dissolve first during heating and probably represent mostly KFeCl<sub>3</sub>. This identification was confirmed by the nearly identical Raman spectrum of KFeCl<sub>3</sub> compound that was produced by chemical synthesis. Raman mapping has shown that some salt melt inclusions can probably contain 3 different phases with a spectrum similar to KFeCl<sub>3</sub>.

The FIB-SEM-EBSD analytical technique was used to investigate salt melt inclusions in three different samples from various depths of the deposit. The technique enabled the progressive abrasion of targeted areas with inclusions using a focused beam of Ga ions (FIB technique), surface imaging using BSE and SE, semiquantitative chemical analyses of exposed daughter minerals (EDS) and measurements of back-scattered electron diffraction (EBSD) patterns. Prior to milling, solid phases in inclusions have been analysed by Raman spectroscopy. EDS analyses have shown the presence of 5 to 7 different chloride minerals, containing major cations Na, K+Ca (in atomic ratios ~1:1 or 2:1), Fe+K (in three different ratios ~1:1, 2:1 or 1:2), K+Na+Fe (in ratios 3:1:1, 3:2:1 or 3:1:2) and K+Ca+Fe+Na (2:1:1:1). The accompanying EBSD patterns always showed a clear agreement of the Nabearing phase with halite. The K-Na-Fe phase and K-Fe phase with 2:1 ratio had a good fit with the structure of synthetic KFeCl<sub>3</sub>. The K-

Ca and K-Fe-Na phases (with Fe $\geq$ Na) showed cubic Fm3m symmetry similar to halite or sylvite. Other phases did not show any fit or similarities with any other known mineral. In some inclusions EDS has also shown the presence of small phases containing Ba+Pb+S (barite), Ca+F (fluorite?), W+Mo+Ca+S (scheelite, powelite or molybdenite?), Pb+S (galena?), Zn+S (sphalerite?), Fe+S (pyrite or pyrrhotite?), Zn+K+Fe+Cl±Na (?). The Ba+Pb+S phase had a good EBSD fit with barite, but other phases were not analysed by EBSD.



Figure 1: Typical FIB-SEM image with interpreted semiquantitative EDS analyses

The combination of FIB-EDS, FIB-EBSD and Raman spectroscopy seems to be a suitable methodology for the identification of daughter minerals in salt melts. Unfortunately, the limits of these methods do not allow the unequivocal identification of all phases. The major limit is the size of inclusions, since for the application of FIB methods inclusions larger than 10  $\mu$ m are not suitable. Thus, the size of individual daughter minerals is significantly smaller than the excitation volume of EDS and Raman analyses. In the interpretation of EBSD analyses the major limit is the absence of information on the structure of unknown analysed phases.

Unambiguously we can only interpret that all inclusions contain NaCl and KFeCl<sub>3</sub> that were identified by several methods. The presence of KFeCl<sub>3</sub> can be also assumed from the phase diagram of the system NaCl-KCl-FeCl<sub>2</sub>, where KFeCl<sub>3</sub> is the last phase undergoing eutectic

crystallisation [2]. This corresponds to the behaviour of this phase during microthermometric measurements. А clear identification of other phases, except of barite is problematic. EDS analyses indicate the presence of KCaCl<sub>3</sub>, which is known as the rare mineral chlorocalcite, but this mineral does not have a cubic structure which was apparent from EBSD analyses of chemically similar phases in inclusions. Furthermore, it is possible to expect the presence of NaK<sub>3</sub>FeCl<sub>6</sub>, which is the mineral rinneite, but again EBSD analyses of chemically similar phases in inclusions do not agree with that (rinneite has trigonal symmetry while the measured EBSD pattern fit with the orthorhombic system). Finally, a phase with composition  $K_2$ FeCl<sub>6</sub>, which is another possible stable phase in the system NaCl-KCl-FeCl<sub>2</sub> at higher K/Fe ratio [2], could be also present here. The results of Raman mapping indicate the presence of structurally similar phases in inclusions that could correspond to K<sub>2</sub>FeCl<sub>6</sub>, NaK<sub>3</sub>FeCl<sub>6</sub> or KCaCl<sub>3</sub> in addition to KFeCl<sub>3</sub>. Disagreement of crystal symmetry with structure of rinneite and chlorocalcite could be tentatively explained by different structural arrangement due to their polymorph modifications. The composition and structure of the tabular mineral with OH group also remains mysterious, but it was possible to confirm that it contains Fe, Cl and probably K. Chemical synthesis of the suggested mineral phases can in future help in identification of salt melt inclusion minerals.

#### Acknowledgements

This work was supported by grants APVV-0537-10 and VEGA- 1/0560/15 and Centre of Excellence for Integrated Research of the Earth's Geosphere (ITMS: 26220120064)

#### References

[1] Koděra P., Heinrich Ch.A., Wälle M. & Lexa J. (2014) Magmatic salt melt and vapour: Extreme fluids forming porphyry gold deposits in shallow volcanic settings. Geology, 42, 495-498.
[2] Robelin C., Chartrand P. & Pelton A.D. (2004) Thermodynamic evaluation and optimization of the NaCl+KCl+MgCl<sub>2</sub>+CaCl<sub>2</sub>+MnCl<sub>2</sub>+FeCl<sub>2</sub>+ CoCl<sub>2</sub>+NiCl<sub>2</sub> system. Journal of Chemical Thermodynamics, 36, 809-828.

# A Record of Cu-Au Mineralizing Fluids over a 2-km Vertical Range in the Ertsberg East Skarn System, Ertsberg-Grasberg District, Papua, Indonesia

J. Richard Kyle, Matthew Ledvina, & Stefanie Frelinger

Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin, Texas, USA. <u>rkyle@jsg.utexas.edu</u>

The Ertsberg East Skarn System (EESS), a 3.6-Gt orebody at 0.6% Cu and 0.44 ppm Au, is located in the Ertsberg-Grasberg mining district, a 50 km<sup>2</sup> region of world class Cu-Au porphyry and skarn deposits in the highlands of Papua, Indonesia [1]. Subduction of the Australian plate beneath the Pacific plate ca. 12 Ma [2] uplifted and deformed a succession of Upper Cretaceous siliciclastic to Paleogene carbonate strata that serve as host rocks for skarn orebodies. The nearby Grasberg porphyry Cu-Au deposit is proposed to have formed when batholith-sourced hydrothermal fluids periodically were released into the overlying magmatic complex [3]. However, the nature of and fluid flow controls for the EESS Cu-Au mineralizing fluids have not been constrained.

The EESS occurs within and adjacent to the 2.8-Ma Ertsberg Diorite, the youngest major magmatic and mineralization system in the Ertsberg-Grasberg district [1]. Cu-Au ore extends from the surface at ~4200 m to the deepest level of drilling below 2000 m elevation. Several structural and stratigraphic pathways have been proposed as fluid conduits connecting a deep fluid source with favorable EESS host rocks [4,5]. EESS Cu-Au concentrations occur as quartz-sulfide veins and as disseminated Cu sulfides in the altered diorite and sedimentary strata that host these ESEM-cathodoluminescence veins [4,5]. imaging of vein quartz reveals complex textures (Fig. 1) that reflect changes in P-T-X conditions, growth rates, and fracture pathways during hydrothermal fluid input. When partnered with fluid inclusion analysis, it may be possible to constrain fluctuations in the depositional conditions of vein quartz formation to identify the pathways of mineralizing fluid migration in the EESS and characterize fluid evolution within the 2-km vertical ore zone.

Previous and on-going studies have established a paragenetic sequence for EESS

skarn and vein development [4,5,6,7,8,9]. Reconnaissance fluid inclusion studies of early calc-silicates and quartz from the upper EESS documented the presence of typical porphyrystyle vapor-dominant and salt-rich fluid inclusions with homogenization in the 390-540 °C range; lower temperature and salinity fluid inclusions were documented in late-stage quartz [7].



**Figure 1:** A: Skarn-hosted quartz-pyrite vein at 2665 m with oscillatory zoned quartz (qz1) typical of porphyry-style veining. B: Diorite-hosted quartz vein at 2107 m with oscillatory zoned quartz (qz1) cross-cut by CL-dark fracture fill (qz2), younger CL-bright fracture fill (qz3) and late CL-black quartz (qz4). Ep=epoxy, py=pyrite, wr=wallrock.

This study explores the variation in vein quartz CL textures by elevation, host lithology, and vein/halo mineralogy. Individual SEM-CL images are taken along vein-perpendicular transects and stitched into composite panoramas. CL imaging of EESS quartz reveals euhedral oscillatory zonation, mosaic textures, rounded/embayed cores, CL-dark fracture fill and late CL-black quartz – textures consistent with porphyry-style veining (*Fig. 1*) [10]. Multiple generations of quartz overgrowths on quartz breccia clasts, CL-bright quartz after CL-dark quartz in fractured porphyry style veins, and symmetrically

banded CL in veins implies that fractures were repeatedly reopened and healed while the hydrothermal system was active. A sheeted quartz vein system as much as 20-m wide has been documented at the 2600-2700-m level and reflects these processes at the macroscale; sulfide minerals occur in intercrystal pores and late fractures in this zone.

Fluid inclusion petrography complements the SEM-CL imagery. In porphyry systems, highsalinity daughter salt-bearing inclusions coexisting with vapor-dominated inclusions are interpreted to record phase separation. The low-salinity parent fluid is recorded in intermediate-density inclusions, which contain 30-50% vapor, commonly with a chalcopyrite daughter crystal. A boiling zone is defined as the fluid region in which brine, vapor, and intermediate-density inclusions are observed. At the Bingham porphyry deposit, this zone spans ~500 m of elevation and occurs below the high-grade Cu ore zone [11,12].

High salinity, vapor-rich, and intermediatedensity fluid inclusions have been identified in EESS vein quartz from 1748- to 3581-m elevation. This relationship suggests phase separation of magmatic-hydrothermal fluids over a remarkable elevation range, and this cumulative effect may account for the great vertical range of the ore system. Fluid inclusion studies are continuing to extend petrographic documentation and to complete fluid temperature and composition analysis to constrain the alteration-mineralization history.

#### Acknowledgements

We are grateful to PT Freeport Indonesia for its long-term support of applied research in the Ertsberg-Grasberg district.

#### References

[1] Leys C.A., Cloos M., New B.T., & MacDonald G.D. (2012) Copper-gold±molybdenum deposits of the Ertsberg-Grasberg District, Papua, Indonesia: Society of Economic Geologists, Special Publication 16, 215-235.

[2] Cloos M., Sapiie B., Quarles van Ufford A., Weiland R.J., Warren P.Q., & McMahon T.P. (2005) Collisional delamination in New Guinea: The geotectonics of subducting slab breakoff: Geological Society of America, Special Paper 400, 51 p.

[3] Cloos M., & Sapiie B. (2013) Porphyry copper deposits: strike–slip faulting and throttling cupolas: International Geology Review, 55, 43-65.

[4] Gandler L.M. (2006) Calc-silicate alteration and Cu-Au mineralization of the Deep MLZ skarn, Ertsberg District, Papua, Indonesia: M.S. thesis, University of Texas at Austin, 273 p.

[5] Kyle J.R., Gandler L., Mertig H., Rubin J.N., & Ledvina M. (2014) Stratigraphic inheritance controls of skarn-hosted metal concentrations: Ore controls for Ertsberg-Grasberg District Cu-Au skarns, Papua, Indonesia: Acta Geologica Sinica, 88, 529-531.

[6] Mertig H.J., Rubin J.N., & Kyle J.R. (1994) Skarn Cu-Au orebodies of the Gunung Bijih (Ertsberg) district, Irian Jaya, Indonesia: Journal of Geochemical Exploration, 50, 179-202.

[7] Rubin J. N. (1996) Skarn formation and ore deposition at the Gunung Bijih Timur (Ertsberg East) Complex, Irian Jaya, Indonesia: PhD dissertation, University of Texas at Austin, 310 p.

[8] Rubin J.N., & Kyle J.R. (1998) The Gunung Bijih Timur (Ertsberg East) skarn complex, Irian Jaya, Indonesia: Geology and genesis of a large, magnesian Cu-Au skarn, in Lentz, D.R., ed., Geol. Assoc. Canada, Short Course Notes, 26, 245-288.

[9] Gibbins S.L. (2006) The Magmatic and Hydrothermal Evolution of the Ertsberg Intrusion in the Gunung Bijih (Ertsberg) Mining District, West Papua, Indonesia: PhD dissertation, University of Arizona, 385 p.

[10] Rusk B. (2012) Cathodoluminescent Textures and Trace Elements in Hydrothermal Quartz, in Möckel J.G.a.R., ed., Quartz: Deposits, Mineralogy and Analytics: Springer, 307-329.

[11] Redmond P.B., Einaudi M.T., Inan E.E., Landtwing M.R., & Heinrich C. A. (2004) Copper deposition by fluid cooling in intrusion-centered systems: New insights from the Bingham porphyry ore deposit, Utah: Geology, 32, 217-220.

[12] Landtwing M.R., Pettke T., Halter W.E., Heinrich C.A., Redmond P.B., Enaudi M.T., & Kunze K. (2005) Copper deposition during quartz dissolution by cooling magmatic-hydrothermal fluids: The Bingham Porphyry: Earth and Planetary Science Letters, 235, 229-243.

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

**Hector M. Lamadrid<sup>1</sup>**, Lowell Moore<sup>1</sup>, Daniel Moncada<sup>2</sup>, Donald Rimstidt<sup>1</sup> & Robert J. Bodnar<sup>1</sup>.

<sup>1</sup>Department of Geosciences, Virginia Tech, Blacksburg, VA 24061 USA. lamadrid@vt.edu <sup>2</sup>Department of Geology and Andean Geothermal Center of Excellence (CEGA), Universidad de Chile, Plaza Ercilla 803, Santiago, Chile

During the last 20 years several groups have presented equations relating splitting of the Raman Fermi diad as a function of the density of  $CO_2$ . The results have been used to estimate the concentration of  $CO_2$  in fluids trapped in different geological settings, including the CO<sub>2</sub> content of melt inclusions. In some settings in which the relative amount of CO<sub>2</sub> in the fluids is small, such as epithermal precious metal deposits, oceanic vents and some melt inclusions, the density of  $CO_2$  in the vapor bubble is low. Moreover, these densities are lower than those used to develop most of the various published densimeters, resulting in relatively large errors in estimating CO<sub>2</sub> densities and concentrations of CO2 in the fluid calculated from these densities.

To address this problem, we measured the splitting of the Raman Fermi diad at ~ 22  $\pm$ 1°C and pressures ranging from 9 psi (0.062 MPa) to the pressure on the  $CO_2$  liquid-vapor curve (~880 psi, or 6.07 MPa) using a High Pressure Optic Cell (HPOC). These data were used to develop a dependent equation relating the splitting of the Fermi diad to CO<sub>2</sub> density and pressure. The resulting equation was compared to other published equations for the Raman densimeter. At 22°C, our revised densimeter predicts CO<sub>2</sub> densities that are in general agreement with results from Fall et al. [1], Song et al. [2] and Rosso and Bodnar [3]. Densities predicted by the equation of Kawakami et al. [4] are significantly higher than those predicted by our revised equation, whereas those from Wang et al. [5] are slightly lower.

#### References

[1] Fall, A., Tattitch, B., & Bodnar, R.J. (2011) Combined microthermometric and Raman spectroscopic technique to determine the salinity of  $H_2O$ - $CO_2$ -NaCl fluid inclusions based on clathrate melting. Geochimica et Cosmochimica Acta, 75, 951-964.

[2] 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.

[3] Rosso K. M. & Bodnar R. J. (1995) Detection limits of  $CO_2$  in fluid inclusions using microthermometry and laser Raman spectroscopy and the spectroscopic characterization of  $CO_2$ . Geochim. Cosmochim. Acta, 59, 3961–3975.

[4] Kawakami Y., Yamamoto J. & Kagi H. (2003) Micro-Raman densimeter for the  $CO_2$  inclusions in mantle-derived minerals. App. Spectr. 57, 1333–1339.

[5] Wang, X., Chou, I. M., Hu, W., Burruss, R.C., Sun, Q., & Song, Y. (2011) Raman spectroscopic measurements of CO2 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.

# Using synthetic fluid inclusions as mini batch reactors to monitor serpentinization reactions in the oceanic lithosphere.

Hector M. Lamadrid<sup>1</sup>, Esther Schwartzenbach<sup>1</sup>, Donald Rimstidt<sup>1</sup> & Robert J. Bodnar<sup>1</sup>

<sup>1</sup>Department of Geosciences, Virginia Tech, Blacksburg, VA 24061 USA. lamadrid@vt.edu

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. The atypical geochemical characteristics of these fluids have been also proposed to be an ideal environment for the origin of life. 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 are using the synthetic fluid inclusion technique to monitor the hydration dehydration 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 low water/rock ratios. Prefractured 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 [1]. The loaded capsules then were placed into high-pressure vessels, and the P-T was increased to 5.6 kbar and 600 °C for 30 days. 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.

Preliminary results show that the reactions start after a few days in some of the fluid inclusions of the 3.5 wt% H<sub>2</sub>O-NaCl-MgCl<sub>2</sub> fluid. Brucite and serpentine (lizardite and/or chrysotile) are the new minerals formed. The salinity of the fluid inclusions increases constantly (~0.5 wt% every 5 days) as soon as the minerals nucleate. Salinity increases were observed until the newly formed minerals completely clogged the sample (~7.1 to 7.5 wt%). To reproduce these observations, we conducted the same experiments at constant temperature by using a Chaixmeca stage at the same experimental conditions. Brucite and serpentine are the minerals forming and salinity increases were observed qualitatively by performing Raman spectra collections of the  $H_2O$  peaks.

TOF-SIMS analyzes will be performed to characterize the chemical composition of the new formed phases and the host at different stages of the reaction to better constrain the reaction progress. The fluids will also be analyzed by TOF-SIMS by using a cryogenic stage and analyzing the ice composition. Synthetic fluid inclusions trapped in olivine can be modeled as mini batch reactors and empirical laws will be applied to determine rates of reactions using with different fluid compositions, concentrations and temperatures.

#### References

[1] 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.

# Different carbon reservoirs of auriferous fluids in African Archean and Proterozoic gold deposits? Constraints from stable carbon isotopic compositions of quartz-hosted CO<sub>2</sub>-rich fluid inclusions.

**Volker Lüders**<sup>1</sup>, Reiner Klemd<sup>2</sup>, Thomas Oberthür<sup>3</sup> & Lisa Richter<sup>4</sup>,

<sup>1</sup>Helmholtz Zentrum Potsdam, Deutsches GeoForschungsZentrum, Potsdam, Germany. volue@gfz-potsdam.de <sup>2</sup>GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Erlangen, Germany.

<sup>3</sup>Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany

<sup>4</sup> TU Bergakademie Freiberg, Freiberg, Germany

The genesis of gold deposits worldwide has been a matter of continuous research and debate for decades. Most of the Earth's gold is concentrated in orogenic gold-lode and placer deposits including auriferous quartz pebble conglomerates. Considered sources for gold are metamorphic rocks, felsic to intermediate magmas, or deeply buried iron-rich or pyriterich sedimentary rocks.

Quartz from orogenic gold deposits is mostly characterized by contents of low-salinity, aqueous-carbonic fluid inclusions, which may also contain variable amounts of other volatiles such as N2 and/or hydrocarbons. Since the origin of CO<sub>2</sub> may be closely linked to the origin of Au, studies of aqueouscarbonic fluid inclusions provide a means to infer P-T-X constraints of the ore-forming fluids and depositional conditions of auriferous quartz mineralization. Proposed sources for CO<sub>2</sub> in fluid inclusions include mantle origin, dehydration of mafic volcanic rocks, or decarbonation of sedimentary and/or metamorphic carbonaceous rocks as inferred by analysis of stable carbon isotopic compositions of carbonates from orogenic gold deposits. However, in cases where carbonates are absent, no statement can be made about the origin of the CO<sub>2</sub> in fluid inclusions without direct analysis of the latter. This study present analyses of carbon and, when present, nitrogen stable isotopic ratios of gas-rich inclusions hosted in quartz from selected gold deposits. The samples studied here originate from several Late Archean and world-class Early Proterozoic gold deposits in Africa.

The study revealed a striking difference in stable carbon isotopic composition of  $CO_2$  in quartz-hosted fluid inclusions from Archean and Paleoproterozoic orogenic gold deposits (Fig.1) and point to different sources of  $CO_2$  in

the studied deposits. Whether this finding can be generalized for other Archean and Proterozoic orogenic gold deposits worldwide remains open and must be the matter of future significant research. However, a  $CO_2$ contribution by mantle degassing can be ruled out for every deposit studied. Felsic magmas and/or devolatization of greenstone belt rocks are the most likely sources for CO<sub>2</sub> in some Archean gold deposits in Zimbabwe, whereas  $CO_2$  in Proterozoic vein-type deposits in the West African Craton is most likely derived from Corg-bearing metasedimentary rocks. The  $\delta^{13}C_{CO2}$  values of high-density CO<sub>2</sub>-rich, water-poor inclusions in vein quartz from the Ashanti deposit in Ghana differ considerably from  $\delta^{13}C_{CO2}$  values of similar high-density CO<sub>2</sub>-rich inclusions hosted in quartz pebbles from the world-class Au-bearing conglomerate deposits at Tarkwa (Ghana) and disprove the idea of derivation of the Tarkwaian quartz (and gold?) from an older equivalent to the Ashanti vein-type gold deposits.



**Figure 1:**  $\delta^{13}C_{CO2}$  values of quartz-hosted fluid inclusions from African Archean and Proterozoic orogenic gold deposits.

# The effects of densimeter choice on reconstructing the pre-eruptive CO<sub>2</sub> content of magmas based on Raman analysis of vapor bubbles in melt inclusions

Lowell R. Moore<sup>1</sup>, Héctor M. Lamadrid<sup>1</sup>, Daniel Moncada<sup>2</sup>, Robert J. Bodnar<sup>1</sup>

<sup>1</sup>Department of Geosciences, Virginia Tech, Blacksburg, USA

<sup>2</sup>Department of Geology and Andean Geothermal Center of Excellence (CEGA), Universidad de Chile, Plaza Ercilla 803, Santiago, Chile

The style, frequency and intensity of volcanic eruptions are controlled by the degassing of volatiles such as CO<sub>2</sub> and H<sub>2</sub>O. The degassing process results in a rock record that is mostly volatile-free when rock/glass is sampled in bulk. However, melt inclusions (MI) trapped by crystals that grow before or during magma degassing preserve samples of undegassed material. As a MI cools, it depressurizes so that the less soluble volatiles (e.g.  $CO_2$ ) form a separate vapor phase -- a bubble. Thus, it is necessary to quantify both the  $CO_2$  contained in the glass and the  $CO_2$ that has exsolved into the bubble. While the analytical techniques for determining the volatile content of the glass have been relatively well established, Raman spectroscopic analysis of the vapor phase is a technique that is still being developed. In particular, there are many equations that proposed have been by different researchers that relate the density of CO<sub>2</sub> in a vapor phase to the splitting of the Fermi diad in the Raman spectrum. These "densimeters" yield different results when applied to melt inclusions, and we have compared their effect on calculated melt compositions and trapping pressures in this study.

We compared the results of Raman analyses of vapor bubbles in the literature [1, 2] to determine the effect on the reconstructed CO<sub>2</sub> concentrations of the MI using different densimeters. The Fermi diad splittings ( $\Delta$ , cm<sup>-1</sup>) were relatively uniform at approximately 103.8 cm<sup>-1</sup>. When the equation of Lamadrid et al. (in prep) is used, the calculated densities are approximately  $0.05 \text{g/cm}^3$ . When the equation of Kawakami et al. [1] is used, the calculated densities are approximately  $0.15 \text{ g/cm}^3$ . As a result, the reconstructed CO<sub>2</sub> concentrations vary by 1000s of ppm depending on the densimeter choice. We used volatile-melt solubility models to calculate trapping pressures for the subset of inclusions for which the glass had been analysed. As an example, Figure 1 shows the reconstructed CO<sub>2</sub> contents from Moore et al. [2]. The resulting calculated trapping pressures vary by as much as 2 kbar as a result of densimeter choice (depending on the relative volume of the bubble).

We conclude that 1) the pre-eruptive  $CO_2$ content of a melt calculated using bubblebearing MI is affected substantially by the choice of  $CO_2$  densimeter, and 2) that selection criteria need to be established to select the proper densimeter for such calculations.



**Figure 1:** Reconstructed volatile concentrations from bubble-bearing melt inclusions calculated using two different CO<sub>2</sub> Raman "densimeters."

#### References

[1] Moore L.R., Gazel E., Tuohy R., Lloyd A.S., Esposito R., Steele-MacInnis M., Hauri E.H., Wallace P., Plank, T., and Bodnar R.J. (2015) Bubbles matter: An assessment of the contribution of vapor bubbles to melt inclusion volatile budgets, American Mineralogist, 100, 806-823.

[2] Hartley, M. E., Maclennan, J., Edmonds, M., Thordarson, T. (2014) Reconstructing the deep CO2 degassing behavior of large basaltic fissure eruptions. Earth and Planetary Science Letters, 393, 120-121.

[3] Kawakami, Y., Yamamoto, J., Kagi, H. (2003) Micro-Raman Densimeter for CO<sub>2</sub> Inclusions in Mantle-Derived Minerals, Applied Spectroscopy, 57, 11, 1333-1339.

# How Mineral Infillings Crystallize In Multiphase Inclusions From UHP Fluid Phase: First In Situ Synchrotron X-ray Measurements

Nadia Malaspina<sup>1</sup>, Matteo Alvaro<sup>2</sup>, Marcello Campione<sup>1</sup>, Fabrizio Nestola<sup>3</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, Università degli Studi di Milano Bicocca, Milano, Italy, nadia.malaspina@unimib.it, <sup>2</sup>Department of Earth and Environmental Sciences Università degli Studi di Pavia, Pavia, Italy, <sup>3</sup> Department of Geosciences, Università degli Studi di Padova, Padova, Italy

Remnants of the fluid phase at ultrahigh pressure (UHP) in subduction environments may be preserved as primary multiphase inclusions in UHP minerals. Saline aqueous inclusions with variable solute load prevail in high pressure (HP) rocks (e.g. [1,2]), whereas multiphase solid inclusions in some UHP rocks have been attributed to silicate-rich fluids or hydrous melts at supercritical conditions (e.g. [3-7]). These inclusions are frequently hosted by minerals stable at mantle depths, such as garnet, and show the same textural features as fluid inclusions (Fig. 1).



**Figure 1:** Photomicrograph (plane polarised transmitted light image) of a multiphase solid inclusion in metasomatic garnet from Maowu Ultramafic Complex (Dabie Shan, China). Inset represents the relative orientation of the spinel {100} surface lattice (light blue) with respect to the garnet {100} surface lattice (violet) for the coincidence at  $\theta = -45^{\circ}$ 

The mineral infillings of the solid multiphase inclusions are generally assumed to have crystallized by precipitation from the solute load of dense supercritical fluids equilibrating with the host rock. Notwithstanding the validity of this assumption, the mode of crystallization of daughter minerals during precipitation within the inclusion and/or the mechanism of interaction between the fluid at supercritical conditions and the host mineral are still poorly understood from a crystallographic point of view.

A case study is represented by garnet orthopyroxenites from the Maowu Ultramafic Complex (China) deriving from harzburgite precursors metasomatised at ~4 GPa, 750 °C by a silica- and incompatible trace elementrich fluid phase. This metasomatism produced poikilitic orthopyroxene and inclusion-rich porphyroblasts. Solid multiphase garnet primary inclusions in garnet display a size within a few tens of micrometers and negative crystal shapes. Infilling minerals (spinel: 10-20 vol.%; amphibole, chlorite, talc, mica: 80-90 vol.%) occur with constant volume ratios and derive from trapped solute-rich aqueous fluids [5]. To constrain the possible mode of precipitation of daughter minerals. we performed for the first time a single-crystal Xray diffraction experiment by means of Synchrotron Radiation at Diamond Light Source. In combination with electron probe microanalyses, this measurement allowed the unique identification of each mineral phase and, most importantly, of their reciprocal orientation with uncertainties typically smaller than  $2^{\circ}$  (see [8] for further details). Applying this methodology for the first time to multiphase solid microinclusions, we have been able, for example, to infer possible epitaxy and to quantify preferred crystallographic orientation.

We demonstrated the epitaxial relationship between spinel and garnet (Fig. 1) and between some hydrous minerals. Epitaxy drives a first-stage nucleation of spinel under near-to-equilibrium conditions, likely promoted by a dissolution and precipitation mechanism between the UHP fluid and the host garnet. A second-stage nucleation involved hydrous phases (amphiboles, chlorite and phlogopite), which nucleate in a nonregistered manner and under far-fromequilibrium conditions. From the mineral chemistry of the mineral infillings and the sequence, crystallization nucleation and subsequent precipitation of the mineral phases occurred as a consequence of a fluid/garnet interaction. This conclusion is in agreement with previous studies on multiphase solid inclusions from UHP rocks which claimed that the precipitation process is due to postentrapment modifications, such as dissolution and precipitation of the host mineral walls [9] and/or passive water diffusion from the inclusion to the host [10]. Such information is discussed in relation to physico-chemical aspects of nucleation and growth shedding light on the mode of mineral crystallization from a fluid phase at supercritical conditions.

#### References

[1] Scambelluri M., Philippot P. (2001) Deep fluids in subduction zones. Lithos, 55, 213–227.

[2] Touret J.L.R., Frezzotti M.L. (2003) Fluid inclusions in high pressure and ultrahigh pressure metamorphic rocks. In: Carswell D.A., Compagnoni R. (eds) Ultrahigh-pressure metamorphism, vol 5. EMU notes in mineralogy, Eötvös University Press, Budapest, pp 467–487.

[3] Stöckhert B., Duyster J., Trepmann C., Massonne H.J. (2001) Microdia- mond daughter crystals precipitated from supercritical COH + silicate fluids included in garnet, Erzgebirge, Germany. Geology, 29, 391–394.

[4] Van Roermund H.L.M., Carswell D.A., Drury M.R., Heijboer T.C. (2002) Microdiamond in a megacrystic garnet websterite pod from Bardane on the island of Fjørtoft, western Nor- way: evidence for diamond formation in mantle rocks dur- ing deep continental subduction. Geology, 30, 959–962.

[5] Ferrando S., Frezzotti M.L., Dallai L., Compagnoni R. (2005) Mul- tiphase solid inclusions in UHP rocks (Su-Lu, China): remnants of supercritical silicate-rich aqueous fluids released during continental subduction. Chemical Geology, 223, 68–81.

[6] Korsakov A.K., Hermann J. (2006) Silicate and carbonate melt inclusions associated with diamonds in deeply subducted carbonate rocks. Earth and Planetary Science Letters, 241, 104– 118.

[7] Malaspina N., Hermann J., Scambelluri M., Compagnoni R. (2006) Polyphase inclusions in garnet-orthopyroxenite (Dabie Shan, China) as monitors for metasomatism and fluid-related trace ele- ment transfer in subduction zone peridotite. Earth and Planetary Science Letters, 249, 173– 187.

[8] Nestola F., Nimis P., Angel R.J., Milani S., Bruno M., Prencipe M., Harris J.W. (2014) Olivine with diamond-imposed morphology included in diamond. Syngenesis or protogenesis? International Geology Review, 56, 1658–1667.

[9] Van den Kerkhof A.M., Hein U.F. (2001) Fluid inclusion petrography. Lithos, 55, 27–47.

[10] Frezzotti M.L., Ferrando S., Tecce F., Castelli D. (2012) Water content and nature of solutes in shallow-mantle fluids from fluid inclusions. Earth and Planetary Science Letters, 351– 352, 70–83.

# Effect of CO<sub>2</sub> on salinity determinations for fluid inclusions from the epithermal environment

Daniel Moncada<sup>1,2</sup>, Lowell Moore<sup>1</sup>, Héctor M. Lamadrid<sup>1</sup>, Robert J. Bodnar

<sup>1</sup> Department of Geology and Andean Geothermal Center of Excellence (CEGA), Universidad de Chile, Plaza Ercilla 803, Santiago, Chile <u>dmoncada@ing.uchile.cl</u> <sup>2</sup>Department of Geosciences, Virginia Tech, Plackburg, VA 24061, USA

<sup>2</sup>Department of Geosciences, Virginia Tech, Blacksburg, VA 24061 USA

Fluid inclusion studies of epithermal systems provide information on the temperature, pressure (depths) and the composition of fluids responsible for mineral growth and the variation in fluid PTX in time and space. Detailed petrography of samples is necessary to identify individual fluid events because, samples usually contain numerous growth zones and/or planes of inclusions representing fluids of potentially different compositions trapped at different times. With modern heating and cooling stages equipment, it is possible to collect a large amount of highly accurate data from fluid inclusion assemblages in a relatively short period of time. These data consist of homogenization temperature and melting temperatures of inclusions fluids. Homogenization temperatures provide a good approximation of the temperature of the mineralization or/and fluid event and are not usually subject to errors in interpretation. The major errors in data interpretation are related composition to fluid and pressure determinations.

The salinity of the fluid is obtained based on the assumption that depression of the freezing point (the last melting temperature of ice in the inclusion) is due to dissolved electrolytes (e.g. sodium, potassium and calcium chlorides). However, fluids in epithermal systems often contain small amounts of gases that are not usually detectable by normal petrographic, microthermometric studies, and these gases also contribute to the freezing point depression. Dissolved  $CO_2$  in the pure system H<sub>2</sub>O-CO<sub>2</sub> can result in lowering of the icemelting temperatures. Hedenquist and Henley [1] show that the freezing temperatures from inclusions in geothermal systems (e.g., well BR25 in the Broadlands, New Zealand geothermal system) show salinities that are too high (1.02 wt %) based on the assumption that the freezing point depression is from salt. Hedenquist and Henley found that ~87% of the freezing point depression was from dissolved

 $CO_2$  and the actual dissolved salt concentration is only 0.13 wt.%. Here we combine the  $CO_2$ densimeter of Lamadrid et al. (in prep) with microthermometry of synthetic fluid inclusions of known H<sub>2</sub>O-CO<sub>2</sub> composition to assess the contribution of CO<sub>2</sub> to the freezing point depression.



**Figure 1:** (A)The last melting temperature of ice  $T_m$  versus mole%  $CO_2$  dissolved in the aqueous phase. (B)  $CO_2$  pressure in the fluid inclusions versus mole%  $CO_2$  dissolved in the aqueous phase.

We prepared synthetic fluid inclusions as described by [2]. The amount of  $CO_2$  dissolved in the aqueous phase at the temperature off ice melting was determined by analysing the inclusions with Raman spectroscopy and determining the Fermi diad splitting for  $CO_2$ . This value was then used to calculate the pressure in the fluid inclusion at the temperature of ice melting using the densimeter of Lamadrid et al. (in prep) (Figure 1B). Then, the solubility of  $CO_2$  in H<sub>2</sub>O at that pressure and the temperature of ice melting was calculated using an equation of state. At the temperature of melting ice melting in the fluid inclusions the dissolved  $CO_2$  concentration ranged from 0.01 to 3.11 mole %  $CO_2$ . The result shows the last melting ice for 0.01 mole %  $CO_2$  was -0.3 °C and for 3.11 mole %  $CO_2$  the ice melting temperature was -1.7 °C (Figure 1A).

#### References

[1] Hedenquist, J. W., and Henley, R. W., 1985, The importance of  $CO_2$  on freezing point measurements of fluid inclusions: Evidence from active geothermal systems and implications for epithermal ore deposition: Economic Geology, v. 80, p. 1379-1406.

[2] Sterner, S. M., and Bodnar, R. J., 1984, Synthetic fluid inclusions in natural quartz. I. Compositional types synthesized and applications to experimental geochemistry: Geochim. et Cosmo chim. Acta, v. 48, p. 2659-2668.

# PVTX Evolution and Re-equilibration of Prograde and Retrograde Fluid Inclusions in Diagenetic and Metamorphic Rocks, Central Alps, Switzerland

**Mullis** Josef<sup>1</sup>, & Tarantola Alexandre<sup>2</sup>

<sup>1</sup>Mineralogisch-Petrographisches Institut, Bernoullistrasse 30, CH-4056 Basel, Switzerland (<u>josef.mullis@unibas.ch</u>), <sup>2</sup>Université de Lorraine, CNRS, CREGU, GeoRessources, BP 70239, F-54506 Vandœuvre-lès-Nancy, France.

Careful fabric, host mineral and fluid inclusion analyses of several hundred localities of the of external parts the Central Alps (Switzerland) enable a critical discussion about their application to fluid evolution and fluid thermobarometry. Detailed investigations on fluid inclusions formed during prograde, PT-maximum and retrograde conditions in veins, Alpine fissures and slickenside systems from diagenetic to metamorphic terrains have been carried out.

Once trapped, fluid inclusions may reequilibrate by changing their volume and composition [1]. This occurs by stretching, leakage and decrepitation of fluid inclusions when fluid pressure largely exceeds the confining pressure during further burial [2] and during heating [3; 4]. Fluid inclusions are reset by static or dynamic recrystallization of the host minerals [5]. Furthermore, fluid inclusions are also modified under deviatoric stress and post-entrapment ductile deformation [6; 7; 8; 9]. During retrograde evolution, stretching and decrepitation of high dense fluid occur isothermal inclusions may by decompression [3; 10].

Our observations show that:

1. Fluids trapped at an early stage along the prograde path have mostly left the host mineral, due to fluid overpressure, decrepitation and recrystallization. Remaining fluid inclusions do not reflect composition and density of the fluid trapped during mineral growth.

2. Only very small fluid inclusions formed during prograde temperatures may be preserved and can reflect the prograde fluid composition, as recrystallization is not complete.

3. Hydrocarbon-saturated water-rich and water-saturated hydrocarbon-rich fluid

inclusions formed at *PT*-maximum and during retrograde conditions are of reliable quality for geothermometry and geobarometry.

4. Fluid inclusions exposed to conditions of larger confining pressures than internal fluid inclusion pressure show three-dimensional implosion features, and do not reflect the original trapping density.

5. Fluid inclusions exposed to post-entrapment ductile deformation by deviatoric stress form a two-dimensional halo of neonate inclusions, revealing possible densities of the involved shearing event.

6. High dense fluid inclusions that were stretched or decrepitated by local and temporary decompression during retrograde conditions (due to seismic pumping or seismic valving) do not reflect the true composition and density of the original fluid.

7. High dense fluid inclusions that were stretched or decrepitated during "isothermal" uplift do not reflect composition and density of the original fluid.

Significance of this study:

Fluid inclusions deformed during prograde and retrograde conditions improve the interpretation of the pre-deformational fluid properties as well as the relative thermal and pressure evolution controlled dominantly by tectonic events.

#### References

[1] Bodnar R.J. (2003) Re-equilibration of fluid inclusions. In: Samson IM, Anderson AJ, Marshall DD (eds) Fluid inclusions: analysis and interpretation. Mineralogical Association of Canada, short course series, vol 32, pp 213–232.

[2] McLimans R.K. (1987) The application of fluid inclusions to migration of oil and diagenesis

*in petroleum reservoirs. Applied Geochemistry 2, 585-603.* 

[3] Mullis J. (1987) Fluid inclusion studies during very low-grade metamorphism. In: Low temperature metamorphism (Ed. by Frey, M.). Blackie, Glasgow, pp.: 162-199.

[4] Tarantola A., Mullis J., Vennemann T., Dubessy J., & De Capitani C. (2007) Oxidation of methane at the  $CH_4/H_2O$  transition zone in the external part of the Central Alps, Switzerland: Evidence from stable isotope investigations. Chemical Geology 237, 329-357.

[5] Wilkins R.W.T., & Barkas J.P. (1978) Fluid inclusions, deformation and recrystallization in granite tectonites. Contributions to Mineralogy and Petrology 65, 293-299.

[6] Diamond L.W., Tarantola A., & Stünitz H.
(2010) Modification of fluid inclusions in quartz by deviatoric stress II: Experimentally induced changes in inclusion volume and composition. Contributions to Mineralogy and Petrology 160
(6), 845-864. [7] Tarantola A., & Diamond L.W. (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, 825-843.

[8] Tarantola A., Diamond L.W., Stünitz H., Thust A., & Pec M. (2012) Modification of fluid inclusions in quartz by deviatoric stress III: Influence of principal stresses on inclusion density and orientation. Contributions to Mineralogy and Petrology 164 (3), 537-550.

[9] 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, 107-119.

[10] Sterner S.M., & Bodnar R.J. (1989) Synthetic fluid inclusions – VII. Re-equilibration of fluid inclusions in quartz during laboratorysimulated metamorphic burial and uplift. Journal of metamorphic Geology 7, 243-260.

# Fluid Inclusions in Quartz from the Gold Mineralization at a Depth of 10 km

Vsevolod Yu. Prokofiev, Konstantin V. Lobanov, Mikhail V. Chicherov, & Alexander A. Pek

Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 119117 Russia, vpr@igem.ru

In the core of the Kola super-deep boreholl (SG-3) of 12262 m depth, the gold-enriched rocks of Archaean age were found out in the depth range of 9.5-11.0 km. These rocks were overprinted Proterozoic by regional metamorphism of amphibolite facies at temperatures of 520-650 °C and pressures of 3-4 kbar. Zones of the greenschist facies of dislocation metamorphism are also established in the Archaean section of the well. Gold mineralization at the present-day surface and at a depth of 9.5-11.0 km is spatially associated with the zones of regressive transformations (1760-1700 Ma) [1].

We have studied fluid inclusions in quartz from the quartz veinlet located at a depth of 9907.5 m within the gold enriched depth interval. Quartz contains 3 types of fluid inclusions, confined to cracks and areas within quartz grains: 1) gas inclusions of the dense carbon dioxide, 2) gas-liquid two-phase aqueous solutions, and 3) three-phase inclusions of chloride brines with the NaCl cubes.

Fluid inclusions have been studied in double polished plates, first optically, then with a THMSG-600 'Linkam' freezing/heating stage equipped with Olympus-80 objective at IGEM RAS, Moscow, Russia.

Bulk inclusion analysis was carried out by gas chromatography, ion chromatography, and ICP-MS was carried out according to the techniques reported by [2] at TsNIGRI by analyst Yu.V. Vasyuta. The analyzed samples were 0.5-g aliquots of milled quartz (0.25- to 0.5-mm sieved fraction).

Carbon dioxide in gas inclusions of the type 1 homogenised into the liquid phase at temperatures ranging from +21.2 to -6.1 °C. Its melting point varies from -57.1 to -58.9 °C, which indicates the absence of significant impurities of low-boiling gases. The density of carbon dioxide is  $0.76-0.96 \text{ g}/\text{cm}^3$ .

The cryometric studies showed that the twophase inclusions of the type 2 are the brines containing chlorides and bromides of calcium and sodium (eutectic temperature in the range from -55 to -74 °C) with the salt concentrations of 25.9-30.2 wt. % -eq. CaCl<sub>2</sub> (ice melting temperature from -33 to -63 °C), the homogenization temperature of 137-185 °C and the density of 1.10 1.15 g / cm<sup>3</sup>.

Three-phase inclusions of the type 3 homogenize into the liquid phase at °C. They contain temperatures 231-123 sodium and calcium chlorides (eutectic of -64 °C) temperature with the salt concentrations of 28.7-33.5 wt. %- eq. NaCl and density of  $1.11-1.14 \text{ g}/\text{cm}^3$ .

According to the bulk analysis, Ca, Na, and Mg are the major cations in the fluids, while K is the minor one. The following concentrations (g / kg H<sub>2</sub>O) of Cl<sup>-</sup> (290), HCO<sub>3</sub><sup>-</sup> (336), CO<sub>2</sub> (110), CH<sub>4</sub> (0.3), Br (4.2), B (2.7), Sr (2.2), Fe (0.7) and Ba (0.4) was established. In addition, Rb, Li, As, Cs, Mo, Cu, Ag, Sb, Cd, Pb, Bi, U, Ga, Ge, Ti, Mn, Co, Ni, V, Cr, Sn, W, Tl, and REE were detected in the fluids.

A large number of manifestations of gold metamorphic hydrothermal mineralization of Proterozoic age are known at the present-day level of erosion of the Baltic Shield. Near the site of the super-deep borehole the South Pechenga linear structural zone is traced. This zone includes a series of ore gold occurrences: Dzhevannet (Norway), Porovarvi, Schuon, Kaplya, Ansem, Vesikyavr, Valunnoe, Bragin et al. The highest gold contents (up to 3.5 g / t) with enhanced concentrations of As, Sb, Bi are established in chlorite-carbonate. the chlorite. biotitecarbonate, carbon-carbonate, carbon-chlorite and sericite-chlorite schists. This area has

experienced transformations during the Svecofennian tectono-magmatic activization (1750 Ma) and underwent impact of the different processes: cataclase, mylonitization, metasomatism, retrogressive metamorphism et al., which caused the metasomatic alterations of all types of volcano-sedimentary rocks.

It is interesting to compare the results obtained by studies of fluid inclusions in the deepseated quartz and in quartz from the Proterozoic gold mineralization at the presentday erosion level. To do this, we have studied fluid inclusions in quartz from the vein ore of the Poroyarvi gold occurrence exposed at the present-day erosion surface in the South Pechenga structural zone.

Two types of fluid inclusions were found in quartz from the gold veins of the Poroyarvi deposit: 1) two-phase (at room temperature) carbon dioxide-aqueous inclusions with a large gas bubble filled with liquid carbon dioxide and 2) gaseous inclusions also containing liquid carbon dioxide (three-phase with the carbon dioxide gas bubbles coated by the aqueous solution rims). Gas inclusions were captured synchronously with the carbon dioxide-aqueous inclusions (confined to the same zones or cracks) indicating а heterogeneous state of the fluid.

Homogenization temperature of the carbon dioxide-aqueous inclusions of the type 1 in the quartz vein is 319-276 °C, the concentration of salts in the solution is 4.9-6.4 wt. %-eq. NaCl and the concentration of the carbon dioxide is 6.2-4.3 mol per kg of solution. Judging by the eutectic temperature (-30 to -33 °C) Na and Mg chlorides are the dominant species in the solution. Fluid density is 0.98-1.05 g / cm<sup>3</sup>.

Carbon dioxide in the mostly gaseous inclusions of the type 2 homogenizes into the liquid at temperatures of -2.1 to +12.7 °C, and its melting point varies from -57.1 to -58.7 °C, which is slightly below the melting point of pure CO<sub>2</sub> (-56.6 °C) and indicates a small admixtures of the low-boiling gases. The density of carbon dioxide is 0.84-0.93 g / cm<sup>3</sup>. Evaluation of pressure from the data of these two types of syngenetic inclusions gives 1.3-2.5 kbar.

According to bulk analysis, Na, Mg, and Ca are the major cations in these fluids too, while

K is the minor one. The following concentrations (g/kg  $H_2O$ ) of  $HCO_3^-$  (25.6),  $CI^-$  (0.3),  $CO_2$  (277),  $CH_4$  (11.5), Br (0.3), and B (0.3) was established. As, Li, Rb, Cs, Sr, Cu, Sb, Pb, Bi, Sb, Ga, Ge, Mn, Co, Zr, Sn, Ba, W, Hg, Tl, and REE were detected in the fluids also.

The physical properties and chemical composition of fluid inclusions in quartz from the deep-seated gold mineralization and Poroyarvi gold occurrence are markedly different which probably indicates that they have come from the different sources. According to the ideas of [3], high salinity chloride brines in quartz from the deep-seated Au mineralization could be formed during metamorphism in the deep zones of the Earth's crust. At the same time, the ore-forming fluids of the Poroyarvi gold occurrence are in all respects similar to the typical ore-forming fluids of orogenic gold deposits described in the classic review [4]. However, the source, from which these fluids had come, is still unknown.

#### Acknowledgements

This work was supported by the Program of the Presidium of RAS "Search in basic research for the development of the Arctic zone of the Russian Federation".

#### References

[1] Lobanov K.V., Kazansky V.I., Chicherov M.V. (2013) Gold mineralization in the Kola super-deep boreholl and present-day erosion surface in the Pechenga ore district // Proceedings of the International conference «Gold of the Fennoscandinavian Shield", Petrozavodsk, 121-125 (in Russian).

[2] Kryazhev S.G., Prokofiev V.Yu., Vasyuta Yu.V. (2006) The application of ICP-MS technique to determine composition of mineralizing fluids, Geological Bulleten MSU, 4, 30–36 (in Russian).

[3] Ridley J.R., Diamond L.W. (2000) Fluid Chemistry of Orogenic Lode Gold Deposits and Implications for Genetic Models, Gold in 2000, SEG Reviews, 13, 141–162.

[4] Yardley B.W.D., Graham J.T. (2002) The origins of salinity in metamorphic fluids, Geofluids, 2, 4, 249–256

## Microthermometric data of stretched and super-cooled liquid water obtained from high-density synthetic fluid inclusions

Chen Qiu<sup>1</sup>, Yves Krüger<sup>1</sup>, Max Wilke<sup>2</sup>, Dominik Marti<sup>3</sup>, Jaro Rička<sup>1</sup>, and Martin Frenz<sup>1</sup>

<sup>1</sup>Institute of Applied Physics, University of Bern, Switzerland, <u>chen.qiu @iap.unibe.ch</u>

<sup>2</sup>Deutsches GeoForschungsZentrum GFZ Potsdam, Germany

<sup>3</sup>Department of Photonics Engineering, Technical University of Denmark, Copenhagen, Denmark

The metastable state of liquid water spans a wide range of p-T conditions between the liquid-vapour equilibrium curve and the mechanical stability limit of the liquid state, the so-called spinodal. The spinodal curve starts at the critical point and runs to negative pressures (tensile stress) with decreasing temperature. At low temperatures, however, the p-T trend of the spinodal curve is controversial and different theoretical models have been proposed in the literature, e.g. [1, 2]. This low-temperature region of the metastable liquid state is of particular importance to elucidate the anomalous thermodynamic properties of water, e.g. the density maximum at 4°C and the minimum in the isothermal compressibility at 46°C.

In the low-temperature metastable region, the liquid water is super-cooled and stretched and thus, metastable with respect to both the vapour and the ice phase. Experimental data from this part of the water phase diagram are scarce but they are of great importance to evaluate and improve theoretical models.

The major problem that hinders experimental studies in the metastable region of liquid water is heterogeneous nucleation of the vapour phase. Different experimental techniques have been used to approach the stability limit of liquid water, but by far the highest negative pressures of up to -1.4 kbar have been achieved by isochoric cooling of synthetic fluid inclusions in quartz crystals [3]. Due to their microscopic size and strong hydrogen bonds between water and quartz, spontaneous heterogeneous nucleation of both, the vapour and the solid phase, is strongly hampered and the water remains in a stretched and supercooled metastable state down to low temperatures and high negative pressures.

While previous studies have measured temperatures of spontaneous vapour bubble nucleation  $T_n(V)$ , we present here a series of new microthermometric data from synthetic high-density pure water inclusions in quartz

that do not feature spontaneous bubble nucleation upon cooling but remain in the metastable liquid state down to ice nucleation. The inclusions were synthesised using an internally heated pressure vessel between 420 and 520°C and 7.1 to 8.6 kbar. The densities of the encapsulated water range from 0.996 to 0.917 g/cm<sup>3</sup> corresponding to  $T_h$  values between 30 and 150°C.



**Figure 1**: Schematic p–T diagram of water based on IAPWS-95 illustrating the microthermometric measurements performed in this study.

Figure 1 illustrates the different measurements in a schematic p-T phase diagram of water displaying the liquid-vapour (L+V) and liquid-solid (L+S) equilibrium curves, three liquid isochores and the liquid spinodal. Note that the spinodal we show in the diagram passes through a pressure minimum and returns to positive pressure at low temperatures and thus corresponds to the thermodynamic model proposed by Speedy [1] but been questioned by Poole [2]. Single ultrashort laser pulses were used to stimulate bubble nucleation (1) in the metastable liquid precondition for subsequent [5], a liquid-vapour measurements of the homogenisation temperature  $T_h$  (2) and, thus, an accurate determination of the density of the water in the inclusions. Besides prograde homogenisation (upon heating), we also retrograde measured liquid-vapour

homogenisation temperatures  $T_{hr}$  upon cooling (3). Furthermore, we measured ice-nucleation temperatures  $T_n(ice)$  both in absence (4a) and in presence (4b) of the vapour bubble. Confocal Raman spectroscopy was used to monitor the appearance of the ice phase in situations when the phase transition could not be visually observed. Finally, we measured ice-melting temperatures  $T_m(ice)$  mostly in absence (5) but in a few cases also in presence (triple point) of the vapour bubble.

Water densities and the volume of the inclusions were calculated based on the measured prograde homogenisation temperatures  $T_{h(obs)}$ additional and measurements of the vapour bubble radius [6] using a thermodynamic model that is based on IAPWS-95 and that accounts for the effect of tension surface on liquid-vapour homogenisation [7]. Additionally, we applied a correction for the temperature-dependent



**Figure 2**: Results of  $T_n(ice)$  (pink dots) and  $T_m(ice)$  (light blue dots) measurements plotted in a  $\rho$ -T diagram and compared to the extrapolated L+S curve (blue dash line) and the extrapolated spinodal (red dash line) of IAPWS-95.

volume change of the quartz host [8].The measured  $T_h - T_{hr}$  data pairs are in excellent agreement with IAPWS-95. Since we were able to precisely determine the density of the inclusions, we plotted the measured data into the  $\rho$ -T diagram, as illustrated in Figure 2. The ice melting temperatures  $T_m(ice)$  show a slight deviation from the extrapolated L+S curve. A potential reason for this deviation might be elastic volume changes of the inclusions due to tensile stress acting on the inclusion walls. Note however, that we observed three-phase inclusions at 0.0°C which confirmed the purity of the water. The ice nucleation temperatures  $T_n(ice)$  in individual inclusions were determined with a fairly good reproducibility of about 0.3°C. Above the L+V curve, the nucleation temperatures seem to follow the previously reported values observed in supercooled water. Following the L+V curve we observed the ice nucleation at around -38°C, which indicates the termination point of the L+V curve. Particularly interesting are the results in the metastable regime below L+V: there, the measured  $T_n(ice)$  lay well beyond the reentrant IAPWS-95 spinodal, in the supposedly unstable region. Thus, our data appears to provide evidence to studies questioning the reentrant model [2]. In any case, we take our findings as yet another indication of the importance of exploring the doubly metastable region, in the stretched and super-cooled state.

#### Acknowledgements

This work was supported by the Swiss National Science Foundation (Nr.200021-140777/1). We thank R. Schulz and H.P. Nabein for technical support.

#### References

- [1] Speedy, R.J., 1982. Stability-limit conjecture. An interpretation of the properties of water. J. Phys. Chem. 86, 982–991
- [2] Poole, P.H., et al., 1992. Phase behaviour of metastable water. *Nature* 360, 324–328
- [3] Zheng, Q., et al., 1991. Liquids at large negative pressures: Water at the homogenious nu-cleation limit. *Science*, New Series 254, 829–832
- [4] Wagner, W. and Pruß, A., 2002. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data 31, 387–535
- [5] Krüger, Y., et al., 2007. Femtosecond lasers in fluid inclusion analysis: Overcoming metastable phase states. *Eur. J. Mineral.* 19, 693–706
- [6] Spadin, F., et al. Technical Note: How accurate can stalagmite formation temperatures be determined using vapour bubble radius measurements in fluid inclusions?, *Clim. Past Discuss.*, 10, 3689-3713
- [7] Marti, D., et al., 2012. The effect of surface tension on liquid-gas equilibria in isochoric systems and its application to fluid inclusions. *Fluid Phase Equilibr*. 314, 13–21
- [8] Marti, D., et al., 2009. Fluid inclusion liquidvapour homogenization in the vicinity of the density maximum of aqueous solutions. ECROFI XX Abstract

# Fluid inclusion study on LCT pegmatites from Bikita, Zimbabwe craton - constraints on a magmatic-hydrothermal model

Lisa Richter<sup>1</sup>, Thomas Dittrich<sup>1</sup>, Steffen Hagemann<sup>2</sup>, Thomas Seifert<sup>1</sup> & David Banks<sup>3</sup>

<sup>1</sup>TU Bergakademie Freiberg, Department of Mineralogy Brennhausgasse 14, 09596 Freiberg, Germany, lisa.richter@gmx.net, <sup>2</sup> University of Western Australia, Centre for Exploration Targeting, 6009 Crawley, WA, <sup>3</sup> University of Leeds, School of Earth and Environment, Leeds, LS2 9JT, U.K.

The pegmatites at Bikita host significant Liand Cs-bearing minerals, such as pollucite, which occurs in economic quantities only at Bikita (Zimbabwe) and Tanco (Canada). Recent genetic models for the mineral formation of pollucite argue for either a product of primary alkali-metal fractionation [1] or a late metasomatic alteration [e. g. 2].

The Bikita pegmatite is located within the Bikita Tin field, 65 km NE of Masvingo. The pegmatites are hosted within metavolcanic and metavolcanic rocks of the Bulawayan system [3] that form part of the Masvingo greenstonebelt.

The zoned pegmatites at Bikita consist of wall, intermediate and core zones [4]. In this study, samples of the intermediate zones were analysed from five different locations: the Bikita Quarry (BQ), Dam Site (DS), Mauve Kop (MK), Nigel Tin (NT) and West pegmatite (WP). The major minerals of the intermediate zones constitute feldspar (Kfeldspar and albite), petalite, spodumene, pollucite, white mica and quartz, with minor apatite, Ta-Nb-oxides, cassiterite and beryl.

Primary and pseudosecondary fluid inclusions were analysed in quartz (Qtz), pollucite (Pol), petalite (Pet), spodumene (Spd) and apatite (Ap). Microthermometric measurements, laser raman spectroscopy and LA-ICP-MS analysis were conducted at the University of Western Australia and the University of Leeds, respectively.

Fluid inclusion assemblages (FIA) in quartz form clusters and internal trails and are interpreted as pseudosecondary inclusions [based on 5]. Inclusions can be grouped into: (1) liquid-rich (>70 vol.-% liquid) H<sub>2</sub>O-salt-inclusions, (2) vapour- and liquid-rich H<sub>2</sub>O-salt $\pm$ CO<sub>2</sub> $\pm$ CH<sub>4</sub>-inclusions (10-90 vol. % liquid) and (3) liquid- and vapour-rich (10-90 vol. % liquid) H<sub>2</sub>O-salt $\pm$ CO<sub>2</sub> $\pm$ CH<sub>4</sub> $\pm$ H<sub>2</sub>S-inclusions.

Inclusions in pollucite occur either isolated or in cluster and interpreted as primary and pseudosecondary fluid inclusions [based on 5]. They are (1) liquid-rich (>60 vol.-% liquid) H<sub>2</sub>O-salt±solid phase inclusions, (2)monophase-liquid  $H_2O$ -salt-inclusions or (3) liquid- and vapour-rich (10-90 vol.-% liquid) H<sub>2</sub>O-salt±CO<sub>2</sub>±CH<sub>4</sub>-inclusions. Petalite hosted fluid inclusions are elongated and located parallel to the prominent cleavage direction, therefore interpreted to be of primary origin. These inclusions are liquid- and vapour-rich (90-30 vol.-% liquid) and contain H<sub>2</sub>O±salt. Inclusions trapped in spodumene are liquidrich (>75 vol. % liquid), H<sub>2</sub>O±salt inclusions in apatite contain 70 to 90 vol.-% liquid H<sub>2</sub>Osalt inclusions. Microthermometric results are summarised in Table 1. Several FIA within quartz, pollucite and petalite show variable liquid-vapour ratios (Fig. variable 1). compositions (different salinities and vol. % CO<sub>2</sub>-CH in the vapour phases) and different modes of homogenisation. This is evidence for, at least local fluid immiscibility at temperatures between 280 to 330 °C at BQ and 360 to 380 °C at WP and MK.



**Figure 1:** FIA in Pol with variable liquid-vapour ratios (V-rich homogenize into V); the figure also provides salinities in wt. % NaCleq and homogenisation temperatures in °C.

European Current Research On Fluid Inclusions (ECROFI-XXIII), Leeds - UK, 27 - 29 June, 2015, Extended Abstracts' Volume

Location	Mineral	Gas-phase(s)	Te <sup>1</sup>	Salinity in wt% NaCl/ CaCl <sub>2</sub> eq <sup>1</sup>	Th <sub>TOT</sub> / Th <sub>DECREP</sub> <sup>1</sup>	into
BQ	Qtz	-	-45 to -30	5.6 – 14.8 [9.6]	300 - 370/310 - 345	L and $V^2$
		$CO_2 \pm CH_4$	-61 to -56.8	3.9 – 14.2 [9.7]	280 - 355/320 - 340	L and $V^2$
		$CO_2 \pm CH_4 \pm H_2S$	-72	1.9 – 4.2 [2.9]	350 - 380	L and $V^2$
	Pol	-	-40 to -30	3.9 – 7.4 [5.6]	280 - 350/200 - 280	L
		$CO_2 \pm CH_4$	-58.4 to -56.6	2.9 – 13 [6.6]	230 - 285	L
	Pet	_3	-40 to -30	4.2 – 15 [8.6]	350 - 400	L
	Spd	_3	-35 to -30	4.9 – 7.4 [6.8.]	- /320 - 450	-
	Āp	-	-35 to -25	5.7 – 11.7 [7.8]	215 - 265	L
NT	Qtz	-	-40 to -35	19.4 – 20.1 [19.6]	460 - 465/435	L
DS	Qtz	$CO_2 \pm CH_4$	-58 to -57	3.9 – 4.1 [3.9]	340 - 350	L
	Pol	$CO_2 \pm CH_4$	-57 to -56.6	3 – 5.7 [4.5]	330 - 380	L
WP	Qtz	-	-35	5.9 – 7.4 [7]	360 - 390	$L^2$
		$CO_2 \pm CH_4$	-63 to -61.3	[1]	355 - 380	L and $V^2$
MK	Qtz	-	-30	10.6 - 21.8	360 - 380	$L^2$
		$CO_2 \pm CH_4$	-59.5 to -57.8	4.2 – 11.1 [7.7]	360 - 380	$\mathbf{V}^2$

Table 1: Results of microthermometry on fluid inclusions within the Bikita pegmatite deposit

<sup>1</sup> within different FIA; <sup>2</sup> "fluid immiscibility", <sup>3</sup> no raman spectroscopy; Te, Th<sub>TOT</sub> and Th<sub>DECREP</sub> in °C

La-ICP-MS analyses were conducted on fluid inclusions in four quartz and two pollucite samples (Table 2). The aqueous phases of inclusions trapped in quartz are dominated by Na, Li, K, Ca and Cs. Pollucite hosted inclusions contain mainly K, Ca, Li, Be and Cu (Na and Cs).

 Table 2: Results of LA-ICP-MS analyses of fluid inclusions trapped in quartz and pollucite

 D002 D012 D022 D001 D012 D001

Sampla	BQ03	) BQI∠	2 BQ23	0201	BQI	2 D S 0 1
Sample	Qtz	Qtz	Qtz	Qtz	Pol	Pol
Sal. <sup>*</sup>	3	4.6	11.8	4	5.6	4.5
	as %	as %	as %	as %	as %	as %
Li	19.5	6.5	26.6	13.3	13.8	19.1
Na	31.7	30.8	22.2	29.9	_1	- <sup>1</sup>
Κ	21.1	8.2	20.7	16.1	26.7	23.6
Ca	9.5	5.8	10.1	19.9	20.7	28.8
Be	1	2.3	1.5	4.6	13.1	9.9
Mn	2.9	1.6	1.3	1.4	4.4	3.7
Fe	6.2	4.0	2.7	1.9	5.5	6
Cu	3.8	2.8	1.5	7.8	13	6.3
Cs	2.6	37.2	12.9	3.6	-1	- <sup>1</sup>

\* wt.-% CaCl<sub>2</sub>/ NaCl; <sup>1</sup> calculation without Na and Cs; other elements constitute less than 2 %

The magmatic-hydrothermal evolution of raremetal-bearing minerals in highly fractionated granitic pegmatites is still under discussion. In Bikita, fluid inclusion data suggest a late hydrothermal formation from a low to moderate salinity, Na, Cs, K, Ca, Li, Be-rich fluid from 280 to 350 °C. Fluid immiscibility of a H<sub>2</sub>O-salt $\pm$ CO<sub>2</sub> $\pm$ CH<sub>4</sub> fluid could play a key role in the formation of pollucite. Further work will concentrate on the evolution of the hydrothermal system and the key processes resulting in the precipitation of significant amounts of Li- and Cs-bearing minerals.

#### Acknowledgements

This work was supported by Rockwood Lithium GmbH. We also acknowledge Thomas Becker and the facilities at the CMCA, University of Western Australia.

#### References

[1] Treetstra D.K. & Černy P. (1995) First natural occurrences of end-member pollucite: a product of low-temperature reequilibrium. European Journal of Mineralogy, 7, 1137-1148.

[2] Wright G.M. (1963) Geology and origin of the pollucite-bearing Montgary pegmatite, Manitoba. Geological Society of America Bulletin, 74, 919-946.

[3] Dixon C.J. (1979) Atlas of Economic Mineral Deposits. Springer Science + Media Dordrecht.

[4] Martin H.J. (1964) The Bikita Tinfield. Rhodesia Geological Survey Bulletin, 58, 114-132.

[5] Roedder E. (1981) Origin of fluid inclusions and changes that occur after trapping in L.S. Hollister and M.L. Crawford (editors), Fluid Inclusions: Applications to Petrology. Mineralogical Association of Canada Short Course Handbook, 6, 101-137.

# Deep porphyry veins at Cerro de Pasco, Peru: Constraints from mineral, fluid and silicate melt inclusions in hydrothermal quartz

**Bertrand Rottier<sup>1</sup>**, Kalin Kouzmanov<sup>1</sup>, Markus Wälle<sup>2</sup>, Luís Fontboté<sup>1</sup>

<sup>1</sup> Section of Earth and Environmental Sciences, University of Geneva, 1205 Geneva, Switzerland

(\*correspondence: <u>Bertrand.Rottier@unige.ch</u>)

<sup>2</sup> Institute of Geochemistry and Petrology, ETH Zürich, 8092 Zürich, Switzerland

The Miocene epithermal base metal deposit of Cerro de Pasco located along the eastern margin of a large diatreme-dome complex [1] is the second largest known epithermal base metal ("Cordilleran") deposit after Butte in Montana, USA. Recently multiple porphyry events at Cerro de Pasco have been reported [2]. Two types of porphyry mineralization have been found: (i) hornfels and magmatic clasts with typical A- and B-type quartzmolybdenite veins incorporated in the diatreme-breccia and also in E-W trending quartz-monzonite porphyry dykes; and (ii), in the central part of the diatreme breccia, a porphyritic andesitic plug crosscut by a stockwork of quartz-magnetite-chalcopyritepyrite veins. This contribution reports results of the hornfels and magmatic clasts with Aand B-type quartz-molybdenite veins.

Around 20% of the hornfels and porphyritic clasts found in the diatreme are crosscut by 1 to 15 mm-large quartz-molybdenite porphyry veins. The clasts are mostly fine-grained and a majority of them is affected by hightemperature K-alteration (K-feldspar-biotiteandalusite-albite) assemblage. In places, the clasts are overprinted by lower-temperature argillic alteration (kaolinite-dickite-(illite)) assemblage.

Two types of high-temperature veins with silicate melt and fluid inclusions have been recognized in the clasts. Veins of the first type are thin (1-2 mm) and irregular in shape (Atype). Quartz contains glassy melt inclusions as well as two distinct sets of mineral inclusions: (i) K-feldspar-biotite-rutile- titanite i.e., an assemblage typical of potassic alteration, and (ii) actinolite-pyroxene-titaniteapatite assemblage, pointing to sodic-calcic alteration. These thin quartz veins are sulfidepoor (around 1%), the main sulfides being molybdenite, pyrite, and chalcopyrite. The second type of high-temperature veins are up to 2 cm thick and regular (B-type), and crosscut the A-veins. They are almost free of mineral inclusions and host scarce crystallized melt inclusions. These veins are also sulfide-(<1%). mainly pyrite and rare poor molybdenite. Commonly, A- and B- veins are re-opened and/or crosscut by late epithermal veins consisting of quartz, pyrite, sphalerite with "chalcopyrite disease", galena, chalcopyrite and fahlore group minerals.

Mineral thermometers applied on the different vein types indicate distinct temperatures of formation. In the A-veins associated with Kfeldspar, biotite, titanite and rutile, the Ti-inthermometer gives quartz an average temperature of  $680 \pm 45^{\circ}$ C (n=16) using the equation [3], the Zr-in-titanite thermometer gives temperature of 725  $\pm$  4°C using the equation [4] and the Zr-in-rutile thermometer gives temperature of 691±15°C using the equation [5]. In the A-veins with actinolite, pyroxene, titanite, and apatite inclusions, the Ti-in-quartz thermometer gives an average temperature of  $615 \pm 43^{\circ}$ C (n=33) and the Zrin-titanite thermometer gives a temperature of  $708 \pm 17^{\circ}$ C (n=3). In the B-veins the Ti-inauartz thermometer gives an average temperature of  $509 \pm 52^{\circ}C$  (n=32) using the equation [3].

Silicate melt inclusions are small (<10 µm in diameter) and isolated. They have been analyzed by LA-ICP-MS, using as an internal standard Al which is fairly constant in all whole rock analyses of the district  $(\text{mean}=16.02 \pm 0.52 \text{ wt\% Al}_2O_3, \text{n}=36)$ . Due to their small size, SiO<sub>2</sub> content could not be quantified. Glassy melt inclusions hosted in Aveins and crystallized melt inclusions hosted in B-veins correspond to a highly evolved melt with low MgO, CaO and TiO<sub>2</sub>. They are strongly enriched in incompatible elements such as Rb, Cs, Y and depleted in compatible element such as Sr (Table 1). Crystallized melt inclusions are Na-deficient due to postentrapment diffusion and enriched in

incompatible elements compared to the glassy melt inclusions.

	K2O (%)	Na2O (%)	Fe2O3 (%)	CaO (%)	MgO (%)	TiO2 (%)
Glassy	4.66	3.2	1.1	1.89	0.045	0.18
σ	0.84	0.23	0.3	0.84	0.058	0.17
Crystallized	5.42	0.17	0.89	0.62	0.056	0.018
σ	1.55	0.32	0.57	0.59	0.054	0.0008
	Mn (ppm)	Rb (ppm)	Sr (ppm)	Cs (ppm)	Y (ppm)	Zr (ppm)
Glassy	318	332	55	57	47	120
σ	27	48	16	13	29	73
Crystallized	459	450	9	90	33	26
σ	113	95	2	10	4	8

 Table1: Composition of the silicate melt inclusions

Metals have been detected only in crystallized melt inclusions: Cu ( $177\pm 45$  ppm,), Sb ( $121\pm 47$  ppm), W ( $48\pm 29$  ppm), Pb ( $76\pm 18$  ppm); Zn and Mo have not been detected. Increase of differentiation of melt inclusions trapped in Bveins compared to those hosted in A-veins is coherent with the relative timing of vein formation.

A-veins host two types of fluid inclusion assemblages (FIAs): 1) High-density CO<sub>2</sub>-rich vapor-dominated inclusions with 60 to 90 vol % vapor phase. These inclusions commonly have daughter crystals of anhydrite, hematite opaque minerals. Microthermometry and results on FIAs yield homogenization temperatures (Th) between 380° and 525°C, salinities from 11.5 to 18.4 wt% NaCl equiv., CO<sub>2</sub> contents between 12 and 25 mol%, and densities from 0.4 to 0.6 g/cc. Such fluid temperature and composition are indicative of high pressure of entrapment, superior to 2 kbar [6]; 2) Late secondary liquid-dominated fluid inclusions with 15 to 20 vol% vapor. Microthermometry analyses vield homogenization temperatures from 230° to 270°C, and salinities from 19 to 25.5 wt% NaCl equiv. B-veins host two distinct types of Hypersaline fluid inclusions FIAs: 1) containing liquid, 40 to 50 vol% vapor, halite, and an unidentified daughter mineral. In addition, these inclusions often contain hematite crystals. Homogenization temperature is  $> 600^{\circ}$ C and final halite melting temperatures vary from 360° to 400°C, corresponding to salinities of 43.3 to 47.4 wt% NaCl equiv. Minor amounts of CO<sub>2</sub> have been detected by Raman. Minimum entrapment pressure for such inclusions is >125 MPa. 2) Low-density vapor inclusions not spatially associated with the hypersaline fluid inclusions; microthermometric experiments could not be performed on them.

LA-ICP-MS analyses have been done on the different fluid inclusion types. The high-density CO<sub>2</sub>-rich vapor inclusions are strongly enriched in Fe and K (several wt%), enriched in Zn and Mn (1000s ppm), Cu is around 1000 ppm and Pb does not exceed 500 ppm. The hypersaline fluid inclusions are also strongly enriched in Fe and K (up to 10 wt.%), Zn and Pb contents are around 5000 and 1000 ppm, respectively; Cu is relatively low (mean=500 ppm). Late secondary liquid-dominated fluid inclusions are highly depleted in metals; only Cu has been detected at around 200 ppm.

Both A- and B-veins in studied clasts formed at near magmatic pressure and temperature. They represent two successive episodes of fluid exsolution from the same differentiated melt. An increase of melt differentiation is recorded in melt inclusions trapped in these porphyry veins. Differentiation results in increase of the metal content of the residual melt. The high-density CO<sub>2</sub>-rich vapordominated inclusions most probably represent the pristine magmatic volatile phase released from the crystallizing magma. These inclusions are extremely rich in Zn, Mn, Fe and relatively poor in Cu compared to other porphyry systems.

#### References

[1] Baumgartner R, Fontboté L, Spikings R, Ovtcharova M, Schneider J, Pace L, Gutjahr M (2009) Bracketing the age of magmatichy drothermal activity at the Cerro de Pasco epithermal polymetallic deposit, central Peru: a U-Pb and 40Ar/39Ar study. Economic Geology, 104: 479-504.

[2] Rottier B, Kouzmanov K, Casanova V, Bendezú R, Cuéllar D, Fontboté L. First evidence of multiple porphyry events in the Cerro de Pasco polymetallic district, central Peru. 12th Swiss Geoscience Meeting, Fribourg 2014. 87-88.

[3]Huang R, and Audétat A (2012) The titaniumin-quartz (TitaniQ) thermobarometer: A critical examination and re-calibration: Geochimica et Cosmochimica Acta, 84: 75-89.

[4]Hayden L, Watson B, Wark D (2008) A Thermobarometer for sphene (titanite). Contrib Mineral Petrol. 155: 529-540.

[5]Tomkins HS, Powell R, Ellis DJ (2007) The pressure dependence of the zirconium-in-rutile thermometer. J Metamorphic Geol.25:703–713

[6]Schmidt C, Bodnar R, (2000) Synthetic fluid inclusions: XVI. PVTX properties in the system H2O-NaCl-CO2 at elevated temperatures, pressures, and salinities, 64: 3853-3869
# Hydrothermal evolution from porphyry to epithermal system: Insights from fluid inclusion and stable isotope studies of the Qibaoshan Cu-Au deposit, southeastern North China Craton

Hong-Rui Fan & Wen-Gang Xu, Fang-Fang Hu, Kui-Feng Yang

#### Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China. <u>fanhr@mail.iggcas.ac.cn</u>

The Qibaoshan deposit is a large breccia pipehosted Au-Cu mineralization located in the southeast North China Craton. The deposit is spatially associated with the late Mesozoic Qibaoshan sub-volcanic complex emplaced at shallow crustal levels in the Cretaceous volcanic and sedimentary sequence. All rocks of Qibaoshan sub-volcanic complex exhibit the same isotopic features, and were produced in consecutive time within the range of 132-123 Ma by LA ICP-MS U-Pb zircon dating, and shared a same magma source, namely enriched lithospheric mantle altered by crustal materials of Yangtze Craton. An Rb-Sr isochron defined by five pyrite grains from ores yields an age of  $117 \pm 3$ Ma, showing the mineralizing time just late than sub-volcanic activity.

Ore bodies are hosted by augite dioriteaugite monzonite and quartz dioritic porphyrygranodiorite porphyry, and controlled by cryptoexplosive structure which generated a breccias pipe with length and width of 400m and 120-300m, respectively. The open-pit mining workings are extensive and drilling holes have obtained deep information to a depth of 800m on porphyry-style system. The ore minerals mainly comprising specularite, pyrite, chalcopyrite, quartz and breccias, display an obviously vertical zonation with copper in the lower part and gold in the upper part. Gangue minerals include quartz, siderite, dolomite and barite. Gold mineralization is mainly occurred in hydrothermal sulfide minerals, and less common in specularite.

Three types of fluid inclusions are recognized in the magmatic quartz phenocrysts collected from the deep located altered porphyry: Type 1, halite-bearing inclusions; Type 2, pure vapour inclusions; and Type 3, vapour-rich inclusions. They commonly show coexistence in samples. Two types of fluid inclusions in quartz veins with different ore minerals representing different hydrothermal stages, and in quartz crystal column collected from the shallow open pit are identified in this study: Type 4, liquid-rich inclusions with vapour volume fraction of 5-8%; Type 5, aqueous inclusions with vapour volume fraction of 10-20%, which can be subdivided into 5a and 5b according to their differential occurrences.

Microthermometric analyses indicate that Type 1 inclusions homogenized via halite dissolution at temperatures of 375–450°C with calculated salinities of 43.8-52.2 wt.% NaCl equiv.; Type 3 inclusions displayed a critical homogenization mode based on the comparison between homogenization pressures and critical pressures at the same homogenization temperatures (347–420°C) with calculated salinities of 0.8 to 7.1 wt.% NaCl equiv.; Type 4, 5a and 5b inclusions homogenized to liquid phase at temperatures of 221-327°C, 199-379°C and 109-193°C, respectively, with calculated salinities of 2.4 to 7.8 wt.% NaCl equiv., 10.2 to 16.8 wt.% NaCl equiv., and 0.3 to 4.0wt.% NaCl equiv., respectively. Type 2 inclusions were not analyzed in this study due to high vapour volume fraction (>80%), which makes observation of homogenization behaviours difficult.

The coexistence of Type 1, 2 and 3 inclusions in the magmatic quartz phenocrysts is not caused by fluid immiscibility, because the homogenization pressures (Ph) of Type 1 inclusions (P=623.46 to 1111.81bar) are much higher than those of Type 3 inclusions (P=139.18 to 362.47bar). According to previous experimental researches, fluids represented by Type 2 and 3 inclusions are believed to be directly exsolved from the melts in the early crystallization stage at low to intermediate pressure, which hosted abundant gold bisulfides, while the brine represented by Type 1 inclusions exsolved later at high pressure caused by crystallization and system resealing following brecciation, which enriched the Fe-chlorine complex. A mixing process is proposed in this study to interpret the coexisting phases.

According to the H-O-S isotopic studies, hydrothermal fluids represented by Type 4 and 5a inclusions in the epithermal system are of magmatic origin, which would be mixed by meteoric water in the late stage generating a low salinity and fluids represented by Type 5b inclusions. Based on the fact that, both Type 3 and 4 inclusion fluids are magmatic origin, sharing a same salinity range (5-7wt.% NaCl equiv.), and display a gradually increasing density from 0.4101 to 0.8816 g/cm3 with temperature decreases from ca. 450°C to ca. 250°C, it can be demonstrated that Type 4 inclusions-representing fluid is produced by contraction of Type 3 inclusions-representing fluids at the elevated pressures, reflecting the hydrothermal transition from porphyry to epithermal system. The vapour contracting

liquid fluids have physical ability to mix with any other aqueous ones including the brine represented by Type inclusions 1 in cryptoexplosion structure, which can consequently consume the HS- in brine causing the gold precipitation, and form the epithermal mineralization in this district. The meteoric water influx may also play a role in gold precipitation in the Oibaoshan epithermal deposit.

### Acknowledgements

This study was financially supported by the Natural Science Foundation of China (41172083), Public Welfare Scientific Research Project of the Ministry of Land and Resources (201411024-5).

# Liquid-vapor partitioning behavior of sodium and potassium in the system $H_2O$ -NaCl-KCl at 600-800<sup>o</sup>C and 500-750 bars.

**D. Matthew Sublett<sup>1</sup>** & Robert J. Bodnar<sup>1</sup>

### <sup>1</sup>Department of Geosciences, Virginia Tech, Blacksburg, VA 24061.<u>dsublett@vt.edu</u>

Magmatic-hydrothermal fluids are responsible for transporting metals such as copper and molybdenum in porphyry copper deposits (PCD), and also facilitate the characteristic alteration patterns that are observed. Analyses of fluid inclusions from PCD have shown that sodium, potassium, and chlorine are all commonly major components in the fluids and the three component H<sub>2</sub>O-NaCl-KCl system has been used to approximate these types of fluids [1].Magmatic-hydrothermal fluids in PCD often go through a "boiling" stage where the single phase fluid separates into two coexisting immiscible fluid phases, a low salinity vapor phase and a high salinity liquid phase. The metal compositions of these two fluid phases control the types of ore that will be deposited, and the major element composition determines the types of alteration assemblages that will occur. Thus, understanding how sodium and potassium partition between the two fluid phases in the H<sub>2</sub>O-NaCl-KCl system at temperatures and pressures commonly associated with PCD formation will advance our understanding of the conditions associated with the formation of this important class of ore deposit.

In this study, partitioning of sodium and potassium between two immiscible fluid phases in the H<sub>2</sub>O-NaCl-KCl system during "boiling" at 600-800°C, and 500-750 bars, and for Na:K molar ratios of 2:1, 1:1, and 1:2 were determined using the synthetic fluid inclusion technique. Figure 1A shows an example of a low salinity vapor-rich inclusion and figure 1B shows a high salinity liquid-rich inclusion. At room temperature, inclusions that trapped the vapor phase contain a small amount of liquid with the composition of the vapor that was trapped at elevated P & T, and the inclusions that trapped the liquid phase contain daughter minerals of halite and sylvite at room temperature. Salinities and atomic ratios (Na/(Na+K)) for the vapor-rich inclusions were obtained by freezing the inclusions and measuring the dissolution temperature of sylvite and the melting temperature of ice as

the inclusions were heated. Compositions were calculated from the microthermometric data using the FORTRAN program "SALTY" [2]. The salinities and atomic ratios for the liquid-rich inclusions were determined by heating the inclusions and measuring the dissolution temperatures of the daughter minerals (halite and sylvite) and compositions were also calculated using "SALTY" [2]. The resulting atomic ratios were used to calculate partition coefficients for sodium and potassium between the liquid and vapor phases  $(D_{Na}^{l/\nu} \text{ and } D_K^{l/\nu})$  and found to be nearly unity over the experimental range of temperature and pressure. The data also show that sodium very slightly prefers the vapor phase over the liquid phase and potassium very slightly favors the liquid phase over the vapor phase, although this effect does not produce partition coefficients that stray far from unity.



**Figure 1:** Image of fluid inclusions that trapped a low salinity vapor phase (A) and fluid inclusions that trapped a high salinity liquid phase (B).

### References

[1] 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.

[2] 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, Computer of Geosciences, 15, 1, 19-41

# Source of brines and metal transport in the Kiruna district, Sweden: Evidence from fluid inclusions

M.P. Smith<sup>1</sup>, S.Gleeson<sup>2</sup>, N. Bernal<sup>2</sup> & B.W.D. Yardley<sup>3</sup>

<sup>1</sup>School of Environment and Technology, University of Brighton, UK, <u>martin.smith@brighton.ac.uk</u> <sup>2</sup> Dept. of Earth and Atmospheric Sciences, University of Alberta, Canada. <sup>3</sup> School of Earth and Environment, University of Leeds, UK.

The Kiruna district, Norrbotten, Sweden, hosts a large number of mineral deposits that haven been related to the Iron oxide-copper-gold (IOCG) class. The deposits are hosted in metvolcanic and metasedimentary rocks of Protoerozoic age, which have undergone sodic alteration, including the formation of scapolite and albite, on a regional scale [1]. The deposits themselves range from iron oxide-apatite deposits (IOA), dominated by either magnetite or hematite, with only minor, late sulphide assemblages (e.g. Kirunavaara), through IOCG deposits with chalcopyrite mineralisation associated with magnetite, and alteration ranging from sodic to potassic (e.g. Pahtohavare, Rakkurijarvi), to deposits with similar alteraton characterisitics, but with evidence for subsequent metamorphism and deformation (e.g Nautanen). The major economic Cu deposit at Aitik may be related to the later class, although deformation has to some extent obscured its primary characteristics. In all the Cu-bearing deposits mineralisation is related to, and often hosted in, quart veins, whilst in the iron oxide-apatite deposits quartz veins cut the main ore bodies, but without significant chemical alteration of the wall rocks, suggesting they may be related the main ore stage fluids. In this to presentation we summarise the results of investigations into the microthermometry, chemistry and isotopic systematics of the inclusion fluids to provide constraints on the origin and evolution of the mineralising systems.

The microthermometric characteristics of fluids associated with different deposit types are distinct, albeit with some overlap between IOA and IOCG systems, and with representation of the full range of potential fluids in the deformed IOCG systems [4]. The inclusions in quartz from the IOA

deposits range in salinity from ~30-40 wt. % with hydrothalite NaCl eq., melting characteristics consistent with Na-dominated brines, and T<sub>h</sub> from ~100-150°C. Inclusions from IOCG systems extend from these conditions to ~60 wt. % NaCl eq., again Nadominated, and T<sub>h</sub> upto 200°C. The quartz veins from deformed IOCG systems show the same range of fluids as normal IOCG systems, but these are overprinted by a major secondary population of inclusions with salinites from ~10-20 wt. % NaCl eq. and CO<sub>2</sub> contents from 0.05-0.29 XCO<sub>2</sub>, occurring on secondary trails with CO<sub>2</sub>-dominated inclusions. All deposits show a late secondary population of aqueous liquid plus vapour inclusions with very low ice melting temperatures and hydrohalite melting temperature consistent with high Ca contents (Na:Ca ~0.3-0.4 by mass). These microthemometric characteristics are consistent with trapping in excess of 200-300MPa and 200-300°C in the Fe oxideapatite bodies, and 250 to >300 MPa and 300-500°C in the IOCG deposits. The aqueouscarbonic and carbonic inclusions are consistent with aqueous-carbonic fluid immiscibility at ~150 MPa.

Crush-leach analysis of hand-picked quartz separates for Br and Cl contents indicates that the origin of the inclusions cannot be accounted for by purely magmatic brines. The ratio of Cl/Br extends from values comparable magmatic volatiles to much more Cl-enriched compositions, consistent with salinity sourced by the dissolution of halite. No single group of inclusions or sample type shows a range of ratios consistent with a single fluid source, nor do high Cl/Br ratios correlate with the highest salinity fluids. This indicates that halite dissolution was not the only mechanism which generated highly saline brines. Analyses of the Cl stable isotope ratio of the same leachates shows veins in Fe-oxideapatite deposits have  $\delta^{37}$ Cl values from -3.1% to -1.0‰, those from inclusions in the Greenstone and Porphyry hosted Cu-Au prospects have  $\delta^{37}$ Cl values from -5.6 to -1.3‰ and the deformed Cu–Au deposits have values that range from -2.4‰ to +0.5‰. The higher ratios are consistent with both halitederived and magmatic brines, but the values below  $\sim -2\%$  are not, and do not correspond to any reasonable magmatic source. They are most comparable to fluids expelled from accretionary prisms which have undergone extensive halogen exchange with minerals [2]. Analyses of scapolite from the regional alteration and intense deposit scale sodic alteration gives  $\delta^{37}$ Cl values ranging from -0.1% to +1.0%. Simple Rayleigh fractionation calculations suggest removal of Cl to scapolite of this composition could result in <sup>37</sup>Cl depletion of the hydrothermal fluid. This suggests that the fluids involved in sodic alteration may have been subsequently involved in mineralisation at deposit scale. This thus supports models of IOCG deposit genesis as a result of metal leaching by saline brines from pre-existing source rocks, and subsequent deposition in structurally controlled sites [3].

The complex assemblages, inclusion particularly in the deformed IOCG deposits means that bulk crush-leach techniques may only sample the most saline populations, with some admixture from low salinity secondary inclusions. LA-ICPMS has therefore been used to analyse metal contents of individual inclusions. Element ratios suggest the alkali content of the fluid exceeded the buffer capacity of the host rocks. Iron and other transition metal contents correlate strongly with Cl concentrations, with secondary controls on solubility from pH, redox and temperature. Copper and Ag contents are higher in lower salinity aqueous-carbonic brines (up to 5000 ppm Cu, 900 ppm Ag) than in the most saline brines (up to 2297 ppm Cu, 837 ppm Ag). This may reflect differences in metal source between deposit types, but is also consistent with the complexation of Cu by bisulphide in the lower salinity fluids.

In conclusion fluid inclusion data, combined with other information, support models for IOCG mineralization involving the mixing of magmatic and halite-derived brines, with the leaching of metals by these brines as a result of district scale circulation resulting in sodic alteration. The distinction between IOA and IOCG type fluids may results from variations in the relative contributions of fluids at different stages. However, a critical factor in the formation of the most enriched deposits in the Norrbotten area is the circulation of aqueous-carbonic brines during deformation and metamorphism of the primary metal accumulations. Aqueous-carbonic brines with salinities down to 10wt. % NaCl eq. have Cu contents as high the most saline aqueous brines. Secondary circulation of magmatic sourced fluids may therefore have had a critical influence in either the redistribution of Cu, or the addition of new metal, in the formation of the most economic deposits.

### Acknowledgements

This work was originally supported by EU Regional Development Fund Georange Program Grant 89121. LA-ICPMS work was carried out at the NERC JIF sponsored facility at the University of Leeds, UK (NER/H/S/2000/853).

### References

 [1] Frietsch R., Tuisku P., Martinsson O. and Perdahl J. A. Early Proterozoic Cu (Au) and Fe ore deposits associated with regional Na–Cl metasomatism in northern Fennoscandia. Ore Geol. Rev., vol. 12, 1–34, 1997.
 [2] Gleeson S. A. and Smith M. P. The sources and evolution of mineralising fluids in iron oxide–

copper–gold systems, Norrbotten, Sweden: constraints from Br/Cl ratios and stable Cl isotopes of fluid inclusion leachates. Geochim. Cosmochim. Acta, vol. 73, pp. 5658–5672, (2009).

[3] N. H. S. Oliver, J. S. Cleverley, G. Mark, J. S. Cleverley, A. L. Ord Feltrin. Modeling the role of sodic alteration in the genesis of iron oxide–copper–gold deposits, Eastern Mount Isa block, Australia. Econ. Geol., vol. 99, pp. 1145–1176, (2004).

[4] M.P. Smith, S.A. Gleeson, B.W.D. Yardley. Hydrothermal fluid evolution and metal transport in the Kiruna District, Sweden: Contrasting metal behaviour in aqueous and aqueous–carbonic brines. Geochim. Cosmochim. Acta, vol. 102, pp. 89-112, 2013.

# **Volatile Exsolution Experiments: Trapping Exsolved Fluids**

Brian C. Tattitch<sup>1</sup> & Jon M. Blundy<sup>1</sup>

<sup>1</sup>School of Earth Sciences, University of Bristol, Bristol, UK. <u>Brian.Tattitch@bristol.ac.uk</u>

The conditions of volatile exsolution exert a strong control on the composition of exsolved magmatic volatiles phase(s), as well as on their parental magmas. Understanding the complexities of volatile exsolution in arc magmas is crucial for assessing the conditions that are ideal for the formation of porphyry copper deposits (PCD). At the most basic level, the likelihood of forming a PCD is controlled by the efficiency by which ore metals (Cu, Au, Mo) are removed from a melt "proto-ore magmatic fluids". bv Yet. additional aspects of volatile exsolution, such as the cation or ore metal ratios in the fluid(s), may ultimately play a role in generating the range of styles and grade observed in PCD globally. However, in order to investigate the interplay between melts and volatile phases we need experimental methods to simulate magmatic volatile exsolution, which is generally poorly preserved in the rock record.

Previous experiments have focused on evaluating the exchange of elements between aqueous fluids and silicate melt under equilibrium conditions (e.g. [1]. [2]). However, the large mass proportion of fluid to melt required by these experiment designs is unrealistic for natural systems. As a result, the idealized or simplified compositions of the aqueous fluids may exert a strong control on melt compositions for which they are out of equilibrium, especially at low melt fractions. The inability to examine low melt fraction systems is rather limiting as a large portion of ore metals are likely to be extracted from the melt during late stage crystallization [3]. In order to investigate the extraction of ore metals from magmas during this critical period of volatile exsolution, along with associated effects on magma/intrusive compositions, we present a new variation on magmatic ore metal partitioning experiments.

In order to better simulate the process of volatile exsolution that occurs in the arc environment we have developed a two-stage fluid-melt experimental design. Stage one is focused on generating super-liquidus hydrous melts, as analogues for melts that would be ascending/evolving from deep levels in the crust. Several trial stage one melts were generated by first crushing a natural rhyolite glass from the Laguna del Maule volcano in Chile (LMR#1-4). The glass powder was combined with H<sub>2</sub>O, Cl, S, Cu, Au, Mo, and other trace elements and synthesized into a hydrous melt (8% H<sub>2</sub>O) at 975°C and 250 MPa. After quenching the melts to a hydrous glass, each cylindrical glass slug was cut into 5 smaller sections for use in stage 2 volatile exsolution experiments.

The stage two experiments are designed to allow the stage one melt/glass to crystallize, exsolve a coexisting volatile phase(s), and trap the volatile phase(s) as synthetic fluid inclusions. LMRG glass was heated to 850°C for 2 hours and the resulting melt was then cooled to temperatures between 760°C and 700°C at 100 to 200 MPa to achieve variable degrees of crystallization. Each stage two capsule also contained and un-fractured single crystal quartz core and a mixture of other SiO<sub>2</sub> phases used to promote trapping samples of the fluid as synthetic fluid inclusions. Because the volume of exsolved fluid is low compared to equilibrium experiments, a pressure spiking technique has been developed to improve fluid inclusion trapping. A series of high to low intensity, low duration pressure spikes are used in conjunction with a thermal shock to insitu fracture [4] the quartz core as well as squeeze bubbles of exsolved fluid out of the crystal mush and into contact with the quartz core.

We present results from trial stage 2 experiments (VEM120 through VEM141) which produced synthetic fluid inclusions of coexisting vapour and brine, consistent with literature values of water solubility [5] and fluid-melt chlorine partitioning [6]. Improved techniques utilized in VEM141 led to generation of fluid inclusions of sufficient size (Figure 1) for LA-ICPMS analysis of trace elements. Major and Trace element data for starting melt LMRG4 (Table 1) and fluid inclusions from VEM141 (Table 2) are shown below. These trace element data allow for direct evaluation of the efficiency by which Cu, Mo and Li were removed from the melt, while Au data requires further methods to improve precision. We can then compare these extraction efficiencies to those for similar experiments at different conditions or for different melt compositions. These experiments then provide us a tool to evaluate the interplay between late evolved melts and volatile phases and their role in generating the diverse porphyry ore deposits observed worldwide.



**Figure 1**: Fluid inclusion photomicrographs of vapour-rich inclusions from experiment VEM141. Each inclusion contains a liquid field, vapour contraction bubble and small opaque daughter crystal (Cp/Po)

Table 1A: Melt [LMRG4] Composition		
Major Elements (Wt%)		
Na <sub>2</sub> O	4.07	
Al <sub>2</sub> Õ <sub>3</sub>	11.72	
SiŌ	70.73	
K"O	4.45	
CāO	0.42	
FeO	0.57	
CI	0.12	
Trace Elements (ppm)		
Li	70.5	
Cu	13.5	
Мо	3.7	
Au	0.27	

**Table 1:** Major and Trace element data for starting melt LMRG4. Melt also contains  $7\% H_2O$ .

Table 1B. VEM141 FIA-LA-ICPMS	
Na/K Ratio	1.8/1
Li (ppm)	368 +/ <del>-</del> 150
Cu (ppm)	118 +/ <del>-</del> 50
Mo (ppm)	15.5 +/- 12
Au (ppm)	< 2.0

**Table 2:** Trace element data for fluid inclusions from experiment VEM141. Uncertainties are  $2\sigma$ .

### Acknowledgements

We would like to thank Robert Bodnar and Luca Fedele for their assistance with characterization of fluid inclusions by LA-ICPMS at Virginia Tech. This work was supported by the BHP Billiton-Bristol Porphyry Copper Project.

#### **References:**

[1] Candela P.A. and Holland H.D. (1984) The partitioning of copper and molybdenum between silicate melts and aqueous fluids. Geochim. Cosmochim. Acta 48, 373–380.

[2] Simon A.C., Pettke T., Candela P.A., Piccolli P.M. and Heinrich C.A. (2006) Copper partitioning in a melt–vapor–brine- magnetitepyrrhotite assemblage. Geochim. Cosmochim. Acta 70, 5583–5600.

[3] Candela P.M. and Piccoli P.M. (1998) Magmatic contributions to hydrothermal ore deposits: an algorithm (MVPart) for calculating the composition of the magmatic volatile phase. Tech. Hydrothermal Ore Deposits Geol. 10, 97–108

[4] Sterner S.M. and Bodnar R.J. (1991) Synthetic fluid inclusions.10. Experimentaldetermination of P–V–T–X properties in the  $CO_2$ –H<sub>2</sub>O system to 6-kb and 700-degrees-C. Am. J. Sci. 291, 1–54.

[5] Newman S. and Lowenstern J.B. (2002) VOLATILECALC: a silicate melt-H<sub>2</sub>O-CO<sub>2</sub> solution model written in Visual Basic for excel. Comput. Geosci. 28, 597–604.

[6] Webster J.D. and Holloway J.R. (1988) Experimental constraints on the partitioning of Cl between topaz rhyolite melt and  $H_2O$  and  $H_2O + CO_2$  fluids – new implications for granitic differentiation and ore deposition. Geochim. Cosmochim. Acta 52, 2091–2105.

# Hydrosilicate liquids: unconventional agents of metal transport in porphyry ore systems

**Jamie J. Wilkinson<sup>1,2</sup>**, Olga Vasyukova<sup>3</sup>, Jamie S. Laird<sup>4</sup>, Chris Ryan<sup>4</sup> & Dima Kamenetsky<sup>3</sup>

<sup>1</sup>Department of Earth Sciences, Natural History Museum, London SW7 5BD, UK <u>j.wilkinson@nhm.ac.uk</u> <sup>2</sup>Department of Earth Science and Engineering, Imperial College London SW7 2AZ, UK <sup>3</sup>CODES, Private Bag 126, University of Tasmania, Hobart, Tasmania 7001, Australia <sup>4</sup>CSIRO Earth Science and Resource Engineering, School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia

The conventional view of separation of an  $H_2O$ -rich magmatic volatile phase from crystallizing porphyry magmas may ignore the potential for more complete miscibility between silicate melts and aqueous liquids, as has been demonstrated for subduction zone conditions. This interval, near the magmatic solidus, has proved difficult to understand, largely because of the transient, reactive nature of volatile phases released during magmatic cooling and partly because of the simplified systems studied in experimental petrology.

The existence of low temperature ( $<400^{\circ}$ C) hydrous silicate "melts" has been reported from granite pegmatites in which elements such as Li, B, P, F, plus carbonate anions and water are thought to have acted as fluxing agents. Under certain conditions, immiscibility may occur between a conventional granitic melt and a supercritical, H<sub>2</sub>O-rich (up to 45 wt% H<sub>2</sub>O) melt/silicate-rich aqueous liquid. Laboratory analogues of this latter fluid type, liquid down to 330°C, have also been produced in low pressure (100-500 MPa) synthetic fluid inclusion experiments involving  $H_2O$ , Na, K,  $HCO_3$ ,  $CO_3^{\frac{1}{2}}$  and quartz. The existence of such intermediate fluid phases has important ramifications for metal transport in magmatic-hydrothermal systems, such as those associated with porphyry ore deposits.

Here, we present data on the occurrence of unusual, low density "melt"+vapour inclusions in veins from the Las Pampas porphyry, part of the Bajo de la Alumbrera porphyry Cu-Au complex in Argentina. These inclusions (Fig. 1) occur in primary arrays in quartz from laminated quartz-magnetite stockwork veins. They contain consistent phase proportions comprising ~50% vapour in curviplanar contact with the remaining inclusion contents, several solid phases and a non-crystalline phase that occupies the remainder of the cavities with a refractive index very close to the host quartz. Heating experiments show that the boundary between the vapour bubble and this transparent phase becomes convex at temperatures well below 400°C with the vapour bubble eventually becoming spherical at higher temperatures. This indicates that the transparent phase is "solid" at ambient temperatures but liquefies (reversibly) on heating to sub-magmatic temperatures.



**Figure 1:** Transmitted light image of hydrosilicate vapour-"melt" inclusions from the Las Pampas porphyry, Argentina. Inset shows PIXE image illustrating metal distribution in the inclusion shown lower left (in two planes of focus).

Analysis of inclusions by LA-ICP-MS and PIXE techniques reveals that they contain approximately equal concentrations of Na, K and Fe, several wt% Mn and Zn, and ~1 wt% Pb and Cu. PIXE images (Fig. 1) show that some of the metal load is contained within daughter phases (e.g. Mn, Fe). Na and K are probably present in chloride crystals (or in a separate chloride brine phase), implying that the transparent phase is not a salt melt. Clearly, this unconventional fluid is loaded with metals and further work is essential to establish its potential role in metal transport.

# CO<sub>2</sub>-rich Fluid Inclusions in Vein Gold-Copper Mineralization of the Sarekoubu-Qiaxia District, Southern Altaides, China

Jiuhua Xu, Longhua Lin, Rui Yang, Xing Xiao

Resource Engineering Department, University of Science and Technology Beijing, Beijing 100083, China. jiuhuaxu@ces.ustb.edu.cn,

The southern Altaides has undergone intensive NW-SE compression since the Late Devonian to the Early Permian, resulting in collision, metamorphism. and hvdrothermal mineralization. This is an important epoch for vein gold and copper mineralization after early Devonian VMS deposition [1]. The Sarekoubu gold deposit and the Qiaxia copper-gold deposit, located near Altay town, both occur in the lower Devonian Kangbutiebao Formation  $(D_1k_2^2)$  (Fig.1). Three hydrothermal-vein quartz systems can be distinguished: (I) a pyrite-disseminated and early white quartz vein (QI) which is characterized by lenticular white quartz veins parallel to foliated wall rocks and filled openings in the shear zone (Fig.2); (II) a sulfide-quartz vein (QII) characterized by veinlet and disseminated pyrite with a small amount of quartz filling the white quartz vein, or a polymetallic sulfide and grey quartz veins composed of chalcopyrite, sphalerite, galena, pyrrhotite and bismuth; and (III) a carbonate-quartz veins. QI and QII consist of main gold mineralization stages.



*Figure 1:* A Sketch map of the Qiaxia-Sarekoubu area (Modified after [2])



**Figure 2:** Cu(Au)-quartz veins in the Sarekoubu and Qiaxia area, southern Altay region A-Gold-rich pyrite veinlets (Py) filling in the fissures of

A-Gold-HCh pyrite ventiers (1y) futing in the fissaries of white quartz vein (QI) that occurs in the shear zone, Sarekoubu; B-Tiny quartz(QII) and pyrite veinlets (Py) occurring in the shear zone, Sarekubu; C-A pyrite (Py)quartz (QI) vein hosted in a chlorite shear zone, Sarekoubu; D-A copper(Cu)-bearing quartz vein(QI) in meta-basic volcanic rocks, Qiaxia

There are three types of fluid inclusions in the quartz veins: CO<sub>2</sub>-H<sub>2</sub>O fluid inclusions, carbonic inclusions, and salt-aqueous inclusions. The CO<sub>2</sub>-H<sub>2</sub>O fluid inclusions  $(L_{CO2}-L_{H2O})$  are commonly found both in the early quartz veins (QI) and the late chalcopyrite-bearing quartz veins (OII). Carbonic fluid inclusions are also commomly observed and may be of primary in the chalcopyrite-quartz veins, but a large number of these inclusions are of secondary. The fluid inclusion assemblage (FIA) method [3] was applied in petrography study and thermometry analysis. The melting temperatures of the frozen phases ( $T_{m,CO2}$ ) for CO<sub>2</sub>-H<sub>2</sub>O inclusions and carbonic inclusions of QI at the Sarekoubu deposit are -60.8~-56.5℃ (9FIAs and 7 non-FIAs), and those of QII are -62.5~-56.5 °C (12FIAs and 9non-FIAs). These inclusions a FIA has a very narrow range, such as from -59.5~-59.0 °C in sample SR19c. The homogenization temperatures  $(T_{h,CO2})$  are 5.6

°C~28.4°C for QI (7FIAs and 7 non-FIAs) and  $-34.9^{\circ}C \sim +31.0^{\circ}C$  for QII ( $T_{h,CO2}$ ) (12 FIAs and 9 non-FIAs). In the Qiaxia deposit, the  $T_{m,CO2}$ of CO<sub>2</sub>-H<sub>2</sub>O inclusions in QI ranges from -63.0°C to -57.7°C (18FIAs and 55non-FIAs), and the  $T_{\rm h,CO2}$  ranges from 17.3 °C to +29.5 °C (18FIAs and 55non-FIAs), those in QII are -67.1~-59.3 °C ( $T_{m,CO2}$ ) (5FIAs and 5 non-FIAs) and 22.7 °C ~28.3 °C ( $T_{h,CO2}$ ) (5FIAs and 8non-FIAs). The total homogenization temperatures  $(T_{h,tot})$  for the CO<sub>2</sub>-H<sub>2</sub>O inclusions of QI range from 243°C to 395°C (Sarekoubu, 6FIAs and 19non-FIAs) and 201 °C to 382 °C (Qiaxia, 8FIAs and 27non-FIAs). The CO<sub>2</sub>-H<sub>2</sub>O inclusions in QII have a  $T_{h,tot}$  from 208°C to 328°C (Sarekoubu, 7FIAs and 9non-FIAs) and 207 °C to 365 °C (Qiaxia, 5FIAs and 5non-FIAs).





A- Isolate  $CO_2$ - $H_2O$  inclusions in QII, SR806; B- An isolate  $CO_2$ - $H_2O$  inclusion in QII, SR22; C- An isolate  $CO_2$ - $H_2O$  inclusions in QII, SR23; D- A  $CO_2$ - $H_2O$  fluid inclusion FIA in QI, QI101; E- Salt-aqueous inclusions FIA in QII, QI112; F- A carbonic fluid inclusion FIA in QII, SR4005; G- A carbonic fluid inclusion FIA in QII, SR21; H- A carbonic fluid inclusion FIA in QII, QI103 C

A Laser Raman microprobe analysis showed that carbonic inclusions are a non-aqueous  $CO_2\pm CH_4\pm N_2$  system; the percent molar fraction of  $CH_4$  ranges from 0.20 to 0.23, and the molar volume ranges from 42 to 57

 $cm^3/mol$  based on the topology VX diagrams of [4].

According to densities of CO<sub>2</sub> based on the Th.CO2 of carbonic fluid inclusions of the Sarekoubu and Qiaxia deposits with Th,tot of the paragenetic L <sub>CO2</sub>-L<sub>H2O</sub> type fluid inclusions, we estimated that the minimum trapping pressures may range from 110 to 330 MPa on the high T-P diagram of a CO<sub>2</sub> system [4]. we assume that liquid carbonic fluids in the southern margin of the Altaides were produced after the peak regional metamorphism from the Carboniferous to the early Permian due to decomposition of marble and calcareous siltstone in the Lower Devonian Kangbutiebao Formation, whereas most of water in those metamorphic rocks entered biotite, chlorite and other waterbearing minerals forming altered rocks. The high density CO<sub>2</sub>-rich fluids were related to an intensive compressing NE-SW striking orogenic environment, and the corresponding regional metamorphism of the Devonian to the end of the early Permian periods. The mineralizing effect of this environment can be observed in two ways: to strongly reform the existing VMS; and to form gold mineralization in shear zones with a high background value for Au, such as exists at the Sarekoubu deposit.

### Acknowledgements

This research is funded by National Nature Science Foundation of China (41372069).

### References

[1] Xiao WJ., Pirajno F., & Seltmann R.(2008) Geodynamics and metallogeny of the Altaid orogen. Journal of Asian Earth Sciences 32(2-4), 77-81.

[2] Xu JH, Craig,H, & Wang LL, et al., (2011) Carbonic fluid overprints in volcanogenic massive sulfide deposits: examples from the Kelan volcano-sedimentary basin, Altaids, China. Economic Geology, 106,145-158.

[3] Chi GX., Dube' B., & Williamson K., et al., (2006) Formation of the Campbell-Red Lake gold deposit by  $H_2O$ -poor,  $CO_2$ -dominated fluids. Mineralium Deposita, 40, 726–741.

[4] Van den Kerkhof A. & Thiéry R., (2001) Carbnic inclusions. Lithos, 55, 49-68

# Isotope Geochemistry (<sup>87</sup>Sr/<sup>86</sup>Sr, δ<sup>18</sup>O, δ<sup>34</sup>S, δD), Fluid Inclusion and Raman Micro-Spectroscopy of Celestine Deposits from the Evaporitic Sarkısla-Celalli Sub-Basin in the Tertiary Sivas Basin, Turkey.

**Ali Ucurum<sup>1</sup>**, Cigdem Sahin Demir<sup>1</sup>, Greg B. Arehart<sup>2</sup>, Ernst Pernicka<sup>3</sup>, Ferenc Molnar<sup>4</sup>, Ronald J. Bakker<sup>5</sup>

<sup>1</sup> Dept. of Geological Engineering, Cumhuriyet University, 58140 Sivas-TURKEY. <u>aliucurum@cumhuriyet.edu.tr</u> <sup>2</sup> Dept. of Coological Sciences <sup>6</sup>, Engineering, University of Neurola, Bong, USA

<sup>2</sup>Dept. of Geological Sciences & Engineering, University of Nevada-Reno, USA.
 <sup>3</sup>Institute for Archeological Sciences, University of Tubingen, GERMANY.
 <sup>4</sup>Geological Survey of Finland, P.O. Box 96, Espoo, FINLAND.
 <sup>5</sup>Resource Mineralogy, Montanuniversität Leoben, Leoben AUSTRIA.

different Twenty-three of 28 celestine deposits/mineralization/occurrences in host rocks of Eocene, Oligocene and Miocene ages from the evaporitic Sarkisla-Celalli sub-basin [1] in the Tertiary Sivas Basin have been studied (Fig.1). All of these deposits are associated with evaporites containing gypsum, and anhydrite of sedimentary origin or as open space filling in the contact zone of sedimentary units associated with evaporites. Celestine has been classified as vuggy filling in Eocene shallow shelf-lagoon; nodular in Oligocene coastal sabkha-alluvial: and massive in Miocene shallow lagoon environments in the Ulas area [2] . Strontium (<sup>87</sup>Sr / <sup>86</sup>Sr), oxygen ( $\delta^{18}$ O) and sulfur ( $\delta^{34}$ S) isotope ratios have been measured in 90 celestine and in 5 gypsum mineral separates. values and <sup>87</sup>Sr/<sup>86</sup>Sr ratios of  $\delta^{34}$ S.  $\delta^{18}$ O celestine are between 20-40‰, 13-29‰, and

0.70558-0.70908; gypsum values range from 11-25‰, 13-18‰, and 0.70741-070782 respectively. A relationship between  $\delta^{18}$ O- $\delta^{34}$ S and  ${}^{87}$ Sr/ ${}^{86}$ Sr- $\delta^{34}$ S shows (Fig 2A and 2B) that only 5 or 6 of the celestine deposits, and a couple massive gypsum samples have signatures consistent with marine evaporites [3]. High  $\delta^{34}$ S values of celestine indicate that the dissolved sulfur in basinal brines had undergone partial reduction to sulfide, probably in a restricted non-oceanic environment. Seawater Sr isotope values are low in the Paleocene and get higher as the rocks get (Oligocene-Miocene). younger When  ${}^{87}{\rm Sr}/{}^{86}{\rm Sr}$ compared to Cenozoic seawater, ratios of celestine minerals  $({}^{87}Sr/{}^{86}Sr =$ 0,70773-0,70786 in Paleocene; 0,70768-0,70788 in Eocene; 0,70776-0,70820 in Oligocene and 0,70819-0,70912 in Miocene) [4] suggest that deep basinal brines may have



**Figure 1:** Geological map of evaporitic Sarkısla-Celalli Sub-Basin of the Tertiary Sivas Basin showing location of celestine deposits/mineralization/occurrences. Outline map is modified [1]. Inset Figure: NAFZ = North Anatolian Fault Zone; ITS = Inner Tauride Suture; CATB = Central Anatolian Thrust Belt; CACC = Central Anatolian Crystalline Complex, SB = Sivas Basin, KB = Kangal Basin.



**Figure 2:**  $\delta^{18}O$  vs  $\delta^{34}S$  and  ${}^{87}Sr/{}^{86}Sr$  vs  $\delta^{34}S$  diagram of celestine and gypsum samples from Ulas-Celalli evaporitic sub basin in Tertiary Sivas Basin.

mixed with other circulating fluids (meteoric hydrothermal) that had interacted with local volcanoclastic sediments and had undergone Sr isotope exchange.

 $\delta^{18}$ O and  $\delta$ D from celestine mineral separates of the largest open-pit celestine mine in the Sivas Basin (Akkaya, Eocene in age [5], and plotted in Tertiary Marine Evaporite box on Fig. 2) are consistent with derivation primarily from seawater or a combination of seawater and meteoric-hydrothermal fluids. Based on petrographic observation, liquid filled, L+V, L+V+S phase appear as primary and L, L+V as secondary inclusions in celestine. Fluid inclusion petrography (Fig.3) and microthermometry suggest that celestine was deposited from heterogeneous brine-gas fluids at a low temperature (<50-70°C [6]). Raman microspectroscopy (Fig.3) proved the presence of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in inclusions. Salinities of fluid inclusions are highly variable between 0 and 21 NaCl equiv wt. %. High salinities (1021 NaCl equiv. wt. %) are characteristic of primary fluid inclusions and low salinities (0-10 NaCl equiv. wt. %) of secondary inclusions.



**Figure 3:** Photomicrograph of primary fluid inclusion including liquid + gas+ solid phases (halite, celestine, gypsum) Yuva Mezrasi celestine mine.

#### References

[1] Yilmaz and Yilmaz, (2006), Characteristic features and structural evolution of a post collisional basin: The Sivas Basin, Central Anatolia, Turkey. J. Asian Erath Sci., v.27, p. 164-176

[2] Tekin, E., 2001. Stratigraphy, Geochemistry and Depositional Enviroment of the Celestinebearing Gypsiferous Formations of the Tertiary Ulaş-Sivas Basin, East-Central Anatolia (Turkey). Turkish Journal of Earth Sciences, v. 10, p. 35-49.

[3] Palmer, M. R., Helvaiı, C., Anthony, E. Fallick, (2004), Sulphur, sulphate qxygen and strontium isotope composition of Cenozoic Turkish evaporites. Chemical Geology 209, 341-356.

[4] McArthur, J.M., Howard, R.J., Shield, G.A., (2012), Strontium isotope Stratigraphy <u>in</u> The Geologic Time Scale 2012, Felix M. Gradstein, James G. Ogg, Mark Schmitz and Gabi Ogg (Eds.): Elsevier, Cp.7, p 127-144.

[5] Sahin, C., Ucurum, A., 2008, Geological and Geochemical Features of Akkaya Celestine Mine from Tertiary Sivas Basin, Turkey, 33<sup>rd</sup> International geological Congress, MPC-01 General Contri-bution to Geochronology and Isotope Geology, August 06-14, Oslo, Norway, Abstract.

[6] Goldstein, R.H., and Reynolds T.J., (1994), Systematics of Fluid Inlusions in Diagenetic Minerals: SEPM Short Course v. 31, 199 pp.

# Poster Presentations

### How microthermometry and eq. mass fraction NaCl can spoil your highly sophisticated LA-ICP-MS data of fluid inclusions

### **Ronald J. Bakker**

Resource Mineralogy, Department of Applied Geosciences and Geophysics, Montanuniversity Leoben, Leoben, Austria. <u>bakker@unileoben.ac.at</u>

Laser ablation-ICP-MS is an analytical technique to determine qualitatively element contents of single fluid inclusions (e.g. [1]). This method has been improved during the last decades by lower detection limits and better ablation procedures. Quantification of element concentrations depends on calibration with an internal standard (Na), which is obtained from microthermometry of the same inclusion prior to laser ablation.

Microthermometry is regarded a relative simple and low-cost analytical technique to identify phases in fluid inclusions. However, microthermometry highly depends on the quality of the optical microscope. The absence of nucleation during freezing experiments and other meta-stabilities may conceal valuable information of fluid inclusion properties. Meta-stable phase assemblages in fluid inclusions are more common than expected from fluid inclusion research presented in literature, and H2O-salt-rich inclusions are very susceptible to meta-stabilities [2, 3]. For example, most of reported "eutectic" temperatures are probably temperatures of the first visible aqueous liquid solution, and very much dependent on the visibility and size of fluid inclusions.

A hypothetical case study can be used to illustrate the limitations of microthermometry to quantify LA-ICP-MS data. The standard calculation procedure to obtain quantitative data is the use of equivalent mass% NaCl [4]. This procedure is based on transforming a dissolution temperature  $(T_m)$  of ice (that may be caused by the presence of multiple types of cations and anions) to an equivalent amount of NaCl that represents the same temperature depression. Subsequently, a hypothetical ternary system of H<sub>2</sub>O-NaCl-rest (Fig. 1) is used to calculate the concentrations. The major assumption: the isotherm (line of equal  $T_{\rm m}$  of ice) is straight and perpendicular to the H<sub>2</sub>O-NaCl side. The true composition is given by point A, which is related to point B (i.e. the

equivalent mass fraction NaCl) by a simple mathematical equation:

eq.mass% NaCl = w(NaCl) + 0.5\*w(rest)



Figure 1: Hypothetical ternary diagram of  $H_2O$ -NaCl-rest in mass fractions.

Finally, knowledge of the ratio of cations as obtained from LA-ICP-MS can be used to calculate the concentrations of all the analysed ions. The factor 0.5 can only be applied to the illustrated example, and is a standard value in the software *SILLS* [5]. Although this factor can be changed, the user has no idea about the true value.

This calculation procedure can be applied to a real H<sub>2</sub>O-NaCl-KCl phase diagram to illustrate the uncertainties of this method (Fig. 2). Final  $T_{\rm m}$ (ice) of -15 °C corresponds to 18.6 eq. mass% NaCl (B in Fig. 2). A straight, perpendicular 'isotherm' and a known ratio result in salinities of 12.5 mass% for both NaCl and KCl (A in Fig. 2). The true isotherm, however, result in salinities of 10.8 mass% for both (C in Fig. 2), illustrating a 16% uncertainty (overestimation). Moreover, this uncertainty rises exponential at lower relative concentrations of NaCl. Consequently, this

method is not appropriate to estimated element concentrations.



**Figure 2:** Ternary phase diagram of  $H_2O$ -NaCl-KCl in mass fractions, representing the liquidus surface ( $T_m$  of ice, hydrohalite and sylvite). Diagram is calculated with program AqSo WNK, <u>http://fluids.unileoben.ac.at</u>.

How improve concentration can we Osmotic estimations? coefficients are thermodynamic parameters that can be used directly to relate solubility (concentrations) of multiple cations and anions to  $T_{\rm m}$  depression of ice (e.g. as used in the software Fluids [6]). Most ions known to geologist are involved in this model. Leisen et al. [7] has applied this thermodynamic modelling to the results of LA-ICP-MS of fluid inclusions and improved, thereby, the accuracy of ion concentration estimations. However, they still report a difference up to 20%. The advantage of this method is that you do not have to make any unrealistic assumptions about the depression of  $T_{\rm m}$  (ice). The disadvantage is that you cannot apply the theory of osmotic coefficients at higher salinities, i.e. exceeding the saturation properties of salt solutions, and thermodynamic modelling is restricted to the ice-field (i.e. ice is the last phase to dissolve in the aqueous liquid solution).

In conclusion, element concentration estimations, which are based on calibration with eq. mass fractions NaCl are highly inaccurate, and not suitable for publication, because the uncertainty cannot be specified. Osmotic coefficients are the only reasonable alternative to estimate accurate element concentrations, but are restricted to relative low salinities. Consequently, only undersaturated fluid inclusions with a liquid and vapour phase may provide reliable laser ablation ICP-MS data.

### References

[1] Pettke T et al. (2012) Recent developments in element concentration and isotope ratio analyses of individual fluid inclusions by laser ablation single and multiple collector ICP-MS, Ore Geology Reviews, 44, 10-38.

[2] Bakker R.J. (2004) Raman spectra of fluid and crystal mixtures in the system  $H_2O$ ,  $H_2O$ -NaCl and  $H_2O$ -MgCl<sub>2</sub> at low temperatures, Can. Mineral., 42, 1283-1314.

[3] Bakker R.J. & Baumgartner M. (2012) Unexpected phase assemblages in inclusions with ternary H2O-salt fluids at low temperatures, Cent. Eur. J. Geosci., 4, 226-237.

[4] Heinrich C.A., Ryan C.G., Mernagh T.P. & Eadington P.J. (1992) Segregation of ore metals between magmatic brine and vapor: a fluid inclusion study using PIXE microanalysis. Econ. Geol., 87, 1566-1583.

[5] Guillong M., Meier D.L., Allan M.M., Heinrich C.A. & Yardley B.W.D (2008) SILLS: a MATLAB-based program for the reduction of laser ablation ICP-MS data of homogeneous materials in inclusions, MAC Short Course Series, 29, 47-62.

[6] Bakker R.J. (2003) Package FLUIDS 1. Computer programs for analysis of fluid inclusion data and for modelling bulk fluid properties, Chem. Geol., 194, 3-23.

[7] Leisen M., Dubessy J., Boiron M.C. & Lach P. (2012) Improvement of the determination of element concentrations in quartz-hosted fluid inclusions by LA-ICP-MS and Pitzer thermodynamic modelling of ice melting temperature, Geochim. Cosmochim. Acta, 90, 110-125.

### Composition and metal-bearing capacity of the ore-forming fluids of the Late Mesozoic alkaline complexes in the Aldan shield (Russia)

Andrey A. Boroikov<sup>1</sup>, **Alexandr S. Borisenko**<sup>1,2</sup>, Ivan V. Gaskov<sup>1,2</sup>, Ivan D. Borisenko<sup>1,2</sup>, Anna G. Doroshkevich<sup>3</sup>; Nikolay V. Vladykin<sup>4</sup>, Ilia R. Prokopiev<sup>1,2</sup>

<sup>1</sup>Sobolev V.S. Institute of Geology and Mineralogy SB RAS; Novosibirsk, Russia; <sup>2</sup> Novosibirsk State University; Novosibirsk, Russia; <sup>3</sup> Russian Academy of Sciences Geological Institute of SB RAS, Russia, Ulan-Ude; <sup>4</sup> Vinogradov A.P. Institute of Geochemistry Sb RAS; Irkutsk, Russia;

The Late Mesozoic alkaline ultramafic and alkaline magmatic rocks (160-120 Ma, Ar-Ar and U-Pb dating) are widely distributed in the SE part of the Siberian craton. The formation of large Au (Au-Cu porphyry, Au-skarn, Au-Te), U, Pt, REE, apatite, fluorite, jewelry Crdiopside, charoite and other deposits are temporally and genetically linked with alkaline magmatism, according to data Kochetkov A.Y. (1996, 2006), Korchagin A.M. (1996;), Khitarov D.N. and Miguta A.K. (2003), Boitsov A.E. (2006), Maximov E.P. (2010) et al. Fluid inclusion study was performed by authors in the minerals of igneous rocks and different type ores from the Murun, Inagly, Ryabinovye and Yuhtinsky alkaline massifs. These massifs are composed of ultrapotassic ultramafic (alkaline picrites, lamproites, pyroxenites), alkaline (alkaline and nepheline syenites, leicitites, syenite porphyre) rocks and carbonatites. Using thermometry, rarely cryometry, Raman spectroscopy and LA-ICP-MS it was found that magmatic fluids of different composition, concentration and metal-bearing capacity took part in the formation of the deposits mentioned above.

1. In the Murun massif, authors studied hydrothermal quartz-anataz-bruckite veins with sulfides localized in the alkaline rocks. Primary and preudo-secondary crystal-bearing, multiphase and two-phase inclusions and gasdominant inclusions are found in quartz of these veins (fig.1a,b). Gaseous phase of the multiphase inclusions consists of 98.9-91.9 mol.% CO<sub>2</sub> and N<sub>2</sub> - 8.1-1.1 mol.%. The density of carbon dioxide ranges from 0.89 to 0.87 g/cm<sup>3</sup>. The largest solid phases are represented by thenardite and nakholite. The eutectic temperature of multiphase inclusion solutions is -23.7°C that points out to the NaCl and KCl presence in the composition of solutions. The average Na<sub>2</sub>SO<sub>4</sub> and NaHCO<sub>3</sub> concentrations in the multiphase inclusions are about 42.5 and 17.7 wt.%, respectively. The



**Figure 1:** Cristal-bearing and multiphase fluid inclusions - in the quartz-anataz-bruckite veins (Murun massif) (a, b), in the chromian diopside (Inagly) (c,d); in the quartz of ore veins Au-Cu porphyry deposits Ryabinovye massif (e, f); in the fluorite of the Samolazovsky Au-skarn deposit (Yuhtinsky massif) (g, h).

multiphase inclusions homogenized at the T=168-175°C. In addition to the main elements (Na, K, S), we found increased concentration of B, Cu, Zn, As, Rb, Sn, Sb, Cs, W, Pb, Bi, U, and minor elements such as P, Mn, Fe, Co, Ni, Sr, Ba and Th in the inclusions using LA-ICP-MS analysis.

Gaseous phase of the two-phase fluid inclusions contains  $CO_2$  and  $H_2S$  (96 and 4 mol.% respectively), aqueous phase contains  $HCO_3^-$ ,  $HS^- \varkappa HSO_4^-$  ions. The density of carbon dioxide ranges from 0.82 to 0.6 g/cm<sup>3</sup>. The eutectic mixture melts at the 11.5-10°C giving evidence of the KCl presence, solution concentrations are in the range of 11-13 wt.%. The LA-ICP MS has shown increased concentrations of Rb, Sb, Cs, W, Au, Th, and U, and small quantities of B, P, Fe, Co, Cu, Zn, Sn, Ba and Pb. The crystal-bearing inclusions contain K and Na as main elements, and increased contents of Rb, Cs, W, U, As, Mo, Sn, Sb, and Th.

2. In the Inagly ring intrusion, Crdiopside from dunite and pyroxene from alkaline pegmatite have been studied. Chromian diopside contains mainly sulfate crystal-bearing and multiphase fluid inclusions (fig.1c,d). Multiphase inclusions homogenized in the range of 595-565°C. Salt concentrations change from 65 up to 85 mas.% of Na<sub>2</sub>SO<sub>4</sub>-eq. By the LA-ICP-MS data, Na, K, S and Cl are the main components in the composition of inclusions. The crystal-bearing inclusions besides main Na and K elements contain increased concentrations of Mn, Fe, Rb, Sr, Cs, Ba, and B. The presence of characteristic elements such as Ni, As, Ag, Sb, Th, U, Pb, W, Mo, Cu, Co, Ni, Sn, Au, Bi and Hg has been detected. Multiphase inclusions contain main (Na, K and S) and minor (Ba, Cs, Sr, B, Ni, Zn, Mo, Ag, Sb, Sn, W, Pb) and less abundant ore elements (Th, U, Hg, Bi, Cu, Co). Solid phases such as galena, pyrite, barite, anhydrite and mixture of solid phases containing Cu, Fe, Cl, Cr, K, S, Ba, and Co are detected by the SEM analysis in the opened multiphase inclusions in the Cr-diopside. The opened melt inclusions in pyroxene contain KCl and solid phases corresponding by composition to the Na, Ca, K, Al, Sr, and Ba sulfates. In addition, solid phases of complex composition have been found which contain P. S, Fe, K, Zr, Rb, Sr, Ba, and W.

3. In the Ryabinovye massif, fluid inclusions in quartz of the Au-Cu porphyry deposits with have been studied. In the productive minerals of quartz-hematitechalcopyrite-bornite mineral association. crystal-bearing and multiphase fluid inclusions (fig.1e,f) are found only in aegirine, while aqueous  $(CO_2)$ , and  $CO_2$ -dominant fluid inclusions studied by [Naumov et al., 1995] occur only in quartz. Raman spectroscopy provides data about composition of the main daughter phases (thenardite and nakholite) in the crystallo-fluid inclusions and other phases represented by Ba, Al, Mg, and Cu sulfates,

carbonates, phosphates and salts with complex anion composition. Daughter Cu-bearing phases (kroehnkite, natrochalcite) and chalcopyrite are found in the crystal-bearing inclusions. LA-ICP-MS study of these inclusions showed the abnormally high Cu contents up to 0.4-9.5 mas.%, increased contents of Mn, Fe, Zn, and less quantities of As, Rb, Sr, Mo, Ag, Sn, Cs, Ba,W, Pb, Bi. Two-phase inclusions have liquid with a gas bubble, they are characterized by high Fe, Cu contents and increased concentrations of As, Mo, Ag, Au, Pb and Bi.

4. In the Yuhtinsky massif, we analyzed fluid inclusions in quartz and fluorite from the ore of the Samolazovsky Au-skarn deposit. There are crystal-bearing, multiphase and twophase fluid inclusions in smoky quartz and violet fluorite from quartz-carbonate-fluorite veins (fig.1g,h). Raman-spectroscopy of fluid inclusions has shown that gaseous phase consists of (in mol.%)  $CO_2$  (100 – 91.4),  $N_2$ (8.6-0) and  $H_2S$  (0.1-0). Inclusion solution contains  $SO_4^{2-}$  and  $HCO_3^{-}$  anions. Main solid phases in multiphase and three-phase inclusions are represented by thenardite and syngenite. The other small solid phases are Na, Mg, Cu, Zn, and Pb sulfates, siderite and native sulfur. LA-ICP-MS analysis of inclusions has shown dominant (Na, K, S) and minor Mg, Mn, Rb, Sr, Ba elements, and the presence of Fe, Co,Cu, As, Pd, Ag, Sn, Sb, Cs, W, Pb, Bi, Th, U, and Hg.

Results of fluid inclusion study display following features of fluid regime of the oremagmatic and ore-metasomatic stages in the Aldan shield:

1. Heterophase magmatic fluids are characterized by high redox-potential value corresponding to the sulfate-sulfide equilibrium.

2. Magmatic fluids have chloridecarbonate-sulfate composition that record a progressive decrease in temperature and salinity from carbonate-sulfate dominant composition of highly concentrated fluids of the magmatic stage to the mainly Na-K chloride composition of hydrothermal moderately and low concentrated fluids of post-magmatic stage.

3. The metal-bearing capacity of chloridecarbonate-sulfate fluids depends on Cu, Zn, Pb, Mo, W, Au, and U concentrations in the solution.

### Evidence of sulphate-rich fluid associated with an enriched heavy rare earth element carbonatite, Huanglongpu deposit, China

**Delia Cangelosi<sup>1</sup>** & Martin Smith<sup>2</sup>, Bruce Yardley<sup>1</sup> and David Banks<sup>1</sup>

<sup>1</sup>School of Earth and Environment, University of Leeds, Leeds, UK. <u>ee12dac@leeds.ac.uk</u>, <sup>2</sup>School of Environment and Technology, University of Brighton, UK.

Carbonatite-hosted REE deposits are known to be the world's primary source of LREEs. They are enriched in REEs relative to other igneous rocks but they mainly show a strong LREE enrichment relative to HREE. However, Huanglongpu carbonatites show unusual mid to heavy REE enrichment. The deposit is situated in the north of the north-western part of the Qinling orogenic belt, which is an important metallogenic belt hosting the most important Mo ore camp in China [1]. Economic Mo, Pb-Zn, W and Sb mineralization is mainly hosted by granitic porphyry bodies, with a few porphyry-skarn deposits. However, at Huanglongpu the mineralization is associated with an unusual carbonatite vein mineralisation which has been Re-Os dated at 221±0.3 Ma [2], making this deposit much older than most of mineralisation in the Qinling belt (porphyries are dated from the early Cretaceous) [1]; therefore precluding association with the any porphyry mineralisation. The uncommon Mo and HREE enrichment of the carbonatites has been as a primary feature of interpreted metasomatized mantle-derived igneous rocks [3]. The aim of this study is to understand what may have led to Mid to HREE enrichment specific sites at in the Huanglongpu deposit, by studying the chemistry of fluid inclusions from a quartz vein associated with REE mineralization (allanite, xenotime and REE-carbonate).

Fluid inclusions hosted in the vein quartz can be divided in four types, described here from the earliest to the latest fluid stage: two-phase  $CO_2$ -rich inclusions (Type A) Tmcla around 2.5°C, three-phase  $CO_2$ -rich, solid-bearing inclusions (Type C), three-phase  $CO_2$ -rich inclusions (Type B) with Tmcla from 1°C to 7°C and liquid-vapour inclusions (Type D). Type B and Type C inclusions are considered to be closely related as they are both found in same planar array. Most of the Type D inclusions have Tmice between -7°C and -11°C. Only Type D inclusions have a measurable ThTOT, and these yield a minimum temperature of trapping between 140°C to 230°C. The solids in Type C inclusions have been identified by Raman spectroscopy, and are mainly sulphates (Figure 1) with some calcite. In Type C inclusions, mean concentration of sulphate is approximate to 6 molal which correspond to an inclusion with 13% solid sulphates. SEM analysis of opened fluid inclusions without daughter minerals shows those inclusions are Cl-rich. Raman spectroscopy has revealed a significant amount of sulphate in solution in Type B and C inclusions meaning another ligand is available in the hydrothermal fluid in addition to chloride (Figure 2). LA-ICP-MS analysis shows that the cation load of CO<sub>2</sub>-rich inclusions (Type A, B and C) is dominated by Na, K, and Ca, and contain Mg>Fe. Type 1A inclusions show a significant amount of REEs; in contrast Type A inclusions only contain significant amounts of the LREEs. Due to the stability of the aqueous **REE-fluoride** complexes being one order of magnitude higher comparing to the REE species involving other ligands fluoride complexes have been thought to be the main agent of REE transport in hydrothermal fluids. However, a recent study has shown that chloride and sulphate rather than fluorite would act as transporting agent [4]. Chloride and sulphate ligands are believed to be the main transporting agents for REE in the Huanglongpu hydrothermal fluids; however the highest HREE levels found in this study are in sulphate-rich, CO<sub>2</sub>-bearing fluids, suggesting that these ligands, rather than Cl, were responsible for hydrothermal mid to heavy REE enrichment in the quartz vein studied.



anhydrite

*Figure 1: Example of identified solids by Raman spectroscopy in Type C inclusions with spectra.* 



**Figure 2:** Peak of sulphate in solution (981  $cm^{-1}$ ) superimposes with the spectrum of the precipitated sulphate (peak at 1011  $cm^{-1}$ ).

### Reference

[1] Mao, J.W. et al. (2008) Tectonic implications from Re–Osdating of Mesozoic molybdenum deposits in the East Qinling–Dabie orogenic belt, Geochimica et Cosmochimica Acta, 72, 4607– 4626.

[2] Stein, H.R. et al. (1997) Highly precise and accurate Re-Os ages for Molybdenite from the East Qinling Molydbenum Belt, Shaanx Province, China, Economic geology, 92, 827-83.5 [3] Xu, C. et al. (2010) A unique Mo deposit associated with carbonatites in the Qinling orogenic belt, central China. Lithos, 118, 50-60.

[4] Migdisov, A.A. and Williams-Jones, A (2014) Hydrothermal transport and deposition of the rare earth elements by fluorine-bearing aqueous liquids. Mineralium Deposita, 49, 987-99.

# Magmatic CO<sub>2</sub>-H<sub>2</sub>O-S fluids at Mt. Somma-Vesuvius: Insights from shrinkage bubbles of melt inclusions

**Rosario Esposito<sup>1</sup>**, Hector La Madrid<sup>2</sup>, Leonid V. Danyushevsky<sup>3</sup>, Daniele Redi<sup>3</sup>, Claudia Cannatelli<sup>4</sup>, Matthew Steele-MacInnis<sup>5</sup>, Annamaria Lima<sup>4</sup>, Robert J. Bodnar<sup>2</sup>, Benedetto De Vivo<sup>4</sup>

<sup>1</sup>Department of Earth, Planetary and Space Science, UCLA, Los Angeles, CA 90095-1567 USA r.esposito@epss.ucla.edu

<sup>2</sup>Fluids Research Laboratory, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061 USA

<sup>3</sup>CODES Coe And School of Earth Sciences, University of Tasmania, Hobart, TAS 7001, Australia Institute for Geochemistry and Petrology

<sup>4</sup>DISTAR, Università degli Studi di Napoli Federico II, Via Mezzocannone 8, Napoli, 80134, Italy <sup>5</sup>ETH Zürich, Clausiusstrasse 25, NW CH 8092 Zurich, Switzerland

Plinian eruptions of Mt. Somma-Vesuvius were first described by Pliny the younger in 79 AD during the infamous eruption that destroyed the city of Pompeii. Today, such eruptions are still a concern to the nearly 3 million people living in the Naples metropolitan area. Understanding the source for Mt. Somma-Vesuvius magmas and the coexisting volatile phase is vital to better constrain the long-term eruptive behavior of this volcano.

If a melt contains  $CO_2$  and  $H_2O$  and becomes saturated in volatiles at certain P-T conditions, the vapor phase in equilibrium with this melt must contain both  $H_2O$  and  $CO_2$  in the vapor phase. The  $H_2O$  molar fraction of the vapor will depend on the concentration of  $CO_2$  and  $H_2O$  dissolved in the melt just before volatile saturation occurs. Recent studies discuss and provide direct evidence for the presence of  $CO_2$  in "shrinkage" bubbles of melt inclusions (MI). In contrast, evidence of  $H_2O$  in MI bubbles is lacking in the literature, raising the question of whether significant amounts of  $H_2O$  are exsolved from mafic magmas.

In the present study, ~50 olivine phenocrysts were selected from lavas and pumices produced during mild effusive events referred to as inter-Plinian eruptions, and from highly explosive Plinian eruptions that occurred at Mt. Somma-Vesuvius between 33000 ka and 1631 AD. Selected olivine phenocrysts containing MI were examined petrographically and analyzed for Fo content. Fo varies from 69 to 73 mole% for inter-Plinian olivine crystals and from 84 to 90 mole% (with one zoned olivine containing 76-81 mole% Fo) for Plinian olivine crystals. Investigated MI vary from slightly crystallized to highly crystallized.

Selected crystallized MI were reheated using the Vernadsky stage, and quenched to a homogeneous glass (Group 1), glass plus a vapor bubble (Group 2; see Figure 1), or to dark glass plus bubbles plus crystals (Group 3). MI of Group 1 are hosted in olivine ranging from Fo<sub>72</sub> to Fo<sub>76</sub> and were all erupted from the Pompeii eruption (white pumice deposit). MI of Group 2 are trapped in olivine ranging from Fo<sub>69</sub> to Fo<sub>81</sub> and from Fo<sub>84</sub> to Fo<sub>90</sub>, and the hosts are representative of both Plinian and inter-Plinian events. The only eruption where Group-1 and Group-2 MI coexist is the 79 AD Pompeii eruption.

All the heated MI were photographed and described before and after heating experiments. , Five MI from Group 2 MI (bubble-bearing MI) were slightly crystallized and a "shrinkage" bubble was visible before the experiment (volume<sub>bubble</sub>/Volume<sub>MI</sub>  $<\sim$  5%). One MI showed slightly crystallized glass plus a large bubble (~40%). All the other MI were strongly crystallized appearing as a dark inclusion using the optical microscope with transmitted light. After quenching, Group 2 MI show volume<sub>bubble</sub>/Volume<sub>MI</sub> <4% with the exception of one MI showing volume<sub>bubble</sub>/Volume<sub>MI</sub> <39%. The temperature of quenching of Group 2 MI ranges from 1143°C to 1238°C.

In this study, we focused on Group 2 MIs and the vapor bubbles were further analyzed by Raman to test for the presence of volatiles  $(CO_2 \text{ and/or } H_2O)$  in the vapor bubbles (Figure 1).  $CO_2$  was detected in all MI analyzed.  $CO_2$  density was determined using the difference in peak position between the two Fermi-diad peaks, and ranges between 0.14 and 0.27 g/cm<sup>3</sup> based on Fall et al. [1] densimeter. Six MI also showed evidence for H<sub>2</sub>O in the vapor bubble. In addition, carbonates and native sulfur(only in two bubbles) were detected at the glass-vapor interface of five MI.

Marianelli et al. [2] reported that the H<sub>2</sub>O molar fraction of the CO2-H2O fluid in equilibrium with the melt associated to recent Mt. Somma-Vesuvius recent eruptions (1794-1944 AD) mostly ranges between 0.2 and 0.6 based on volatile content of the glass of MI. We estimated the H<sub>2</sub>O rim thickness of the vapor bubble of R6\_D54\_4\_2 MI based on the density of CO<sub>2</sub> determined from the difference in peak position between the two Fermi diad peaks. Our calculation based on the shrinkage bubble contained in MI R6\_D54\_4\_2 (1631 sub-plinian eruption) show that the thickness of the rim of H<sub>2</sub>O fluid in the vapor bubble at room T is (i) ~0.09 µm if the fluid at the moment of quenching contained a mole fraction of  $H_2O(X_{H2O})$  of 0.2, (ii) is ~0.2 µm if the fluid  $X_{H2O}$  was 0.4, and (iii) is 0.5 µm if the fluid  $X_{H2O}$  was 0.6.

The results of this study provide direct evidence of  $H_2O$  and S in MI shrinkage bubbles, in addition to  $CO_2$  vapor and carbonates. The amount of  $H_2O$  present at early crystallization stages is a key parameter in understanding magmatic systems, influencing both magma dynamics and eruptive behavior, as well as the properties and roles of magmatic volatiles in the subsurface.

The presence of S in the vapor bubble underscores the possibility that not only the  $CO_2$  content may be underestimated if only the glass is analyzed [3 and references therein], but also the original S concentration of the MI could be underestimated if only the S concentration of the glass is considered. In turn, accurate estimation of the pre-eruptive S concentrations of silicate melts is key for understanding such processes as sulfide saturation and metal mobility in ore-forming magmatic-hydrothermal systems.

At present, most published estimates of pressures of saturation obtained from MI are based on  $H_2O-CO_2$ -silicate melt solubility

models. The results of this study suggest that depths of olivine crystallization based on volatile contents of MI will be more reliably determined using a C-O-H-S fluid-silicate melt solubility model.



**Figure 1:** Bubble-bearing MI quenched at 1167°C. Notice the dark crystals showing subhexagonal shape. Raman analysis at the glass/bubble interface show carbonate, sulphur and liquid H<sub>2</sub>O signals.

**Acknowledgements**This work was supported by the 7/PON/ST/2012-4 Enerbiochem project to B. De Vivo. Partial funding for analysis on MI was provided by PRIN2010PMKZX7 to C. Cannatelli.

### References

[1] Fall A., Tattitch B., and Bodnar R.J. (2011) Combined microthermometric and Raman spectroscopic technique to determine the salinity of  $H_2O-CO_2$ -NaCl fluid inclusions based on clathrate melting, Geochimica et Cosmochimica Acta, 75(4), 951-964.

[2] Marianelli P., Sbrana A., Métrich, N., Cecchetti, A. (2005) The deep feeding system of Vesuvius involved in recent violent strombolian eruptions, Geophysical Research Letters, 32(2), L02306.

[3] Moore, L., Gazel, E., Tuohy, R., Lloyd, A., Esposito R., Steele-MacInnis, M.J., Hauri, E.H., Wallace, P., Plank, T., and Bodnar, R.J. (2015) Bubbles matter: An assessment of the contribution of vapor bubbles to melt inclusion volatile budgets, American Mineralogist, 100, 806-823.

# Fluid Chemistry of High Grade Iron Mineralization at Piçarrão-Liberdade Deposit, Brazil

**Sylvio D. Gomes<sup>1</sup>**, Rosaline C. Figueiredo e Silva<sup>1</sup>, Carlos A. Rosière<sup>1</sup>, Lydia M. Lobato<sup>1</sup>, Steffen Hagemann<sup>2</sup> & David A. Banks<sup>3</sup>

<sup>1</sup>Universidade Federal de Minas Gerais-UFMG, Brazil. <u>sylvio.gomes@gmail.com</u>; <sup>2</sup>Center for Exploration Targeting-CET, University of Western Australia-UWA; <sup>3</sup>School of Earth and Environment, University of Leeds

Banded iron formation-BIF of Guanhães Group [1], a geological unit comprised mainly of metapelites, quartzites, BIFs and gneisses, has been recently an important target for mineral exploration, especially for its high grade (>60% Fe) iron orebodies, and also due to the near exhaustion of the giant iron deposits in the Iron Quadrangle. Picarrão iron deposit is located in the eastern border of the southern Espinhaço Range, near Santa Maria de Itabira town, Minas Gerais, Brazil. The mine was exhausted (more than 500,000 t of Fe), but its northern extension, represented by Liberdade deposit, has been mined. The iron orebodies are strongly foliated, 2-20 m wide and is comprised of magnetite-martite. They usually occur parallel and discordant to the BIF bedding.

Quartz veins from Piçarrão-Liberdade deposit were classified according to their hosted rocks in two types: (i) quartz-magnetite veins (Qtz1) in magnetitic-martitic orebodies (Fig. 1A); and (ii) quartz-feldspathic veins (pegmatoid metasedimentary Qtz2) in rocks. Microthermometry and in situ LA-ICP-MS studies were conducted in fluid inclusions (FI) trapped in quartz crystals (Qtz1 & 2) in order to characterize the hydrothermal fluid responsible for the Fe-enrichment and the possible contribution of magmatic fluids at the deposit.

Fluid inclusion assemblage-FIA (Fig. 1B) is represented by two types of pseudosecondary inclusions in Qtz1 with variation in liquid/vapour ratios: Type 1 – aqueous, twophase (Fig. 1C); and Type 2 – aqueouscarbonic, three-phase (Fig. 1C). Locally, FIA in Qtz1 contains only Type 1 FIs. Pegmatoid-Qtz2 crystals contains only pseudosecondary Type 1 FIs with constant L/V ratios (5% vapour). Secondary trails are represented by fine (< 10  $\mu$ m) monophase aqueous FIs (Fig. 1B), along fractures in both Qtz1 and Qtz2 crystals.



Figure 1: A) Hand sample of quartz-magnetite vein; B) Photomicrography of Qtz1 crystal (xpl nicols) showing FIA1 and secondary trails; C) Detail showing types 1 and 2 FIs in FIA1.

*Microthermometry* - Types 1 and 2 FIs trapped in **Qtz1** have low to moderate salinity values (1.0 to 15 eq % NaCl), with homogenization temperatures between 140-240°C for Type 1, and decrepitation temperature between 250-330°C for Type 2 FIs. Type 1 FIs trapped in **Qtz2** have also low to moderate salinity values (1.0 to 10 eq % NaCl), with homogenization temperatures between 240-300°C. Eutectic temperatures between 240-300°C for the two types of quartz and FIs.

LA-ICP-MS – In situ LA-ICP-MS analyzes determined ratios of the elements K, Ca, Mg, Mn, Fe, Cu, Zn, Sr, Ag, Ba, La, Pb and Li in relation to Na. Concentrations (ppm) were calculated using salinity values obtained by microthermometry. Fluid inclusions in Otz1 reveal a similar composition in the two types for the cations K, Ca, Mg and Fe. This is in agreement with low eutectic temperatures determined by microthermometry [2]. suggesting other cations besides Na. Potassium and Fe enrichment may be observed in both types of FIs. On those FIs where Fe is anomalous, Ba concentrations are also high. The Na/K versus Na/Ca diagram display a dispersion in FIs trapped in Qtz1, showing two distinct populations (Fig. 2). Lithium concentrations in Type 1 FIs of Qtz1 from quartz-magnetite veins are below the detection limit. On the other hand, Li is above limit detection in Type 2 FIs of Qtz1, and have similar concentration (300-400 ppm) when compared to Type 1 FIs of Qtz2 from quartzfeldspathic veins. For the case of metals Cu, Pb and Zn, they show similar concentrations (800-1600 ppm Cu, 100-400 ppm Pb, 800-1200 ppm Zn) in both types 1 and 2 FIs of Qtz1 and Qtz2.

Based on microthermometric and LA-ICP-MS data of fluid inclusions, low to moderate salinity and temperature values suggest interaction of different fluids to form the high-grade iron orebodies in Piçarrão-Liberdade deposit. Low temperature FIs (140-240°C) in Qtz1, together with presence of Ba, suggest meteoric water contribution for quartz-magnetite veins. The presence of Li in both, Qtz1 and Qtz2 (quartz-feldsphatic veins), may also indicate a magmatic contribution.



*Figure 2:* Na/K x Na/Ca ratios in FIs in Qtz1 – LA-ICP-MS results.

It is also worth noting that ratios of Na/K and Na/Ca in Qtz1 (quartz-magnetite veins) show two populations, suggesting a possible fluid mixing for the formation of these mineralized veins. This mineralizing process is compatible with other Fe deposits, such as Serra Norte, Carajás, Brazil [3], and Paraburdoo, Western Australia [4], where mixing of two endmember fluids is interpreted, magmatic and meteoric, basinal and meteoric, respectively.

**Acknowledgements** - The authors thank CPMTC-UFMG, Fapemig (APQ-00557-12) and CNPq for financial resources, and scholarship from CAPES.

### References

[1] Grossi Sad J. H., Chiodi Filho C., Santos J. F., Magalhães J. M. M., Carelos P. M (1990), Geoquímica e origem da formação ferrífera do Grupo Guanhães, Distrito de Guanhães, MG, Brasil. SBG, Congr. Bras. Geol., 36, Natal, Anais 3, pp. 1241-1253

[2] Borisenko A.S., (1977), Study of the salt composition of solutions in gas-liquid inclusions in minerals by the cryometric method, Soviet Geology and Geophysics, v. 18, pp. 11–19.

[3] Figueiredo e Silva R.C, Hagemann S.H., Lobato L.M., Rosière C.A, Banks D.A., Davidson G., Vennemann T., Hergt J., (2013), Hydrothermal Fluid Process and Evolution of the Giant Serra Norte Jaspilite-Hosted Iron Ore Deposits in the Carajás Mineral Province, Brazil, Economic Geology, 108, pp.739-779.

[4] Thorne W.S., Hagemann S., Sepe D., Dalstra H.J., Banks D.A., (2014). Structural control, hydrothermal alteration zonation, and fluid chemistry of the concealed, high-grade 4EE iron orebody at the paraburdoo 4E deposit, Hamersley Province, WA

# Development of a deposit model for the giant gold orebody at Lone Star in the Klondike, Yukon.

Matthew Grimshaw, Rob Chapman and Graham McLeod

School of Earth and Environment, University of Leeds, Leeds, UK. ee09mrg@leeds.ac.uk

The Klondike Gold District is world famous for the huge amount of placer gold that has been recovered since the great Gold Rush of 1896. Exploration and research has been driven by the disparity between the 20+ million ounces of placer gold versus only 1240 ounces recovered from in situ occurrences [1]. The largest of these apparently modest lode occurrences is located on the Lone Star ridge which is flanked by the extremely rich Eldorado and Bonanza creeks (~7Moz) (Fig.1) [2]. Previous studies have established that this placer gold was derived from the Lone Star mineralization [2, 3], which indicates that the source of the gold could be a potentially world class deposit [4]. Development of the geological understanding of the area has been hindered by complex lithologies, multiple phases of deformation, deep weathering and a lack of exposure.



geochronology and detailed structural studies have placed vein formation within a period of tectonic uplift and a hiatus in magmatic activity. Consequently, the generation of this small, but exceedingly rich gold mineralization requires an alternative deposit model.

Chapman et al. [2] investigated Au mineralization in the Lone star area through systematic study of the compositions of gold grains derived both from veins and placers in the headwaters of valleys. Two observations emerged from the work: firstly that there was a systematic variation gold in allov compositions with location, and secondly that different compositional populations of gold could be present within a single vein (Fig. 2). These authors concluded that gold was emplaced in a single hydrothermal system but in several episodes, which exhibited overall spatial and temporal zonation. This zonation

may have been influenced by fluid interaction with discrete lenses of gold enriched schist (13g/T Au) and syngenetic sulphides.

studies Three have addressed vein textures and the associated fluid inclusions within auriferous veins in the Klondike region [6-8]. All studies identified low temperature aqueo-carbonic solutions trapped at a range of pressures. Although these broad studies suggest gold deposition within a typical

*Figure 1:* A geological map indicating key historic and current mineralised veins in the Lone Star area of the Klondike.

The auriferous veins are hosted in Permian metamorphic rocks and exhibit characteristics typical of orogenic gold mineralization (Fig.1). Currently accepted generic models for orogenic gold invoke either large fluid movement via regional scale faults, or a magmatic influence [5]. However,

orogenic system, there is no detailed information relating to multiphase vein evolution in the Lone Star area as suggested by the gold compositions. The current project is examining the hypotheses that the fluids may be very locally sourced and that uplift of the host rocks may be an important factor [1].



of factors during deposition (temperature, pressure, pH, Eh, fluid composition and sulphur fugacity) and can be used to interpret the mineralising environment. The present study aims to develop

understanding of the source-transport-trap elements of the deposit model through studies of the auriferous veins. Over two field seasons thorough characterisation and sampling of lode mineralisation and host lithologies has been carried out. Currently, research is focussing on the detailed and systematic petrological characterization of the all visible gold (Fig. 3) and host rock samples, analysis of the trace element chemistry of component minerals by LA-ICP-MS, characterization of the gold compositions using EMPA and LA-ICP-MS (Fig.3), and, fluid inclusion studies of different generations of quartz. The development of a deposit model for the Lone Star auriferous hydrothermal system will not only underpin approaches to local exploration but contribute a case study on an atypical, but economically important gold occurrence to inform the wider debate on orogenic gold genesis.

#### References

[1] Allan, M.M., et al., 'Magmatic and Metallogenic Framework of West-Central Yukon and Eastern Alaska.' Society of Economic Geology 2013. Special Publication (17): p. 111-168.

[2] Chapman, R.J., et al., 'Microchemical Studies of Placer and Lode Gold in the Klondike District, Yukon, Canada: 1. Evidence for a Small, Gold-Rich, Orogenic Hydrothermal



**Figure 3:** Reflected light image of gold from the Buckland vein. The gold is typically found in vein selvages associated with pyrite. The veins are quartz-carbonate with some wallrock sulphidation and ankerite alteration.

System in the Bonanza and Eldorado Creek Area.' <u>*Economic Geology*</u>, 2010. 105(8): p. 1369-1392.

[3] Knight, J.B., J.K. Mortensen, and S. Morison, 'Shape and composition of lode and placer gold from the Klondike District, Yukon, Canada.' 1994: Indian and Northern Affairs Canada, Exploration and Geological Services Division, Yukon Region.
[4]Groves, D.I., et al., 'Gold deposits in metamorphic belts: everyiew of current

metamorphic belts: overview of current understanding, outstanding problems, future research, and exploration significance'. Economic Geology, 2003. 98(1): [5] Goldfarb, R.J., et al., 'Distribution, character, and genesis of gold deposits in metamorphic terranes.' Economic Geology 100th Anniversary Volume, 2005: p. 407-450. [6] Wolff, G.W.R., 'Microstrucutres and Trace **Element Signatures of Orogenic Quartz Veins in** the Klondike District, Yukon Territory, Canada`', in Faculty of Science2012, University of British Columbia. [7] Rushton, R.W., et al., 'A fluid inclusion and stable isotope study of Au quartz veins in the Klondike District, Yukon Territory, Canada; a section through a mesothermal vein system.<sup>2</sup> Economic Geology, 1993. 88(3): p. 647-678. [8] Friedrich, G. and H. K-H, 'Gold and sulphide mineralization in the Hunker Creek

area, Yukon Territory, Canada.' Indian & Northern Affairs Canada/Department of Indian & Northern Development: Exploration & Geological Services Division., 1992.

### Fluid inclusion studies on rare metal enriched pegmatites

Marieta Freitas, Alexandra Carolino, Alexandra Guedes & Fernando Noronha

DGAOT and Earth Sciences Institute (ICT), Pole of the FCUP, Rua do Campo Alegre 4167-007, Porto, Portugal. aguedes@fc.up.pt

### Introduction

In order to contribute to the study of rare metal enriched pegmatites from Central Portugal petrographic and fluid inclusion studies were carried in beryl, hyaline quartz, and lithiophilite from those pegmatites.

### Geology

The studied pegmatites, belong to the important "Iberian Pegmatite Field" (IPF), located in the same segment of the European Variscan chain, the Central Iberian Zone. The IPF from Central Portugal arises in an area of over 100 km<sup>2</sup>, and results of spatial overlap of several vein structures, preferably hosted by granitic rocks of various types and only rarely installed in the metasedimentary formations [1]. The IPF is mainly composed of granitic pegmatites, deserving particular attention the LCT type with lithiniferous minerals such as lepidolite, amblygonite/montebrasite and lithiophilite.

The studied pegmatites, Mesquitela and Companheiro, are located in the Central of Portugal in the West part of the IPF and are primarily composed by quartz and potassium feldspar and subordinated albite and muscovite. Beryl and lithiophilite are the main accessory minerals.

Petrographic study reveals a succession of different overprinting stages: the earlier, corresponding to the pegmatitic texture, is essentially characterized by quartz, muscovite, albite, and K-feldspar. The later, characterized by presence of beryl, albite, quartz and Li-Mn phosphates. Cassiterite, as well as scarce sulphides (arsenopyrite, pyrite, chalcopyrite, sphalerite and molybdenite), can be present.

In quartz richer areas, the Companheiro pegmatite exhibits alternations of milky and clear quartz parallel to a latter N30°E subvertical fracturing system.

Considering the mineralogy and the relationship with orogenic granites, the studied pegmatites belong to the group of orogenic pegmatites, so formed in a collision scenario, and LCT type once they have lithium [1]. According to the classification of Cérny and Ercit [2] they can be classified as REL class; REL-Li subclass, beryl type; subtype - beryl-phosphate with geochemical signature - Be, P (Li, F,  $\pm$  Sn, B) and therefore presenting as typical minerals beryl and lithiophilite.

### Methodology

Fluid inclusion studies were performed using a Chaixmeca and a Linkam stages and a Horiba Jobin-Yvon LabRaman spectrometer interfaced to Olympus microscopes. Raman Spectra were obtained using the 632.8 nm emission line of HeNe laser (20mW).

### Results

Microthermometric and Raman microspectrometric studies performed in the studied minerals reveal the existence of primary, pseudosecondary and secondary fluid inclusions.

The beryl shows primary and pseudosecundary two-phase fluid inclusions containing low salinity H2O-NaCl aqueous fluids (<5 wt% eq. NaCl) revealing trapping conditions of 350°C and 300-500 MPa.

The quartz studies revealed the existence of three-phase primary fluid inclusions and two-phase pseudosecondary fluid inclusions. The primary fluid inclusions contain aqueous carbonic  $H_2O-CO_2-(CH_4-N_2-NaCl)$  fluids and were trapped during quartz crystallization at minimum temperatures and pressures of 330°C and 190-240 MPa.

The lithiophilite reveal the presence of aqueous fluids with  $CH_4$  and  $N_2$  in primary two-phase fluid inclusions and were trapped at temperature conditions between 330 and

500°C and pressures between 150 and 300MPa; similar to the P-T conditions of the aqueous-carbonic fluids studied in hyaline quartz. Finally, the secondary fluid inclusions present in lithiophilite contain aqueous fluids trapped at temperature between 400 and 250°C and pressures between 250 and 100 MPa.

### **Discussion and conclusions**

The origin of pegmatites continues to be debated and there is little doubt that hydrothermal metassomatism occurs namely in rare element pegmatites [3 and 4].

Disequilibrium is dominant all along the late stages of pegmatite crystallization and will be highly enhanced during subsolidus reworking [3 and 5] and the pegmatites usually display aspects of both igneous and hydrothermal systems [6].

Fluid inclusion studies in beryl, revealed the importance of low-salinity aqueous fluids on mineral deposition. The aqueous fluids with CH<sub>4</sub> and N<sub>2</sub>, contained in the lithiophilite reveal similar P-T conditions of the aqueous-carbonic fluids studied in hyaline quartz from Companheiro pegmatite. Finally, the later fluids present in lithiophilite are also aqueous and similar to fluids that occur in lepidolitic pegmatites where the main episode of lepidolite formation occurred around 300°C, and 100 MPa. [4].

The PT evolution of the fluids contained within the studied minerals seems to follow a trend from higher to lower pressure and temperature conditions, with the formation of the beryl and the conditions defined for the deposition of lithiophilite, corresponding to a hydrothermal stage, where the aqueous fluids formed subsequently to the  $CH_4$  and  $N_2$  fluids.

The fluids present in these pegmatitic structures together with the trapping conditions found are similar to those described for late orogenic Variscan hydrothermal systems in Central Iberian Zone [7] and confirm the important role of hydrothermal fluids also in the pegmatite history, especially in those specialised in lithium (lithiophilite and/or lepidolite)



**Figure 1:** P-T-X evolution of the fluids in the studied pegmatites.  $(\Delta)$  – Triple point And-Sil-Ky.

### Acknowledgements

This work was supported by the Project PEst-OE/CTE/UI0039/2014.

### References

[1] Černý P. (1991) Rare-element granitic pegmatites. Part I. Anatomy and internal evolution of pegmatite deposits, Geosci. Can, 18, 49–67.

[2] Černý P., & Ercit T.S. (2005) Classification of granitic pegmatites revisited, The Canadian Mineralogist, 43, 2005-2026.

[3] Charoy B., & Noronha, F. (1999) Rareelement (Li-rich) granitic bodies: A primary or a superimposed signature? Revista Brasileira Geociências, 29, 1, 3-4, 1-8.

[4] Farinha-Ramos J.M. (2010) Aplitopegmatitos com mineralizações de metais raros de Seixo Amarelo-Gonçalo. O Recurso geológico. Geologia e recursos geológicos, PhD thesis, vol.II, capítulo I, 121-130.

[5] Linnnen R.L., Van Lichtervelde M., & Cerny P. (2012) Granitic Pegmatites as sources of strategic Metals, Elements, 8, 4, 275-280.

[6] London D., Kontak D.J. (2012) Granitic pegmatites: Scientific Wonders and Economic Bonanzas, Elements, 8, 4, 263-268.

[7] Noronha F., Ribeiro M.A., Almeida A., Dória A., Guedes A., Lima A., Martins H.C., Sant'Ovaia H., Nogueira P., Martins T., Ramos R., Vieira R. (2012) Jazigos filonianos hidrotermais e aplitopegmatíticos espacialmente associados a granitos, In: Dias R. Araújo A, Terrinha P, Kullberg JC (eds) Geologia de Portugal, Escolar Editora, 1, pp. 403-438.

### Unravelling the Origin of the Bahariya Ironstone of Egypt

Adel Mady Afify<sup>1, 2</sup>, **Laura González-Acebrón<sup>3</sup>**, María Esther Sanz-Montero<sup>1</sup> & Jose Pedro Calvo<sup>1</sup>

1 Dpto. Petrología y Geoquímica, Facultad de Ciencias Geológicas (UCM), Madrid, Spain.

2 Geology Department, Faculty of Science, Benha University, Egypt.

3 Dpto. Estratigrafía, Facultad de Ciencias Geológicas (UCM), Madrid, Spain. lgcebron@geo.ucm.es

Despite the literature on the ironstone deposits of the northern part of the Bahariya Depression is quite large, their origin is still a matter of debate. In this area, the term cherty ironstone is used to describe the ore deposits hosted in the Eocene dolomites of Bahariya where major concentration of iron, manganese, barite and silica occurs closely related to a major fault system. The cherty iron-rich beds show a fine preservation of the primary carbonate sedimentary structures and fossil components as well as karstic features developed during early diagenetic stages [1, 2]. During the Early-Middle Eocene, the carbonate deposits underwent dolomitization. The formation of cherty ironstone deposits took place probably during the Oligocene.

The main mineral assemblage in the cherty ironstone comprises goethite, hematite, quartz and barite. Pyrolusite and jacobsite manganese oxides were found in the lowermost part of the iron-rich succession, while other manganese minerals, i.e., romanechite, psilomelane, todorokite occur as younger pore-filling cements. Silica content increases in the highly porous and fossiliferous beds. Silica occurs as mega-quartz, micro-quartz, and chalcedony and/or banded with the iron-rich laminae. Barite occurs as big lenses, irregular bodies, open-space fillings, fracture fillings. poikilotopic cement and euhedral disseminated and rosette-like crystals only along the main faults and stockwork zones (Figs. 1A and B). Dolomite relics and pseudomorphs are present together with the iron oxide, quartz and barite (Figs. 2A and B).

Fluid inclusion analyses on barite and quartz crystals and overgrowths have been undertaken to develop a model for the origin and evolution of fluids responsible for the formation of the cherty ironstone.



Figure 1: Outcrop view of an open-space cavity infilled with barite (lower part in A) and fracturefilling (B) barite crystals (arrows) within ironstone deposits.

Biphasic fluid inclusions with very small size not exceeding 8  $\mu$ m and with 95:5 to 90:10 liquid/vapour ratios are present in the quartz cement in the ironstones as well as in quartz syntaxial overgrowths of the overlying Oligocene sandstone (Figs. 3A and B). Biphasic fluid inclusions homogenized to the liquid in a temperature range 288-383 °C. The hydrothermalism in such area is supported by the clay mineralogy of the underlying rock unit in contact with ore bodies [3].

On the other hand, barite crystals present primary monophasic liquid fluids as well as minor two-phase aqueous inclusions, ranging in size from 4 to  $32 \mu m$  and showing variable liquid/vapour ratios and concentrated along growth zones and/or randomly distributed in inclusion clouds within barite crystals (Figs. 3C and D).

The fluid inclusion petrography of barite reflects primary monophasic liquid fluid inclusions were affected by stretching resulting in formation of biphasic fluids with variable-sized bubbles. Such bubbles are formed by water vapour and other gases have been discarded by raman. The salinity measurements suggest a low salinity (0.18-4.96 eq. wt.% (NaCl)) aqueous solution. The liquid monophasic inclusions reflect formation in low temperature (<50 °C) phreatic environment. The purified barite crystals were selected for sulfur and oxygen isotope analyses and displayed values of 12.1 - 21.1‰ for  $\delta^{34}$ S and 13.66 - 17.14‰ for  $\delta^{18}$ O. These data reflect their formation from mixing of hydrothermal steam-heated fluids and meteoric water in phreatic zones. The fluid inclusion salinity suggests that hydrothermal fluids rose until shallow levels where they were mixed with meteoric waters.



Figure 2: A. SEM photo of a pseudomorph crystal of dolomite replaced totally by hematite, B. Photomicrograph of a barite crystal showing relics of dolomite.

The integration of fieldwork, petrographic, mineralogical, isotopic and fluid inclusion analyses data confirms a hydrothermal origin of tectonically driven fluids that resulted in the formation of barite, silica and Fe/Mn bearing minerals. The circulation of hot waters strongly corroded the dolomite host rocks and produced silica precipitation. Further, the quiescence of temperatures in mixing with meteoric water resulted in formation of Fe/Mn minerals and ended with barite formation.



**Figure 3:** Photomicrographs showing: Quartz syntaxial overgrowths in sandstone (A), Biphasic fluid inclusion in quartz of the ironstone (B) and monophasic liquid fluid inclusions in growth zones of barite (C, D).

### Acknowledgments

We are grateful to the Egyptian Government for their financial support through a Ph.D. grant for the first author and to Ronald Bakker for his help with raman analysis.

### References

[1] A. M. Afify, M. E. Sanz-Montero and J. P. Calvo, 2015. Cherty ironstone hosted in Eocene marine carbonates: Tectonic and sedimentological controls on iron and silica formation,  $31^{th}$  IAS Meeting of Sedimentology.

[2] A. M. Afify, M. E. Sanz-Montero and J. P. Calvo, 2015. Biotic versus abiotic iron: An example of the fault-related ironstone hosted in Eocene carbonates in the Bahariya area, Western Desert, Egypt, 31<sup>th</sup> IAS Meeting of Sedimentology.

[3] A. M. Afify, X. Arroyo, M. E. Sanz-Montero and J. P. Calvo, 2014. Clay mineralogy in Bahariya area, Egypt: Hydrothermal implications on fault-related iron ore deposits, 7<sup>th</sup> Mid European Clay Conference, 137.

# The Sulphur Isotopes and Fluid Inclusion Characteristics of the Madenköy (İmranlı) Cu-Pb-Zn±Ag Mineralization, Sivas, Turkey

Serkan Şenkaya<sup>1</sup> & Nurullah Hanilçi<sup>2</sup>

<sup>1</sup>Balıkesir University, Dep. of Geological Engineering, Balıkesir, Turkey <u>serkansenkaya@balikesir.edu.tr</u> <sup>2</sup>Istanbul University, Dep.of Geological Engineering, Istanbul, Turkey <u>nurullah@istanbul.edu.tr</u>

The Madenköy Cu – Pb – Zn ± Ag mineralization is located about 100 km east of Sivas, Turkey. The Middle Eocene altered andesitic lavas and tuffs, and the Late Eocene syenitic pluton (Kösedağ pluton) occur in outcrops in the vicinity of the mineralization. The Cu-Pb-Zn±Ag mineralization lies in a NW directed zone within the andesitic and syenitic rocks. The ore zone is approximately 2 km in length, 1 km in width and the mineralization occurs generally in sub-parallel veins. The length and thickness of the ore veins varies between 10 and 100 m, and 0.5 and 3 m, respectively. Their orientation and dip varies between N42W and N55W, and between 77°NE and 85°NE, respectively. While sericitic alteration occurs in the andesitic rocks, carbonation (mostly calcite formation) and kaolinitisation is prominent in the syenitic rocks in the vicinity of the ore zone. Ore minerals are primarily galena, sphalerite, chalcopyrite, arsenopyrite, pyrite, rare bornite, molybdenite, fahlore-group minerals, malachite, hematite, goethite, and quartz and barite as the gangue minerals.

Fluid inclusion studies have been carried out in quartz and sphalerite. Petrographically two types of quartz have been identified. The first quartz occurs early without showing an obvious zonation. The second phase of quartz occurs in growth zones around the first phase of quartz and is zoned. All inclusions in sphalerite and quartz contain liquid and vapour, where the vapour phase occupies approximately 20 % of the inclusion. All homogenisation were to the liquid phase. Microthermometric measurements have been performed on primary inclusions in quartz (Fig. 1a, b) and pseudo-secondary inclusions in sphalerite (Fig. 1c, d).

The characteristics of fluid inclusion of the first phase quartz, early and late phase growth zones in quartz, and sphalerite are;

- The fluid inclusions in first phase quartz has Te values of approximately -23.0°C, and Tmice values of -2.7°C, which represents an average 3.25 % NaCl equivalent salinity. The average Th value of these fluids is 350°C (Fig.2).

- The fluid inclusions in early growth zone around the first phase Qz has average Tm-ice values and salinity of -3.2°C and 5% NaCl equivalent (Fig.2). The average Th value of early growth zones is 263°C. These data show that the salinity of fluids of the early growth zones is higher than those of the first phase of quartz. The fluid inclusions in some early growth zones have low salinity (1% NaCl eq.) which may indicates involvement of meteoric However, homogenisation fluids. the temperature of early growth zones is lower than those of the first phase quartz (Fig.2).



**Figure 1**: Two-phases (L+V), liquid rich fluid inclusions in the quartz (a-b), and sphalerite minerals (c-d; all scale bars are 10 µm).

- The Te values of the late growth zones vary between -27 and -21°C, with the average Tmice values of -5.47°C, corresponding 8.5% NaCl equivalent salinity. The average Th value of the late growth zones is 230°C. These data show that the salinity of the late growth zones quartz is higher than the early growth zones and the first phase Qz (Fig.2). The lower Te values of late growth zones may indicate that the composition of the fluids changed and more KCl [1] was added to the fluids possibly via alteration of wall rocks.

- The microthermometric data of pseudosecondary inclusions in sphalerite are between -49 °C and -47°C for Te, -13.7°C for Tm-ice, indicating 17% NaCl equivalent salinity, and 163°C for Th. Even though these data are obtained from pseudo-secondary inclusions, the sulphide minerals precipitated from solutions with lower temperature and higher salinities, at the least for sphalerite (Fig.2). The high salinity values of fluids and the lower Te values may reflect that the hydrothermal solutions were affected by more intense alteration of wall rocks with CaCl<sub>2</sub> [1] added to the fluids



**Figure 2:** The homogenization temperature (Th) versus wt.% NaCl equivalent salinity diagram of fluid inclusions in quartz and sphalerite in the Madenköy Cu-Pb-Zn±Ag mineralization.

The  $\delta^{34}$ S values of sulphide-bearing minerals vary between -2.77 and +3.94‰ (n=23, average=+0.13‰); between +1.48 and +3.94‰ (n=2, average=+2.69‰) in sphalerite; between -1.02 and +2.36 ‰ (n=3, average= +0.83‰) in pyrites; between -4.22 and +2.42‰ (n=18, average= -0.27‰) in galena. The narrow range and near zero values of the  $\delta^{34}$ S suggest that the sulphur in hydrothermal solutions is probably sourced from a single, homogenous source such as a magmatic system.

### Acknowledgements

This work was supported by the Scientific Research Projects Coordination Unit of Istanbul

University, Project No: TEZ-35908. Author's thanks to ESAN-Eczacıbaşı *Company* for their logistic supports in the field study, and chemical analysis.

### References

[1] Shepard T. J., Rankin A. H., Alderton D. H. M. 1985 – A Practical Guide To Fluid Inclusion Studies. Blackie & Son, Glasgow, 239

# Polymineralic Inclusions Representing *In Situ* Melting in Garnet of Eclogite-Facies Metapelites during Uplift and Heating

**Petra Herms<sup>1</sup>**, Andreas Möller<sup>2</sup>, Peter Appel<sup>1</sup> & Peter Raase<sup>1</sup>

<sup>1</sup>Department of Geosciences, University of Kiel, Germany, (<u>ph@min.uni-kiel.de</u>), <sup>2</sup>Department of Geology, The University of Kansas, Lawrence, KS, USA

Melt inclusions in high-grade metamorphic rocks are an indication for partial melt formation and are often preserved as polymineralic inclusions. There are different processes and geodynamic settings where a partial melt can be produced. Partial melting caused by heating (700 to >900°C) either under fluid-present or under fluid-absent conditions can produce large amounts of melt eventually leading to anatexis of the rock. Decompression is another process to produce partial melt, but the amount of melt is much lower. Melting under fluid-absent conditions is induced by dehydration reactions and can occur under both processes - heating and decompression. Associated with melt formation is the growth of new peritectic minerals like garnet, which can trap the melt in small inclusions.

The polymineralic inclusions under investigation have been found in garnet porphyroblasts of metapelites from the Usagaran Belt, Tanzania. The metapelites are associated with eclogites and represent oceanic crust subducted 2 Ga ago [1]. During uplift, the eclogite-facies rocks passed through а granulite-facies stage indicated bv orthopyroxene-plagioclase coronas developed around garnet in the eclogites. Partial melting occurred at this stage in the metapelites. In spite of the high temperature, the garnet porphyroblasts have preserved their prograde zoning. The polymineralic inclusions occur in the outer part of the core, but not in the rim zones of the porphyroblasts. It has to be pointed out that the polymineralic inclusions are not associated or cut by fractures or veins. A retrograde formation can therefore be excluded.

The polymineralic inclusions consist mainly of quartz, plagioclase, biotite, kyanite and carbonate (dolomite and magnesite). Kyanite and biotite inside the inclusions have euhedral to subhedral shape while quartz and feldspar display granoblastic texture. The polymineralic inclusions (20-50 µm in diameter) partly exhibit euhedral to subhedral negative crystal shapes of the host garnet. In detail, the garnet inclusion interface shows reentrant angles at junctions of two inclusion phases, especially feldspar and quartz. Inside the inclusions these phases have straight grain boundaries with equilibrium angles of about 120°. In addition, many polymineralic inclusions display cuspate or offshoots. Around corners some polymineralic inclusions, fluid inclusion haloes are observed in the garnet host. Both latter observations are interpreted as decrepitation features.

The combined textural evidence suggests crystallization of the polymineralic inclusions at high temperature in the presence of melt and/or fluid, probably during decompression due to uplift of the eclogite-facies rocks. Very similar polymineralic inclusion textures have been described by Stöckhert et al. [2] in UHP rocks from the Erzgebirge and are interpreted to be formed or equilibrated at falling pressures during uplift. Polymineralic inclusions could be interpreted to have crystallized from melt entrapped in peritectic garnet during partial melting of metapelite [3]. However, the prograde zoning with Mn-rich cores argues against a peritectic origin of the garnet porphyroblasts from the Usagaran belt. The Al-rich composition inferred from the kyanite content of the polymineralic inclusions suggests the former presence of phengitic white mica which could have been enclosed in the garnet porphyroblasts during prograde metamorphism with peak conditions of 1.8–2.0 GPa and 750-800°C. During uplift, at pressures of about 1 GPa, temperatures must have increased to at least 900°C, judged from the bulk composition of large antiperthite crystals in leucosome veins. At such conditions, dehydration melting of white mica must have occurred in the metapelite matrix as inclusions well as in inside garnet porphyroblasts. Phengite inclusions should

have reacted with host garnet yielding biotite, kvanite, K-feldspar, plagioclase and some melt. High temperatures could have prevailed only for a short time span, since the prograde garnet zoning is often preserved. After peak temperature at decreasing pressure, the melt in the inclusions must have been consumed reacting with garnet and K-feldspar, finally leading to the observed inclusion assemblage biotite + plagioclase + quartz + kyanite. Pure CO<sub>2</sub> fluid inclusions in garnet and the additional presence of carbonate (mostly dolomite) suggests the presence of  $CO_2$  in the polymineralic inclusions, which probably reacted with the grossular and pyrope components of the host garnet producing dolomite, anorthite and quartz. The high An content of the plagioclase could be explained by this reaction but also by reaction of host garnet with enclosed quartz and kyanite during decompression. At high temperatures during the granulite stage, a CO<sub>2</sub>-bearing fluid phase must have coexisted with a H<sub>2</sub>O-containing melt.

### References

[1] Möller, A., Appel, P., Mezger, K. & Schenk, V. (1995) Evidence for a 2 Ga subduction zone: Eclogites in the Usagaran belt of Tanzania, Geology, 23, 1067-1070.

[2] Stöckhert, B., Duyster, J., Trepmann C. & H-J. Massonne, H.-J. (2001) Microdiamond daughter crystals precipitated from supercritical COH + silicate fluids included in garnet, Erzgebirge, Germany, Geology, 29, 391-394.

[3] Cesare, B., Ferrero, S., Salvioli-Mariani, E., Pedron, D. & Cavallo, A. (2009) "Nanogranites" and glassy inclusions: The anatectic melt in

migmatites and granulites, Geology, 37, 627-63

# Fluid inclusions in apatite indicate low-temperature, metasomaticinfiltration origin of the Evate carbonatite deposit (Mozambique)

Vratislav Hurai<sup>1</sup>, Monika Huraiová<sup>2</sup>

<sup>1</sup>Geological Institute, Slovak Academy of Sciences, Bratislava, Slovakia. <u>vratislav.hurai@savba.sk</u>, <sup>2</sup>Department of Mineralogy and Petrology, Comenius University, Bratislava, Slovakia.

The Evate carbonatite deposit located within the Monapo Klippe (structure) in the Nampula province is the largest phosphate deposit of south-east Africa. The deposit is 3 km long and 850 m wide. Phosphate-rich zones, 5-100 m thick, occur within marble horizons conformable to gneisses of the Metachéria Complex. The phosphate-rich zones contain REE-rich fluorapatite, magnetite, pyrrhotite, forsterite, diopside, phlogopite, and graphite [1, 2]. Preliminary reserve estimates calculated by the Intergeo expedition (1985) indicated 155 Mt apatite ore at 9.3 wt. % P<sub>2</sub>O<sub>5</sub> [1]. In addition, a total of 43 Mt of ore with 6.2 %  $P_2O_5$  is exploitable from the regolith zone by simple beneficiation [3].

Origin of the Evate carbonatite is unresolved. A large K-fenite aureole developed around margins supports an intrusive (magmatic) origin. Previous studies have assumed a close genetic relationship with the A-type alkalifeldspar granite and hornblende syenite of the Ramiane pluton that have intruded the eastern part of the Monapo Klippe. Recently, the carbonatite is correlated with the granodiorites and tonalites of the Namialo pluton [4].

There is a consensus that U-Pb ages of zircons from Ramiane and Namialo plutons ranging at  $637\pm5$  Ma reflect intrusive ages [4,5,6]. A  $584\pm16.5$  Ma age of zircon rims and metasomatic embayements in the Ramiane pluton and the surrounding Metacheria metamorphic complex is correlated either with the cooling-related metasomatic event [5] or with a high-pressure metamorphism [4] indicated by the formation of garnet at the expense of amphibole and biotite.

A 590 Ma U-Pb age was determined for zircon from forsterite-rich marbles of the Evate carbonatite deposit [7]. Hence, its origin is correlated either with the high-pressure metamorphism or with the metasomatic event coincidental with the magmatic activity. Preferable accumulation of industrial minerals, particularly apatite and magnetite, along N-S, W-E and NW-SE fracture zones favours the metasomatic-infiltration origin from deep-seated fluids [1].



**Figure 1:** Various types of primary fluid inclusions in apatite. a) Three-phase aqueous inclusion with vapour bubble (V), aqueous liquid (L) and an unidentified solid phase (S). b) Multiphase inclusion with aqueous liquid, halite (H),  $CO_2$  liquid ( $CO_2L$ ) and vapour phases ( $CO_2V$ ), and unidentified solid phases. c) Two-phase, lowsalinity aqueous inclusion with Th = 122°C. d) High-salinity aqueous inclusion with halite. e) Low-salinity gaseous inclusion with barite-celestite (S) growing in the right tip. f) Lenticular and elongated barite-celestite solid inclusions.

Apatite contains primary fluid inclusions, comprising low-salinity two- and monophase aqueous, low-density gaseous inclusions, and high-salinity, high-density multiphase brines.  $CO_2$  liquid phase rarely occurs in the high-salinity aqueous inclusions (Fig. 1).



Figure 2: Uncorrected multidimensional data matrix recorded by a Labram HR800 Raman spectrometer from a multiphase aqueous fluid inclusion in apatite. Raman mapping based on the factor analysis algorithm (DCLS) included in the Labspec5 computer program from Horiba<sup>™</sup> revealed celestite (Ce), calcite (Cal), barite (Bar), hematite (Hem) and laurionite (Lr) daughter crystals precipitating from chloride-sulphate aqueous solution trapped in the apatite (Ap) host. V denotes the vapour bubble. Note additional Ramaninactive solid phases, including large halite crystal (Hal). The laurionite – PbCl(OH) - is invisible under optical microscope, but it was revealed by cluster analysis according to intense bands at 131 and 142  $cm^{-1}$ .

Apart from halite, Raman mapping revealed other daughter minerals: hematite, celestite, barite, carbonates, and laurionite (Fig. 2). Strong sulphate band at 998 cm<sup>-1</sup> and complicated phase transitions in medium-salinity aqueous inclusions are diagnostic of chloride-sulphate solutions with up to 43 wt. % NaCl eq. Maximum CO<sub>2</sub> density was close to that in the critical point, i.e. 0.466 g.cm<sup>-3</sup>.

Character of fluid inclusions excludes primary magmatic or high-pressure metamorphic origin of apatite. Moreover, lacking re-equilibration textures rule out the possibility that the apatite experienced the cooling from high P-T conditions or some metamorphic overprint. Prevalence of primary low-density gaseous inclusions in some apatites and the coexistence of low- and high-salinity inclusions with variable phase proportions are diagnostic of mixing of groundwater with high-salinity,  $CO_2$ -bearing, probably deep-seated fluids, thus favouring the metasomatic-infiltration origin of the apatite ore.

### Acknowledgements

The laboratory of vibrational spectrometry and fluid inclusion thermometry at the Slovak Academy of Sciences was established thanks to financial support from the European Regional Development Fund under the project of the Centre of Excellence for Integrated Research of Geosphere (ITMS-26220120064).

### References

[1] Cílek V. (1989) Industrial minerals of Mozambique. Czech Geological Office, Prague, 326 p.

[2] Manhica A. (1991) Phosphates and apatite of Mozambique. Fertilizer Research 30, 167-175.

[3] Pekkala Y., Kuivasaari T., Gonçalves R, Deus M., Chaúque F. & Almeida C. (2008) Reviews of industrial minerals in Mozambique. Geological Survey of Finland, Special Paper 48, 289-306.

[4] Macey P.H., Miller J.A., Rowe C.D., Grantham G.H., Siegfried P., Armstrong R.A., Kemp J. & Bacalau J. (2013) Geology of the Monapo Klippe, NE Mozambique and its significance for assembly of central Gondwana. Precambrian Research 233, 259-281.

[5] Karlsson J.P. (2006) An investigation of the felsic Ramiane Pluton, in the Monapo Structure, Northern Moçambique. Examensarbeten I Geologi vid Lunds universitet – Berggrundsgeologi, Nr. 202, 39 p.

[6] Jamal D.L. (2005) Crustal studies across selected geotransects in NE Mozambique: differentiating between Mozambiquian (~Kibaran) and Pan-African Events, with implications for Gondwana Studies. PhD Thesis, University of Cape Town, South Africa.

[7] Siegfried P.R. (1999) The Monapo structure and intrusive complex – an example of large scale alkaline metasomatism in northern Mozambique. In: Stanley C.J., Rankin A.H., Bodnar R.J., Naden J., Yardley B.W.D., Criddle A.J., Hagni R.D., Gize A.P., Pasava J., Fleet A.J., Seltmann R., Halls C., Stemprok M., Williamson B., Herrington R.J., Hill R.E.T., Prichard H.M., Wall F., Williams C.T., McDonald I., Wilkinson J.J., Cooke D., Cook N.J., Marshall B.J., Spry P., Khin Zaw, Meinert L., Sundblad K., Scott P., Clark S.H.B., Valsami-Jones E., Beukes N.J., Stein H.J., Hannah J.L., Neubauer F., Blundell D.J., Alderton D.H.M., Smith M.P., Mulshaw S., Ixer R.A.(Eds.), Mineral Deposits: Processes to Processing. Balkema Press, Rotterdam, 683-686

# CH<sub>4</sub>-N<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub>O-NaCl fluid inclusions in Praid salt rock

(Transylvania, Romania)

Orsolya R. Kátai<sup>1</sup>, **Réka Káldos<sup>1</sup>**, Attila Tóth<sup>2</sup>, Csaba Szabó<sup>1</sup>

<sup>1</sup>Lithosphere Fluid Research Lab, ELTE, Budapest, Hungary <u>rekakaldos@gmail.com</u> <sup>2</sup>SAPIENTIA Hungarian University of Transylvania, Cluj-Napoca, Romania

In the close vicinity of the Neogene calcalkaline volcanic chain of the Eastern Carpathians, the sedimentary cover of the Transylvanian Basin is passed through by salt diapirs. One of these salt diapirs at Praid is a well-known geological formation of the eastern part of the Transylvanian Basin [1, 2]. However, textural features and fluid inclusions of the rock salt have not been studied in details up to now.

In this study we present a detailed petrographic description of the rock salt and a preliminary fluid inclusion study in order to reconstruct the tectonic evolution of the salt diapir. According to petrographic study of salt rock by considering the grain size and morphology of the grain boundaries of halite, three types of textures can be distinguished: 1) primary euhedral texture, which composed of 4–15 mm sized, euhedral to subhedral grains of halite, 2) inequigranular sutured mosaic texture composed of 2–10 mm sized, euhedral to subhedral grains, and 3) inequigranular polygonal mosaic texture composed of also 2-10 mm sized, euhedral to subhedral grains but the triple junctions of grain boundaries are nearly 120°. Randomly distributed solid (crystal) inclusions (e.g. dolomite, anhydrite, pyrite, quartz, albite and mica) were identified by Raman spectroscopy in halite. Beside crystal inclusions, large number of fluid inclusions trapped in halite. Based on we petrographic observations, could distinguish two associations of fluid 1) negative crystal shaped, inclusions: maximum 40 µm in size, one phase (liquid, at room temperature) fluid inclusions appearing in growth zones or randomly distributed in halite that are considered as primary fluid inclusions entrapped during crystallization of the halite, and 2) negative crystal, spherical or irregular shaped, maximum 140 µm in size fluid inclusions, usually containing two-phases (liquid+vapor, at room temperature) and situated along healed cracks are considered as secondary ones by applying the definition of Roedder (1984) with respect to the formation of the host mineral. High-resolution (HR) Raman spectroscopic measurements were performed to study the fluid compositions. Primary, one phase (liquid) inclusions are aqueous fluid inclusions with high salinity (32–40 wt. % NaCl eq.). Secondary two-phase (liquid+vapor) fluid inclusions are also aqueous fluid inclusions however, their vapor phase contain  $CH_4$ ,  $N_2$  and  $CO_2$ .

Microtextures of salt rocks, handled as imprints of deformation "frost" in the rock, thus, can reveal its evolution. Inconstant grain size, sinusoidal and straight grain boundaries salt rocks. which construct the of inequigranular sutured mosaic and the inequigranular poligonal mosaic textures indicate traces of deformation. In contrast, straight grain boundaries intersecting each other at 120° triple junctions represent equilibrium state of the rock. The salt textures together with the fluid inclusion petrography show a complex deformation history of the salt rock. The presence of  $CH_4$ ,  $N_2$  and  $CO_2$  in the vapor phase of the secondary fluid inclusions indicates that these components were probably added to the system during deformation event(s) after the salt formation. Further study of these samples can be an important tool in the study of the diapir forming processes on the eastern part of the Transylvanian Basin.


*Figure 1:* Negative crystal shaped primary aqueous fluid inclusion in halite, 1N.



**Figure 2:** Negative crystal shaped secondary one (aqueous) and two-phase (aqueous+vapour) fluid inclusions in halite, 1N.

#### References

[1] Krézsek, Cs. and Bally, A.W. (2006) The Transylvanian Basin (Romania) and its relation to the Carpathian fold and thrust belt: Insights in gravitational salt tectonics. Marine and Petroleum Geology, 23, 405–442.

[2] Har, N. et al. (2010) New data on the mineralogy of the salt deposit from sovata (mures county-romania). Carpathian Journal of Earth and Environmental Sciences, 5, 127–135.

### Genetical study of the fluorite veins of Pécsely (Balaton Highland, Transdanubian Mountain Range, NW-Hungary)

**Zsuzsa Molnár<sup>1</sup>**, Gabriella B. Kiss<sup>1</sup>, István Dunkl<sup>2</sup>, Tamás Váczi<sup>1</sup>, Federica Zaccarini<sup>3</sup>, & István Dódony<sup>1</sup>

<sup>1</sup>Department of Mineralogy, Eötvös Loránd University, Budapest, Hungary molnarzsuzsa89@gmail.com; <sup>2</sup>Department of Sedimentology & Environmental Geology, Geoscience Center, University of Göttingen, Göttingen, Germany; <sup>3</sup>Department of Applied Geosciences and Geophysics, University of Leoben, Leoben, Austria;

The studied area is located in the Transdanubian Mountain Range, on the southern part of the ALCAPA Megaunit, at the northern side of the Periadriatic-Balaton Lineament System. The Transdanubian Mountain Range was originally situated in a transitional position between the Southern and Eastern Alps. It was pulled out of the Alpine collision zone along with the Velence Mts. during the Late Palaeogene-Early Neogene [1].

Earlier investigations have revealed а radioactive anomaly in the vicinity of Pécsely and Vászoly, which is assumed to be related to a uranium-bearing sedimentary phosporite occurrence. This phosphorite layer, together with some fluorite veins, is located in Triassic limestone and dolomite. It is thought that the fluorite veins formed through the leaching of the carbonate-fluorapatite (the main mineral of the phosphorite layer), but the details of this process is still not known [2]. Therefore, this study aims to answer a few open questions using fluid inclusion study, completed by Raman spectroscopy and geochemical analyses.

Euhedral deep purple zoned fluorite grains (0.1-2 mm) found together with calcite and dolomite in veins and cavities below the phosphorite layers. Finely dispersed fluorite can also be found in the matrix of the host dolomite, in which brecciated clasts of the phosphorite layers can be also found. The cathodoluminescence image of the fluorite shows a fine zonation (*Figure 1*). Raman spectroscopic investigations showed that the purple colouration is caused by strong structural disorder in very fine zones.

Quantitative analyses of the fluorite showed that it contains ~0.01 wt% U and <0.174 wt% total REE (Nb, Dy, Sm, Gd, Eu). The elemental mapping revealed that its REE content is most likely related to submicron sized REE mineral inclusions. Based on ICP-MS investigations, the fluorite shows slight depletion in LREE, while slight enrichment in HREE content is also observable.



**Figure 1:** CL image of finely zoned fluorite grains.

Fluid inclusion study was carried out on the primary and secondary, two-phase, liquid (L) and vapour (V) fluid inclusions in fluorite crystals. Four fluid inclusion assemblages (FIA) were distinguished: a primary (P) and three secondary (S1, S2 and S3). The constant area% of the vapour and liquid phase of the primary inclusions (V=15-20%, L=85-80%) suggest a homogeneous parent fluid. The minimum formation temperature of the P varies between 75-169 inclusions °C (Th=109.2 °C, st.dev.=21.9 °C), whereas the eutectic melting point scatters around -51 °C, suggesting a NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O system. The total salinity varies between 16.23-21.73 NaCl equiv. wt% (0.71-6.14 wt% CaCl2 and 12.44-20.64 wt% NaCl) (Figure 2). The constant area% of the vapour and liquid phase of the S1 inclusions (V=5-10%, L=95-90%) also suggest a homogeneous parent fluid. The minimum formation temperature of the S1 inclusions between 42-121 °C (Th=72 °C. varies st.dev.=12.07 °C) and, based on the eutectic melting points of the inclusions, a NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O system is suggested, too. The total salinity varies between 17.35-22.37 NaCl equiv. wt% (0.65-14.36 wt% CaCl2 and 6.1522.01 wt% NaCl). The fluid inclusion microthermometry measurement was completed by Raman spectroscopic analyses, and the salinities calculated on the basis of the Raman spectra of the aqueous phases match the results from microthermometry (P inclusions: 21.83 NaCl equiv. wt% and S1 inclusions: 20.07 NaCl equiv. wt%.) and verify the validity of this approach [3]. Based on Raman spectroscopy, the vapour phase of the P and S1 inclusions contains H<sub>2</sub> gas. These data suggest that the S1 inclusions formed shortly after the mineral formation (i.e. after the P inclusions), from the same hydrothermal fluid, during the waning of the system.



*Figure 2:* Salinity versus homogenisation temperature diagram of the primary inclusions of fluorite

The origin of the fluorite forming fluid is still uncertain, but the above mentioned characteristics propose the possibility of the establishment of a regional fluid circulation system, with magmatic and/or diagenetic fluid components. The  $H_2$  in the fluorite inclusions may originate from the U-bearing phosphorite layer, found above the fluorite veins [4].

The existence of a possible regional fluid circulation system may be proven by considering a similar fluorite occurrence in the Velence Mts. (~80 km to the east from Pécsely). That locality is situated on the northern side of the Periadriatic-Balaton Lineament System, on the southern part of the Trandanubian Mountain Range. The Velence Mts. is mostly built up by a Variscan postcollisional or synextensional, 274-290 Ma monzogranite [5]. Triassic fluid mobilization event (209-232 Ma) with epigenetic lead-zinc sulphide mineralization was found there, along with the presence of fluorite. The formation conditions of the fluorite are similar to the ones found in Pécsely (fluorite: Th=90-130 °C; 8-13 NaCl equiv. wt%, sphalerite: 80-160 °C, 18-23 CaCl<sub>2</sub> equiv. wt%, hydrothermal quartz: 80-130 °C, 10-25 CaCl<sub>2</sub> equiv. wt%) [6], which supports the possibility of their precipitation from the same regional fluid migration event.

#### Acknowledgements

The University Centrum of Applied Geosciences (UCAG) is thanked for the access to the E. F. Stumpfl Electron Microprobe Laboratory, Leoben. The CL imaging was supported by the European Union and co-financed by the European Social Fund. The ELTE Faculty of Science Research Instrument Core Facility is thanked for the access to the Raman laboratory. The ICP-MS measurements were performed at the University of Göttingen.

#### References

[1] Balla Z. (1985) The Carpathian loop and the Pannonian Basin: a kinematic analyses, Geophysical Transactions, 30, 313-353.

[2] Kiss J. & Virágh K. (1959) An uraniumbearing phosphatic rock in the Triassic of the Balaton Uplands around Pécsely, Földtani Közlöny, 89, 85-97.

[3] Sun Q., Zhao L., Li N. & Lui J. (2010) Raman spectroscopic study for the determination of Clconcentration (molarity scale) in aqueous solutions: Application to fluid inclusions, Chemical Geology, 272, 55-61.

[4] Dubessy J., Pagel M., Beny J.M., Christensen H., Hickel B., Kosztolanyi C. & Poty B. (1988) Radiolysis evidenced by H2-O2 and H2-bearing fluid inclusions in three uranium deposits. Geochimica et Cosmochimica Acta, 52, 1155-1167.

[5] Buda Gy., Koller F. & Ulrych J. (2004) Petrochemistry of Variscan granitoids of Central Europe: correlation of Variscan granitoids of the Tisia and Pelsonia terranes with granitoids of the Moldanubicum, Western Carpathians and Southern Alps, A review: part I. Acta Geologica Hungarica, 47, 117-138.

[6] Benkó Zs., Molnár F., Lespinasse M., Billström K., Pécskay Z. & Németh T. (2014) Triassic fluid mobilization and epigenetic leadzinc sulphide mineralization in the Transdanubian Shear Zone (Pannonian Basin, Hungary), Geologica Carpathica, 65, 177-194.

### Contribution to the genesis of the Covide layered pegmatite (Portugal)

António Moura<sup>1</sup>, Jens Götze<sup>2</sup>, Stuart Kearns<sup>3</sup>

<sup>1</sup>Departamento de Geociências, Ambiente e Ordenamento do Território. Faculdade de Ciências, Universidade do Porto, Portugal and C.G.U.P. (ajmoura@fc.up.pt). <sup>2</sup>TU Bergakademie Freiberg Institut für Mineralogie Brennhausgasse 14 D-09596 Freiberg, Germany. <sup>3</sup> School of Earth Sciences, University of Bristol, GB.

The Covide pegmatite exhibit an unusual striped texture of centimetric layers of Kfeldspar/albite alternating with quartz (Figure 1a). The outcrop is almost circular with about a dozen meters, emerging in an old exploitation of feldspar, near the Covide settlement, about 5 km west of the village of Gerês. The upper and middle part of the intrusion also contains crystals of black tourmaline, willing to radial manner. The country rock is the late-D3 Vieira do Minho granitic pluton interpreted as generated from two different batches of magma of metaigneous crustal sources, around 311±3 Ma [2]. One km to NE outcrops the Gerês post-D3 granite [3]. It is not certain to which intrusion the pegmatite are related [1]. The quartz bands are between 2 feldspar bands, which begin with a millimetric albitic band followed by one or two K-Feldspar generations (Figure 1b). Occasionally we can see small miarolitic cavities in the feldspar bands.



*Figure 1: a-* Sample from the Covide pegmatite (Portugal). *b-* Quartz-Feldspar zonation (adapted from [1]). g.- generation.

In this study the following techniques were applied: fluid inclusion (FI) petrography, cathodoluminescence, microprobe analysis (Ti in quartz), microthermometry and Raman spectroscopy on selected aqueous-carbonic fluid inclusion in quartz. CL measurements were done on a "hot cathode" CL microscope HC1-LM. The system was operated at 14 kV accelerating voltage and a current of 0.2 mA (current density of about 10 µA/mm2). CL spectra in the wavelength range 380 to 920 nm were recorded. Microthermometric characterization of the fluids was performed using a heating-freezing Chaixmeca stage for cryometry, and a Linkan 600 stage for the heating studies. The accuracy was  $\pm 0.1$  °C during cryometry and  $\pm 1$  °C during heating. Both stages were periodically calibrated using synthetic fluid inclusions (SynFlinc). The Analyses were performed on a Cameca SX100 Electron Probe Microanalyser (EPMA) operating at 20 kV accelerating voltage and 80 nA beam current.

The quartz shows the typical short-lived blue (greenish) CL of pegmatite quartz. The luminescence almost disappears after electron irradiation of 120 s. Albite has blue-violet CL. This feldspar contains considerable amounts of REE, which are identifiable by their typical sharp emission lines. In general, feldspars in all layers and all quartz bands show similar luminescence characteristics, which suggest coeval formation.

Quartz is homogenous, macrocrystalline with several centimetres and full of FI. There are two distinct FI population: the majority (more than 95% of the inclusions) is a water-rich low salinity fluid (Lw), the other is an aqueous--carbonic fluid (Lc-w) very often triphasic  $(CO_2 \text{ liquid, } CO_2 \text{ vapour and liquid water) at}$ room temperature. The FI are randomly distributed in the quartz with occasional water fluid inclusion in intragranular trails. The last melting of ice in the Lw fluids are in the range 0.0/-6.0°C and the final homogenization temperatures (Th) between 170 and 300°C. The Lc-w fluids has final melting of CO<sub>2</sub> between -58.0 and -57.4°C (mode at -57.5°C), clathrate melting around +6.5/+9.8°C(mode = 7.2°C),  $CO_2$  homogenization (ThCO<sub>2</sub>) in the range +13.5/+27.0 [mode = 24.4°C (L)] mainly in liquid. Most of these fluid inclusions decrepitate between 300-350°C, only a few attained Th before decrepitating at higher temperature, and the Th are between 300/320°C. Composition of the Lw fluids varies in the range (moles %) 94.1-100% H<sub>2</sub>O and 0-5.9% NaCl. Volatile composition of the Lc-w fluids are in the range 92.0-96.3% CO<sub>2</sub> the remaining being N<sub>2</sub>. Total composition for this fluids are (moles %) 74.0-85.1% H<sub>2</sub>O, 15.9-4.0% CO<sub>2</sub>, 0.6-0.1% N<sub>2</sub>, 4.8-1.1 both Na<sup>+</sup> and Cl<sup>-</sup>. Densities varies from 0.80-0.95 (Lw fluids) and 0.80-0.85 (Lc-w fluids). Compositions and isochores were calculated using [4].

The geothermometer TitaniQ [5] was used. For that, 54 measurements of the Ti content, each around 8 minutes, were performed with the microprobe. The higher value was 209 ppm and the lower 0 ppm. Half (26) measurements were above the detection limit (D.L.=14 ppm Ti). The average was 20 ppm Ti, and the average above the D.L. was 43 ppm. Within the limits of the EPMA, the data suggest that the quartz is inhomogeneous in respect to Ti content, and that the temperature of formation was probably <580°C (<20 ppm Ti), which is in agreement with the Rare Elements/ Miarolitic pegmatite fields (Figure 2) and the fluid inclusion study.



*Figure 2: P*-*T* field for pegmatites, according with published data [6].

The isochoric path of coeval  $H_2O-CO_2-N_2$ -NaCl and  $H_2O-NaCl$  fluids suggests their entrapment at 100 MPa and 330°C and limits the depth of entrapment at 10 km (pressure must have been hydrostatic for meteoric water *43*, 2005-2026.

descent). At this depth and under lithostatic pressure the aqueous-carbonic magmatichydrothermal fluid was at 580-510°C and 265 MPa. The penetration of the H<sub>2</sub>O-NaCl fluids down to 10 km changed the fluid regime to hydrostatic. Mixing of the two fluids and a decrease in temperature, destabilized the hydrothermal system causing precipitation. According with [1] layering was a consequence of horizontal convective stratification of a water-rich magmatic fluid at low viscosity in a temperature and composition (Na,K) gradient regime.

#### Acknowledgements

We are grateful to the Portuguese Foundation of Science and Technology (FCT) for financial support. Fernanda Guimarães (LNEG) and are thanked for their help with microprobe analysis. The measurements in laser Raman were possible by the presence and assistance of Armanda Dória, which we are very grateful.

#### References

[1] Gouanvic, Y. & Gagny, C. (1987) Contribution à l'étude des litages pegmatitiques: l'exemple de la pegmatite de Covide) Nord-Portugal), Geologische Rundschau 71, 1, 125-135.

[2] Martins, H.C.B., Sant'Ovaia, H. & Noronha, F. (2013) Late-Variscan emplacement and genesis of the Vieira do Minho composite pluton, Central Iberian Zone: Constraints from U–Pb zircon geochronology, AMS data and Sr–Nd–O isotope geochemistry, Lithos, 221–235.

[3] Neiva, A.M.R. (1993) Geochemistry of granites and their minerals from Gerez Mountain, northern Portugal, Chem. Erde, 53, 227–258.

[4] Bakker, R.J., (2003) Package FLUIDS 1. Computer programs for analysis of fluid inclusion data and for modelling bulk fluid properties. Chem. Geology 194, 3–23.

[5] Wark, D.A. & Watson, E.B. (2006) TitaniQ: a titanium-in-quartz geothermometer, Contrib. Mineral. Petrol., 152, 743-754.

[6]Černý, P. & Ercit, T.S. (2005) The classification of granitic pegmatites revisited, Canadian Mineralogist,

# *P-T-X* conditions of hydrothermal fluids of base-metal-gold mineralization at the Tesbihdere deposit, Biga Peninsula, NW Turkey

**Fatih Ozbas<sup>1</sup>** Gulcan Bozkaya<sup>2</sup> David A Banks<sup>3</sup>

<sup>1</sup>Department of Geological Engineering, Istanbul University, Istanbul, Turkey

<sup>2</sup>Department of Geological Engineering, Pamukkale University, Denizli, Turkey

<sup>3</sup>School of Earth and Environment, University of Leeds, Leeds, UK.

The Biga Peninsula in NW Turkey hosts a variety of Au-Ag, porphyry Au-Cu-Mo, Fe skarns and epithermal Pb-Zn- Cu-Au deposits and is one of the most actively explored and exploited. Mineralization is related to the closure of the Tethys Ocean and forms part of the Tethyan Eurasian Orogenic Belt that extends to the east eventually joining the Pacific Metallogenic Belt.

The Cu-Pb-Zn-Ag-Au mineralization in this area are largely found in five discrete localities: going from north to south these are the Azitepe, Sarikayalar, Sarioluk, Basmakci and Tesbihdere sectors. (Figure 1). In the Tesbihdere sector, the host rocks are andesitic lavas, whereas in the Azıtepe, Sarıkayalar Basmakci and Sarioluk sectors the host rocks are rhyolitic, dacitic and trachyandesitic pyroclastic rocks with rhyolitic and dacitic lava intercalations Based on the field and petrographic observations, two styles of mineralization redominate in the andesitic lavas: vein-type and stockwork-type. All mineralization in the investigated area exhibit fault-controlled features: a brecciated matrix consisting of veins and vein fragments of medium to coarse-grained quartz. The ore veins are predominantly in WNW-ESE striking fault zones where the volcanic rocks have been extensively altered by the passage of hydrothermal fluids with extensive and widespread argillic alteration along with sericitization and silicification

The sulphide veins consist of primary chalcopyrite, galena, pyrite and sphalerite with lesser amounts of tetrahedrite, chalcocite, covellite, goethite, boulangerite and cerrusite, which are mainly secondary. Pyrite is the most common mineral as euhedral cubes and subhedral crystals of variable size. Mineral assemblages indicate that pyrite was likely the



*Figure 1:* Location and local geology of the main mineralized sectors [1].

forming primary earliest of phase. Fragmentation is commonly observed where early formed pyrite has become fractures and deformed by later phases.Chalcopyrite is the second-most common mineral as anhedral crystals and it is found mainly with galena and Fahlore minerals (tetrahedritepvrite. tennantite) are seen along the fractures of chalcopyrite. Goethite is widespread typically replaced with altered chalcopyrite. Chalcocite and covellite are found along the grain boundaries and fractures in chalcopyrite and considered as one of secondary minerals. Sphalerite appears with chalcopyrite and chalcopyrite disease is often observed. Galena has an intimate relationship with chalcopyrite and sphalerite, and has been replaced by anglesite and cerussite by supergene alteration.

Tesbihdere is one of a number of spatially close epithermal Cu-Pb-Zn-Ag-Au deposits hosted by andesites and rhyolites, typical of deposits in the Biga peninsula. Microthermometry of fluid inclusions shows a wide range of temperatures,  $\sim 360 - 170^{\circ}$ C, and salinities, ~10 - 0.5 wt.% NaCl, in the different deposits studied. Dilution of a moderately saline magmatic? fluid with meteoric water occurred at constant temperature indicating, the temperature of both fluids was controlled by the geological environment. Boiling was not a major factor, but did occur in very minor amounts. The large range of temperatures within individual samples can only reasonably be explained by variations from near lithostatic to hydrostatic pressure during vein and fracture opening. That this pressure decrease did not produce extensive boiling suggests that vein opening was gradual rather than allowing the aggressive, pressure and temperature decrease to follow a path close to the L-V boiling curve. P-T reconstruction places emplacement of these ore veins at between 300 - 500m beneath the surface.

Similarities of LA-ICPMS of fluid inclusions from Tesbihdere, Azitepe and Basmakci, supports the conclusion that they were part of the same contemporaneous mineralizing system. The fluids are dominated by Na, with the concentrations of K>Ca>Mg combined equivalent to the concentration of Na. The range of K/Na ratios is not consistent with the fluid inclusion temperatures as the calculated significantly temperatures are higher indicating the fluids were not close to equilibrium with the enclosing rocks. Elevated K concentrations are consistent with acid-sulphate waters in shallow epithermal systems. Ore metals Cu, Zn and Pb are present in significant concentrations ~500, 300 and 200 ppm respectively and the low Fe/Mn ratios are indicative of a relatively oxidising fluid. The negative  $\delta^{34}$ S values of sulphides are consistent with boiling and oxidising redox.



*Figure 2:* P-T-depth of the mineralized veins. Temperature variability is consistent with Lithostatic to Hydrostatic pressure variation [2].

#### Acknowledgements

This work was supported by the CUBAP (Cumhuriyet University Scientific Research Projects Coordination Unit) Project No: 447.

#### References

[1] Ozbas, F., Bozkaya, G. and Banks, D., 2013. Mineralizing fluids in the Tesbihdere base-metal-Au deposit Biga Peninsula, NW Turkey: Analyses from LA-ICP-MS of fluid inclusions. European Current Research on Fluid Inclusions (ECROFI-XX11), Antalya, TURKEY, 4-9 June. Abstract Volume, p.92., 2013.

[2] Bozkaya G, Banks DA, Ozbas F and Wallington J., Fluid processes in the Tesbihdere base- metal-Au deposit: Implications for epithermal mineralization in the Biga Peninsula, NW Turkey. CEJG, 6 (2), 148-169. (2014)

## Fluid inclusion study in metamorphic veins from the Luarca sector (Asturias, northern Spain): role of fluid pressure in veining

Jorge Pérez-Alonso<sup>1</sup>, Mercedes Fuertes-Fuente<sup>1</sup> & Fernando Bastida<sup>1</sup>

<sup>1</sup>Department of Geology, University of Oviedo, Jesús Arias de Velasco s/n 33005, Oviedo, Spain. <u>mercedf@geol.uniovi.es</u>

#### Introduction

Veins occur in different ways in the Earth crust, and are a valuable source of information for diverse geological disciplines. Quartz veins are common in the Westasturian-Leonese Zone (WALZ), which is an internal zone of the NW Iberian Variscan belt. Along the Cantabrian coast, in the vicinity of Luarca, a sector stands out for the profusion of quartz veins. The study of these veins allows us to better understand the brittle deformation in an overall compressional tectonic regime and to complete the geological history of this area. The present work focuses on the fluids involved in the genesis of these veins and the P-T regime. For this, a fluid inclusion study and mineralogical studies, including SEMcathodoluminescence (SEM-CL) and mineral thermobarometry, have been done in these veins.

#### **Geological Setting**

The Luarca sector is located in the eastern part of the WALZ and characterized by a siliciclastic Ordovician succession. Three main Variscan deformation phases have been recognized in the WALZ, two of them (D<sub>1</sub> and D<sub>3</sub>) are represented in the area: D<sub>1</sub> with tight folds verging toward the external zones and associated cleavage (S<sub>1</sub>), and D<sub>3</sub> with asymmetric open folds, upright or verging westward, and crenulation cleavage (S<sub>3</sub>). Subsequently, late-orogenic structures, mainly sub-horizontal kink bands, were developed [1] [2].

#### Vein description

The veins are mainly hosted by slates, mostly pyrite-rich black slates, and by quartzites. The veins roughly follow the slaty cleavage  $S_1$  and are composed of quartz and, in less proportion, chlorite (ripidiolite), ankerite, white mica, apatite and base-metal sulphides (pyrite, chalcopyrite, sphalerite and galena).

Shortening undergone by the  $S_1$  at the beginning of the  $D_3$  folding produced relaxation in the perpendicular direction to the foliation  $S_1$  and enabled development of veins, subsequently which were folded and plastically deformed during the progress of the D<sub>3</sub>. In quartz infillings, it is possible to distinguish recrystallized new grains and old grains ("old quartz"). SEM-CL images of them show CL-dark quartz with nearly homogenous to mottled textures that are distinctive of metamorphic quartz. Moreover, there are microcracks outlined by fluid inclusions trails and healed by other quartz generation that is CL-brighter. In some cases, younger veintlets that even crosscut the healed microcracks occur. They are infilled by quartz with cathodoluminescence oscillatory zoning.

#### Mineral thermobarometry

Trace-elements in quartz from representative veins were analyzed by LA-ICP-MS in order to use titanium-in-quartz thermobarometry [3]. Ti-contents were homogeneous among old quartz grains, with an average interval of 2.2-3.7 ppm. These contents were used to construct Ti-in-quartz isopleths. These were combined with the isochores obtained from the fluid inclusion study. As regards the last quartz generation with CL-oscillatory zoning, the Ticontent average is similar (2.8 ppm). However, it shows Li and Al in higher amounts and a striking variation in trace element contents along LA-ICP-MS line rasters in a single quartz crystal.

Furthermore, the composition of the chlorite from the veins was used with two geothermometers [4] [5]. The obtained temperature averages for each one are 410°C and 375°C, respectively.

#### Fluid inclusion study

Quartz sampled from veins was collected for fluid inclusion petrography and

microthermometry. Three fluid inclusion types were recognized in all the sampled veins:

1. Aqueous-carbonic fluid inclusions (Type I). They form three-dimensional arrays in "old quartz" being primary or pseudosecondary. Two subtypes are distinguished, Ia and Ib. The former shows higher volumetric fraction of the aqueous phase  $\varphi_{liq}$  =0.7-0.95 (being in Ib  $\varphi_{liq}$ =0.4-0.8) and the carbonic phase is only detected by clathrate nucleation. Both subtypes occur in the same way in quartz crystals and, often, forming part of the same fluid inclusion assemblage (FIA). We consider very close temporal relations between them. Subtype Ib FIs show consistently  $T_m(CO_2)$  = -56.6 °C and  $T_h(CO_2)$  from 21.4 °C to 30.5 °C in the liquid and critical phases.  $T_m(ice)$  ranges from -7.5 °C to -0.2 °C and  $T_m(cla)$  is from 6.7 °C to 10.5 <sup>o</sup>C. The total homogenization  $T_h(total)$  for subtype Ib FIs have two modes, 275°C and 335°C in the liquid phase, and for subtype Ia FIs has a mode of 225 °C in the liquid phase.

2. Aqueous fluid inclusions (Type II). They occur as transgranular fluid inclusion planes (FIPs). They have  $\varphi_{liq} = 0.8-0.95$ . T<sub>e</sub> is around -20.8 °C and  $T_m(ice)$  is from -2.5 °C to -0.2 °C.  $T_h(total)$  is between 140 °C and 251 °C in the liquid phase.

3. Halite-bearing aqueous fluid inclusions (Type III). They have only been found as primary fluid inclusions in the last generation of quartz with CL-oscillatory zoning. The  $\varphi_{liq}$  =0.8-0.95. The liquid–vapour homogenization temperature is from 136 °C to 181 °C in the liquid phase. Total homogenization by halite dissolution is at temperatures of 200±5 °C.

#### Conclusions

The old quartz precipitated from the aqueouscarbonic fluid, thus, the composition of the fluid involved in the formation of the veins is 0.875-0.936 XH<sub>2</sub>O, 0.041-0.110 XCO<sub>2</sub> and 0.015-0.023 XNaCl. After the plastic deformation, an aqueous low-salinity fluid (0.994 XH<sub>2</sub>O and 0.006 XNaCl) circulated during later microfracturing events related to the FIPs of type II fluid inclusions. Lastly, the veins record the circulation of younger brine (32 wt.% NaCl) represented by Type III fluid inclusions. The timing of this fluid circulation is uncertain and we lack of criteria to consider this paleofluid linked to the Variscan orogeny. Considering the aqueous-carbonic fluid as the vein-forming fluid, isochores of type I fluid inclusions were calculated in distinct veins.  $P_{h}$ - $T_h$  pair varies from 250 °C and nearly 25 MPa to 350°C and up to 100 MPa. As constraints on the real trapping conditions, Ti-isopleths and chlorite geothermometers were combined with these isochores. The P-T values obtained are around 375°C with a corresponding pressure interval from 220 MPa to 85 MPa. Fluid pressure shows differences in FIAs from the same vein close to 140 MPa. Considering the lack of evidence for the trapping of these FIAs in a separate time, or for significant postentrapment modifications, we suggest that these veins formed at constant depth with fluid pressure fluctuating from lithostatic to infralithostatic, or even, hydrostatic values. It could be due to pressure drops during sudden enlargement of emerging open spaces after local fluid overpressure. It happened in discrete sites where  $D_3$  deformation favoured the relaxing of foliation  $S_1$ .

#### Acknowledgements

This work has been financed by CGL2011-23628 project from Spanish government and supported by a FPI grant to Jorge Pérez-Alonso.

#### References

[1] Marcos, A. (1973). Las series del Paleozoico inferior y la estructura herciniana del occidente de Asturias (NW de España). Trabajos de Geología, Univ. Oviedo, 6: 1-113

[2] Pulgar, J. A. (1980.) Análisis e interpretación de las estructuras originadas durante las fases de replegamiento en la Zona Asturoccidental-leonesa (NW de España). PhD dissertation, Univ. Oviedo, 334 pp.

[3] Thomas J. B., Watson E. B., Spear F. S., Shemella P. T., Nayak S. K. & Lanzirotti A. (2010). TitaniQ under pressure: the effect of pressure and temperature on the solubility of Ti in quartz. Contrib. Mineral. Petrol., 160, 743–759.

[4] Cathelineau, M. (1988). Cation site occupancy in chlorites and illites as a function of temperature. Clay Minerals, 23, 471-485.

[5] Kranidiotis P. & MacLean W.H. (1987). Systematics of chlorite alteration at the Phelps Dodge massive sulfide deposit, Matagami, Quebec. Economic Geology, 82, 1898-1911.

## Mineralizing Fluids of Two Stage Au Mineralization of Pionersky Ore Cluster, North-East Russia

Vsevolod Yu. Prokofiev, Alexandr V. Volkov, Evgeniya E. Tyukova

Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 119117 Russia, vpr@igem.ru

Gold deposits Igumenovskoe and Rodionovskoe locate at North-East Russia and are the parts of Pionersky ore cluster. These two deposits pertain to vein type gold deposits in terrigenous rocks. The main minerals of vein type gold ores are quartz, pyrite, arsenopyrite, gold (fineness of 870–940‰). The sedimentary terrigenous rocks of Permian age overlapping by rocks of Okhotsko-Chukotsky volcanic belt are the host rock for Au veins. The deposits under consideration are structurally controlled by Ten'kinsky deep fault as well as a number of other deposits in this region including the large gold deposits Natalka and Pavlik. The Au quartz veins are of Early Cretaceous age (135-137 Ma) (the first stage of ore deposition).

Near the turn of the Early and Late Cretaceous (105-112 Ma) the multiphase granitoid massif Ulakhan has intruded into sedimentary rocks in close proximity to deposits of Pionersky ore cluster. This has caused the formation of pyroxene hornstones from the sedimentary rocks, the partially recrystallization of ores at Rodionovskoe and Igumenovskoe deposits and the generation of stockwork-type ores. These ores can be attributed to the second stage of deposition. The gold fineness in ore stockwork-type ores is lesser than in previous case (of 720-870‰). Loellingite, bismuthine, electrum, küstelite and silver minerals appear here in the associations with Au.

Fluid inclusions have been studied in double polished plates, first optically, then with a THMSG-600 'Linkam' freezing/heating stage equipped with Olympus-80 objective at IGEM RAS, Moscow, Russia. Precision at low temperature (cooling) was about 0.1-0.2 °C and about 1 °C at high temperature (heating). Salinity was estimated from final ice melting temperature. The salt composition dominant in aqueous solutions was estimated from the measured eutectic temperature [1]. The total concentration of salts in fluid inclusions of type III was estimated from the temperature of

ice melting on the basis of experimental data for the NaCl–H<sub>2</sub>O system [2]. The salt concentration in inclusions with a high CO<sub>2</sub> content (type I) was estimated from the melting temperature of gas hydrates [3] because most values of the gas hydrate melting temperature were below  $\pm 10^{\circ}$ C. The pressure was determined for heterogeneous fluids by the intersection of the isochore and isotherm. The salt concentration, density, and fluid pressure were estimated using the FLINCOR program [4].

Two types of fluid inclusions were found in the first stage quartz from gold veins of the Igumenovskoe and Rodionovskoe deposits: 1) two-phase (at room temperature) carbon dioxide-aqueous inclusions with a large gas bubble filled with liquid carbon dioxide and 2) substantially gaseous inclusions also containing liquid carbon dioxide (three-phase with the carbon dioxide gas bubbles coated by the aqueous solution rims). Gas inclusions captured synchronously with the carbon dioxide-aqueous inclusions (confined to the same zones or cracks) indicate to а heterogeneous state of the fluid.

Homogenization temperature of the carbon dioxide-aqueous inclusions of the type 1 in the quartz Au vein is 344-275 °C, concentration of salts in the solution is 4.3-10.0 wt. %-eq. NaCl and the carbon dioxide concentration is 7.5-1.7 mol per kg of solution. Judging by the eutectic temperature (-31 to -38 °C) sodium and magnesium chlorides are the dominant species in the solution.

Carbon dioxide in the mostly gaseous inclusions of the type 2 homogenized into the liquid at temperatures of +6.3 to +25.5 °C, and its melting point varies from -57.6 to -60.5 °C, which is slightly below the melting point of pure CO<sub>2</sub> (-56.6 °C) and indicates the presence of the impurities of low-boiling gases. The density of carbon dioxide is 0.70-0.89 g/cm<sup>3</sup>.

The evaluation of pressure from the data of these two types of syngenetic inclusions gives 1060-2250 bar (4.0-8.6 km according to lithostatic gradient).



Figure 1: Diagram "temperature versus pressure" of ore-forming fluid.

1, 2 – Rodionovskoe deposit (1 – stage 1, 2 – stage 2); 3, 4 – Igumenovskoe deposit (1 – stage 1, 2 – stage 2).

Three different types of fluid inclusions were found in second stage quartz from the stockwork-type ores of the Igumenovskoe and Rodionovskoe deposits: 1) two-phase (at room dioxide-aqueous temperature) carbon inclusions with a large gas bubble filled with liquid carbon dioxide; 2) substantially gaseous inclusions also containing liquid carbon dioxide (three-phase with the carbon dioxide gas bubbles coated by the aqueous solution rims), and 3) gas-liquid two-phase aqueous solutions. Gas inclusions captured synchronously with the carbon dioxideaqueous inclusions (confined to the same zones or cracks) indicate to a heterogeneous state of the fluid.

Homogenization temperature of the carbon dioxide-aqueous inclusions of the type 1 in the second stage quartz is 321-293 °C, concentration of salts in the solution is 7.9-8.2 wt. %-eq. NaCl and the carbon dioxide concentration is 6.6-2.4 mol per kg H<sub>2</sub>O of solution. Judging by the eutectic temperature (-31 to -37 °C) sodium and magnesium chlorides are the dominant species in the solution in this case too.

Cryometric studies showed that the two-phase inclusions of the type 3 are solutions containing chlorides of Na and Mg (eutectic temperature in the range from -31 to -36 °C) with the concentration of salts of 1.2-8.4 wt. % -eq. NaCl (ice melting temperature from -31 to -36 °C), the homogenization temperature of 137-447 °C and the density of 0.47-0.94 g / cm<sup>3</sup>.

Carbon dioxide in the mostly gaseous inclusions of the type 2 homogenized into the vapor at temperatures of +10.2 to +23.9 °C, and its melting point varies from -57.8 to -61.4 °C, which is slightly below the melting point of pure CO<sub>2</sub> (-56.6 °C), what indicates the presence of the impurities of low-boiling gases. The density of carbon dioxide is 0.14-0.23 g/cm<sup>3</sup>. The evaluation of pressure from the data for the pairs of syngenetic inclusions of the types 1 and 2 and types 2 and 3 gives 140-650 bar (1.4-6.5 km according to hydrostatic gradient).

The significant pressure drop between the fluids of two stages of gold mineralization formation indicates a change in the depth of ore deposition over the period of time separating them. This can be associated with the lifting of ore-bearing rock block for 2-3 km and the simultaneous erosion.

#### Acknowledgements

This study was supported by the Russian Science Foundation (project № 14-17-00140).

#### References

[1] Borisenko A.S. (1977) Study of Salt Composition of Fluid Inclusions in Minerals with Cryometric Method, Geologiya i Geofizica, 18, 8, 16–27.

[2] Bodnar R.J. and Vityk M O. (1994) Interpretation of Microthermometric Data for H<sub>2</sub>O–NaCl Fluid Inclusions," in Fluid Inclusions in Minerals: Methods and Applications, Siena, Pontignano, 117–130.

[3] Darling R. S., "An Extended Equation to Calculate NaCl Contents from Final Clathrate Melting Temperatures in H2O–CO2–NaCl Fluid Inclusions: Implications for P–T–Isochors Location," Geochim. Cosmochim. Acta 55, 3869– 3871 (1991).

[4] Brown P. (1989) FLINCOR: a Computer Program for the Reduction and Investigation of Fluid Inclusion Data, American Mineralogist, 74, 1390–1393.

## Cyclic injection of metal-rich high-salinity magmatic fluids leading to the formation of the giant base metal deposit of Cerro de Pasco, Peru

Bertrand Rottier<sup>1</sup>, Kalin Kouzmanov<sup>1</sup>, Markus Wälle<sup>2</sup>, Lluís Fontboté<sup>1</sup>

<sup>1</sup> Section of Earth and Environmental Sciences, University of Geneva, 1205 Geneva, Switzerland

(\*correspondence: <u>Bertrand.Rottier@unige.ch</u>)

<sup>2</sup> Institute of Geochemistry and Petrology, ETH Zürich, 8092 Zürich, Switzerland

Cerro de Pasco, as part of the Miocene metallogenic belt of central and northern Peru, epithermal is а large base metal ("Cordilleran") deposit located along the eastern margin of a diatreme-dome complex [1]. It was formed during three main stages by fluids with contrasting fS2, fO2 and pH. During *stage-A*, a number of pyrrhotite pipes that grade outwards into massive Fe-rich sphalerite and galena replacement bodies were emplaced. Following this stage, a massive body consisting mainly of pyrite and quartz with a halo of pervasive sericite-pyrite alteration affecting the diatreme-dome complex was formed (Stage-B). Contemporaneously, the roots of the diatremedome complex (between 1300 and 900 m below the present-day surface) were cut by quartz-pyrite veins with sericite alteration. mineralogical They share and textural characteristics with the pyrite-quartz body. During *stage-C* two types of ore bodies were formed: well-zoned high- to intermediate sulfidation Zn-Pb-(Bi-Ag-Cu) carbonate replacement ore bodies occurring in the eastern part of the deposit and a set of E-W trending Cu-Ag-(Au-Zn-Pb) enargite-pyrite veins hosted by the diatreme-dome complex in the western part of the deposit.

A fluid inclusion study was conducted on products of the three stages of mineralization. Microthermometry has been performed on 109 fluid inclusion assemblages (FIAs) in quartz, Fe-poor and Fe-rich sphalerite, enargite, and Fe-Zn-Mn carbonates, using both transmitted visible and near-infrared light microscopy for gangue and ore minerals, respectively. All fluid inclusions are aqueous, liquid-rich, with 20-30 vol% vapour phase. FIAs from the pyrrhotite pipes and their rims, the pyritequartz body, and the deep pyrite-quartz veins show similar pattern with salinity decreasing with time from 20 to 3 wt% NaCl equiv. at relativelv constant homogenization temperature between 280° and 220°C. No

evidence of boiling has been observed and the possibility of mixing with basinal brines seems limited taking in account registered eutectic temperatures around -20°C. In contrast, FIAs from the high-sulfidation carbonate bodies replacement ore show a clear correlation trend between salinity and homogenization temperature - from 19 wt% NaCl equiv. salinity at 280°C to 1.05 wt% NaCl equiv. at 140°C. Such a pattern is characteristic of mixing of high-salinity (e.g. magmatic) fluids with cooler and low-salinity (e.g. meteoric) waters. The enargite-pyrite veins are mainly characterized by low-salinity FIAs (1.8 -3.5 wt% NaCl equiv). Homogenization temperatures vary from 230° to 195°C in enargite-hosted FIA and from 295° to 260°C in quartz-hosted FIAs.

Fluid inclusion analyses by LA-ICP-MS have been conducted on more than 600 fluid inclusions from 91 FIAs. For all stages, except the enargite-pyrite veins, the results show a strong correlation between metal content (Fe, Mn, Zn, Pb and Sb) and salinity. In FIAs of the high-sulfidation carbonate replacement ore bodies (*stage-C*) metal contents correlate with both homogenization temperature and salinity. The highest concentrations of some of the base metals (Fe, Zn, Pb, and Mn) reach up to several wt%. whereas Sb and Cu concentrations do not exceed 6000 ppm and 1200 ppm, respectively. Less saline FIAs show metal contents which are at least two orders of magnitude lower than high salinity ones. Ratios of Me/(Na+K+Mn) show similar correlation trends to Fe, Zn, Pb, and Cu concentrations for stage-A, for the stage-B deep pyrite-quartz veins and for the stage-Chigh-sulfidation carbonate replacement ore bodies. Such trends indicate that decrease of metal contents is mainly due to precipitation. For the pyrite-quartz body (also *stage-B*) except for Fe, no distinct correlation exists between metal ratios and salinity. In this case, the decrease of metal concentrations in the

fluid is best interpreted as caused by dilution and not by sulfide precipitation. This is in agreement with the mineralogy of the pyritequartz body (only pyrite and quartz). Like metals, concentration decrease of lithophile elements (e.g., Li, B, Rb, Sr, Cs and Ba) correlate with decrease of salinity (stages A and B) or of temperature (carbonate replacement bodies of stage-C). Ratios of lithophile element concentrations with the sum of alkalis (Na+K+Mn) remain constant, thus indicating that such trend is mainly due to fluid dilution. Our results show that all mineralization stages at Cerro de Pasco, except the formation of enargite-pyrite veins, are related to the progressive dilution of magmatic metal-rich fluids.

The diluent fluid involved in the formation of the carbonate replacement bodies of stage-Cwas identified as meteoric waters based on our microthermometry results and previously published oxygen data isotope on hydrothermal quartz For the [1]. mineralization stages A and B, the nature of the diluent fluids is puzzling, as no evidence of input of meteoric water or fluids from sedimentary formations has been recognized so far. The dataset for the early stages of mineralization is indicative of dilution of a magmatic metal-rich fluid by a later magmatic metal-poor fluid (e.g. contracted vapour). Fluid composition and evolution in term of metals and lithophile elements concentrations are similar for all mineralization stages, except the enargite-pyrite veins. This similarity of fluid composition contrasts with the difference in mineralogy observed. It indicates that the main factor controlling the mineralogy of main ore bodies is not the fluid composition itself. but rather the difference in oxidation state of the fluids which is partly controlled by the nature of the host rock and the input of oxidized meteoric water. The sulphur content should also play a role, but the obtained LA-ICP-MS analyses do not allow to quantify it.

Fluids in the enargite-pyrite veins present a pattern differing from the other mineralization styles. Quartz in these veins precipitates always before enargite. Quartz-hosted FIAs have one order of magnitude less metal and lithophile element contents than fluid inclusions hosted in enargite. This difference

may be due to a more important input of magmatic fluid during enargite precipitation. Lead, Zn, Cu and Mn contents are up to 800 ppm for FIAs hosted in guartz. Those of Pb and Mn in FIAs hosted in enargite are up to 8000 ppm. The difference in fluid chemistry between the enargite veins and the other mineralizing stages is hard to explain. Published oxygen isotope data on hydrothermal quartz also indicate a more important input of meteoric water. These veins could results from a mixing of a contracted magmatic vapour and meteoric fluids. However, no evidence of such mixing has been found by the fluid inclusion study.

The obtained fluid inclusion results indicate that the Cerro de Pasco deposit was formed by three cycles of injection of metal-rich highsalinity magmatic fluids diluted by lowsalinity waters. Such cycles imply the presence at depth of a homogeneous high-salinity metalrich magmatic fluid reservoir that was reactivated periodically over less than 1 m.y [1]. Such reservoir of high-salinity fluid could be formed above the magmatic chamber under lithostatic pressure if the crustal rocks behave in a plastic manner at normal strain rate [2]. High-salinity fluids are then released during major breaches of the self-sealed zone. Considering the highest Zn (2.7 wt%) and Pb (1.13 wt%) contents measured in the fluid inclusions, already 1 km<sup>3</sup> of such high-salinity metal-rich fluid are sufficient to form the giant epithermal polymetallic deposits of Cerro de Pasco (considering two times the recognized 175 Mt resource @ 7% Zn and 2% Pb [1]), assuming 100% efficiency of mineral precipitation.

#### Acknowledgements

This research is supported by the Swiss National Science Foundation (grant 200020\_134872). The authors are grateful to the Volcan Compania Minera S.A.A. for the logistic support in the field.

#### References

[1] Baumgartner R., Fontboté L., & Vennemann T. (2008) Mineral zoning and geochemistry of epithermal polymetallic Zn-Pb-Ag-Cu-Bi mineralization at Cerro de Pasco, Peru. Economic Geology, 103, 493-537

[2]Fournier O, Hydrothermal processes related to movement of fluid from plastic into brittle rock in the magmatic-epithermal environment. Economic Geology, 94, 1193-1211

## Preliminary Microthermometric Data of Hayriye, Iclaliye Mineralizations in (Inegöl-Bursa).

Hüseyin Sendir<sup>1</sup>, Kadir Sarıiz<sup>1</sup>,

#### <sup>1</sup>Department of Geology, Eskişehir Osmangazi University, Eskişehir, Turkey

#### E-mail: <u>hsendir@ogu.edu.tr</u>

Western Anatolia (Turkey) experienced widespread Cenozoic magmatism after the collision between the Sakarya and Anatolide-Tauride continental blocks in the pre-middle Eocene. The widespread magmatic activity in NW Anatolia postdates this continental collisional event in the region. The following magmatic episode during the Oligocene and Early Miocene is known to have produced the widespread granitic plutons. Many skarn mineralization associated with plutons formed in the region (such as Hayrive and İclaliye Mineralizations). The study area is located at 30 km southeast of İnegöl (Bursa), includes Hayriye and İclaliye villages. The Paleozoic aged Devlez Metabasite is the oldest unit of the study area. This unit includes amphibolite, glaucophane-lawsonite schist, muscovite schists. The unit has widely spread in area. This units are overlain unconformably by the Geviktepe Marbles. Paleocene aged Domaniç granitoidic intrusives cut other rock series and located as a batholite. Magmatic units present porphyric holocrystalline and textures. Granitoidic intrusions are represented by tonalite, tonalite porphyr, granodiorite, granodiorite porphyr, granite, diorite, diorite porphyries. The Domanic granitoid intruded in to the metamorphides during Paleocene and caused formations of skarn zones and related Cu-Pb-Zn mineralizations along the contacts. Mineralizations are known in the locations

named as Sarıçayıryayla, Arapdede and Hayriye. The mineralizations occur along the metamorphites - plutonics contact, in the pockets and fractures extending towards marble. The thickness of the mineralized bodies can reach up to 1-2 m. Primary minerals are galenite, magnetite, pyrite, chalcopyrite and sphalerite at Hayrive mineralizations and sphalerite, galenite, chalcopyrite and pyrrhotite minerals at the Iclalive mineralizations. Fluid inclusion measurements carried out on quartz and sphalerite minerals. The size of inclusions varies between 1 and 10 µm in quartz, and 1 and 14 µm in sphalerite minerals. The inclusions contain two-phase aqueous fluids (L+V) at room temperature. All fluid inclusions belong to the H<sub>2</sub>O- NaCl-CaCl<sub>2</sub> system. Fluid inclusion homogenization temperatures of Sarıçayıryayla, Arapdede and Hayriye mineralizations are 209-390°C, 220-330 °C, 210-350 °C and salinities equivalent % 5.4-13.9. 3.20 -3.90. NaCl 1.6-3.4 respectively. Primary microthermometric measurement show low to medium salinity and medium to high temperature.

#### Acknowledgements

This study supported by ESOGU BAP (2011150

## Fluid mixing and fault-valve action in the formation of the Nalunaq Gold deposit, Greenland.

M.P. Smith<sup>1</sup>, D.A. Banks<sup>2</sup>, F. Bowers<sup>3</sup>

<sup>1</sup>School of Environment and Technology, University of Brighton, UK, <u>martin.smith@brighton.ac.uk</u> <sup>2</sup>School of Earth and Environment, University of Leeds, UK. <sup>3</sup>C A Blackwell (Contracts) Lt

This study reports the results of petrographic observations, fluid inclusion microthermometry and LA-ICP-MS analyses from quartz samples from the main vein at the Nalunaq gold mine, South Greenland. The deposit consists of shear zone-hosted quartz veins, almost entirely within basaltic greenstones, but also associated with aplitic and pegmatitic granitoid dykes in places (Kaltoft et al. 2000). The study was undertaken in order to develop genetic models for the deposit, and in particular to help in the development of predictive models to account for the extreme variation of gold grade throughout the shear zone system. Eight samples were selected for detailed study, and taken from shear zone sections with Au grades varying from 0.5 to 196g/tonne.

All samples were dominated by quartz, but a defining feature was clear textural evidence for multiple stages of vein opening and quartz deposition, alongside other minerals. This included strike and vein margin parallel fractures indicative of crack seal growth in most samples. Strike-inclined fractures are also common, some close to perpendicular to the main vein strike, possible indicating extensional (or transtensional) fracturing of the vein post formation. Most fractures sets are developed as conjugate pairs, although the conjugate fractures may not be as strongly developed in one orientation. In a number of samples fractures are infilled with minerals distinct from those in the background quartz of the main vein. These included quartz-albite veinlets. quartz-actinolite veinlets with associated sulphides, and quartz-calcitesulphide veinlets. The sulphide assemblage includes pyrite, pyrrhotite and chalcopyrite, and in some instances arsenopyrite and native gold.

Fluid inclusions were observed in all samples. The dominant room temperature phase assemblages are aqueous liquid plus halite plus vapour (Lw+Sh+V), and aqueous liquid plus vapour (Lw+V). No observations have been made in this study of carbonic and aqueous-carbonic fluid inclusions noted by Kaltoft et al. (2000). Some vapour-rich inclusions were observed, but these failed to nucleate an additional vapour bubble following cooling to -120°C.

Four main fluid inclusion populations were identified by microthermometry. *Population A* contains Lw+Sh+V inclusions in which L-V to L homogenisation took place prior to halite dissolution and has salinities ranging from 32 to 44 wt. % NaCl eq. and L-V homogenisation temperature ranging from 130 to 380°C. The L-V homogenisation prior to halite dissolution in these inclusions implies significant pressures at halite dissolution, ranging from 100-300MPa (Lecumbreapproximately Sanchez et al., 2012). Population B contains Lw+Sh+V inclusions in which L-V homogenisation took place following halite dissolution. Salinities in these inclusions range from 28 to 32 wt. % NaCl eq. Liquid-Vapour homogenisation liquid to the phase characteristically occurred over a wide temperature range in these inclusions (130 to 250°C). Such a trend can be indicative of density variations in inclusions resulting from leakage of fluids during deformation or heating, but it may also indicate rapid, large, pressure variations during periods of vein dilation and re-establishment of equilibrium fluid pressures (fault valve action - [3]). This population is associated with some of the highest gold grades. *Population C* contais Lw+V inclusions which nucleate hydrohalite on cooling, and have either exceptionally low ice melting temperatures, or in which halite forms on the melting of hydrohalite and then dissolves below 100°C. First ice melting temperatures in the inclusions are typically

below -50°C, and may be below -60°C. The eutectic temperature for the system NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O is -52.5°C, and so these low first melting temperatures indicate high concentrations of Ca and potentially other divalent cations (Fe, Mg). The combination of low ice melting and hydrohalite melting temperatures in many of these inclusions is consistent with high Ca concentrations relative to Na (Oakes et al., 1990). Bulk salinities of these inclusions range from 18 to 28 wt. % NaCl eq., and homogenisation temperatures from ~130 to 250°C. As with population B, these inclusion are associated with high gold grades. **Population** D contains Lw+V inclusions with high ice melting temperatures. Bulk salinities range from 0 to ~12 wt. % NaCl eq., and T<sub>h</sub> from ~140 to 210°C. There is a clear distinction in salinity between these fluids and all others identified (Fig.1, 3), and this is the only population to occur in low grade samples indicating is not associated with significant gold deposition. Comparison with geothermometry arsenopyrite from [1] suggests trapping pressures as high as 500MPa, by with variations in trapping pressure of up to 2-300MPa within individual populations.

Laser ablation analyses of the inclusions confirm that the populations have distinct cation chemistry, and variation in salinity is not merely a function of dilution. Quality control and interpretation of analyses is at a preliminary stage, but it is clear that highly saline brines (Populations A and B) are distinguished from less saline fluids by higher Fe contents relative to Ca, and high K contents relative to Na. The fluids are also clearly distinguished by their gold content, which correlates with the grade in the bulk samples. The two highest grading samples have dominant salinity populations of 30 wt. % NaCl eq. and 7 wt. % NaCl eq. respectively. Initial estimates based on the LA-ICPMS analyses suggest these populations may have had Au concentrations in the range 10-100ppm, with means of 30ppm and 23ppm

respectively. Lower salinity fluids typically had Au contents below detection levels.

In conclusion the Nalunaq main vein exhibits a complex multistage structural and fluid flow history. Unequivocally primary fluid inclusions have not been identified, but internal vein textures are consistent with a crack-seal vein growth mechanism resulting from fault valve action. The trapped fluid inclusions are widely variable in salinity, ranging from hypersaline brines, to very low salinity aqueous fluids. At least some of the fluid salinities are consistent with mixing of a high salinity fluid with a low to moderate salinity fluid and it is these fluids which show the highest Au contents and correlate with the highest gold grades in bulk samples. These fluids show a wide range in liquid-vapour homogenisation temperature, and hence density, consistent with rapid pressure cycling during vein growth. The combination of fluid mixing with rapid pressure drops on vein dilation may have been responsible for the formation of zones of high gold grade.

#### Acknowledgements

We thank Angel Mining Gold A/S for permission to publish the microthermometric data in this abstract. LA-ICPMS work was carried out at the NERC JIF sponsored facility at the University of Leeds, UK (NER/H/S/2000/853).

#### References

[1] P. Lecumberri-Sanchez, M. Steele-MacInnis, **R.J.** Bodnar. A numerical model to estimate trapping conditions of fluid inclusions that homogenize by halite disappearance. Geochim. Cosmochim. Act, vol. 92, pp. 14-22. [2]K. Kaltoft, D.M. Schlatter, L. Kludt. Geology and genesis of hte Nalunag Palaeoproterozoic shear zone-hosted gold deposit. South Greenland. Trans. Inst. Min. Metall. B: Applied Earth Science, vol. 109, pp. 23-33, 2000. [3] C.S. Oakes, R.J. Bodnar, J.M. Simonson, The system NaCl–CaCl<sub>2</sub>– $H_2O$ : I. The ice liquidus at 1 atm total pressure. Geochim. Cosmochim. Acta vol. 54, pp. 603-610.. 1990. [4] Sibson, R.H., Robert, F., and Poulsen, K.H. (1988) High angle reverse faults, fluid pressure cycling and mesothermal gold-quartz deposits.

Geology vol. 16, pp. 551-555.

### Fluid inclusion studies constrain conditions of Cu mineralization in Cerro Colorado Mine, Northern Chile

Debbie P.W. Tsang<sup>1,2</sup>, **Brian Tattitch<sup>2</sup>** & Simon Wallis<sup>1</sup>

1 Department of Earth & Planetary Sciences, Graduate School of Environmental Studies, Nagoya University, Japan. tsang.pui.wai.debbie@i.mbox.nagoya-u.ac.jp 2 School of Farth Sciences, University of Printed Vinedom

2 School of Earth Sciences, University of Bristol, United Kingdom

Cerro Colorado porphyry copper mine, a BHP Billiton property, is the northernmost copper mine in Chile currently in active production. The accessibility to drilled cores that penetrate into the hypogene zone provides a good opportunity to examine timescales and physical conditions of fluid flow associated with the porphyry ore formation of the region.

In the Cerro Colorado mine, quartz veins are commonly associated with important ore minerals including chalcopyrite and molybdenite. Analysis of these veins has the potential to help identify the conditions of ore formation. Microstructures of veins were examined under reflected and polarized light combined with cathodoluminescence (CL) images. They suggest that there were multiple stages of quartz growth. The first stage (stage I) is associated with a mosaic quartz pattern, which may indicate recrystallization from an amorphous silica state [1]. The quartz grains are generally homogenous and fine-grained. This is followed by the growth of euhedral quartz grains (stage II), which show clear growth zone patterns in CL images. These grains are cut by quartz-filled fractures that show only weak luminescence (stage III). The same type of quartz also shows highly irregular outlines (splatter and cobweb microstructures) where it is in contact with stage II quartz. These microstructures suggest the veins formed in three distinct stages with a period of fracturing, dilation and partial dissolution of stage II quartz prior to the final stage of quartz precipitation.

The economically valuable sulphide minerals, chalcopyrite and molybdenite, are associated mainly with the second stage of the quartz growth evolution. They occur mainly as large grains deposited along the quartz grain boundaries, but also occur as small inclusions within quartz grains and within fluid inclusions. These microstructural observations suggest that stage II quartz growth is coeval with the sulphide ore deposition. Fluid inclusions within this quartz can potentially be used to estimate the formation conditions of both the quartz and sulphide minerals. CL images are important to help identify primary inclusions. Firstly, inclusion trails that crosscut growth zonation shown in CL are clearly secondary. In contrast, inclusions that lie along the growth zone domains are likely to be primary. We focused on inclusions with good microstructural evidence for being primary. Currently only high-salinity three-phase inclusions have been analyzed. Measurement of 31 of fluid inclusions from 2 different veins showed the following characteristics.

1) 80% of the halite dissolution temperatures ( $T_m$ Halite) lie between 220°C to 300°C, suggesting a salinity of 32-38 wt% NaCl.

2) 40% show homogenization temperatures ( $T_hL$ -V) higher than 425°C, which combined with the dissolution temperatures, imply trapping pressures of 250 to  $\geq$  480 bars.

3) 55 % yield  $T_hL$ -V of 280-380°C, indicating a lower range of trapping pressures from 60 to ~180 bars.

4) A few inclusions showed homogenization temperatures above 550°C, which is the high temperature limit for accurate measurement on the Linkam TS600 utilized.

The Cerro Colorado mine area is composed of a series of subvolcanic to volcanic rocks, with andesitic lava and porphyritic dacite being the most common. Taking the range of andesite, granodiorite and quartz diorite density at 2.65-2.91 Mg/m<sup>3</sup> [2], assuming lithostatic pressures, the high temperature population indicates shallow crustal formation depths of about 0.86-1.81km and the lower temperature population implies very shallow depths of about 210–680 m. According to phase equilibrium of  $SiO_2$  in  $H_2O$  system [3], at the pressures indicated by our results, the solubility of  $SiO_2$  in aqueous fluids has a local maximum in the temperature range of 375-410°C. This implies that precipitation of  $SiO_2$  phases will be limited in this temperature range and may account for the bimodal homogenization temperatures.

The multiple stages of quartz growth revealed in this study show that quartz veins formed in several discrete stages and have experienced dissolution and recrystallization. The estimated P-T conditions are compatible with increasing SiO<sub>2</sub> solubility limiting quartz precipitation as temperature decreases through ~400 $^{\circ}$ C (retrograde solubility), which may be recorded in the stage III microstructures. The fluid inclusion data are compatible both with vein formation during a single phase of cooling from above 550°C and also with a formation history that involves multiple stages of fluid influx at temperatures generally varying between 300 and 550°C. More complete integration of the microthermometry results with microstructural observations of quartz, fluid inclusions, and sulphide minerals can help resolve this issue and constrain conditions required for sulphide mineralization.



Figure 1: Inclusion types observed in sampled quartz veins from Cerro Colorado. Lq-liquid, G-gas, Cpy-chalcopyrite, Mo-molybdenite. (a) & (b) show typical 3-phase inclusions including sulphide daughter minerals. (c) A gas phase inclusion with negative crystal shape. (d) Inclusion showing the coexistence of gas phase and liquid phase inclusions, which are close to each other.



Figure 2: (a) Quartz vein that shows two stages of quartz growth. The mosaic and homogenous quartz (stage I) at the rim of vein, and the euhedral quartz showing clear growth zones (stage II) in the centre. (b) Quartz vein composed only of stage I quartz growth; (c) Stage II quartz being cut by late stage quartz veins that have very dull CL intensity.

#### Acknowledgements

This work is a collaboration effort between Nagoya University and the University of Bristol, supported by the BHP Billiton-Bristol PCD project.

#### References

[1] Dong G., Morrison G., Jaireth S. (1995) Quartz Textures in Epithermal Veins, Queensland—Classification, Origin, and Implication, Economic Geology, 90, 1841-1856.

[2] Wohletz K. & Heiken G. (1992) Volcanology and Geothermal Energy. Berkeley: University of California Press.

[3] Steele-MacInnis M., Han L., Lowell R.P., Rimstidt J.D., Bodnar R.J. (2012) The Role of Fluid Phase Immiscibility in Quartz Dissolution and Precipitation in Sub-seafloor Hydrothermal Systems, Earth and Planetary Science Letters 321-322, 139–151.

### Methodology and Application of Evaporate Mound SEM-EDS analysis to Quantify the Solute Chemistry of Quartz-hosted Fluid Inclusions in a Mineralized Granitic Batholith

Fergus Tweedale<sup>1</sup>, Jacob Hanley<sup>1</sup>, Daniel Kontak<sup>2</sup>, and Neil Rogers<sup>3</sup>

1. Department of Geology, Saint Mary's University, Halifax, Nova Scotia B3H 3C3 fergus.tweedale@smu.ca

2. Department of Earth Sciences, Laurentian University, Sudbury, Ontario P3E 2C6

3. Geological Survey of Canada, Ottawa, Ontario K1A 0E8

Given the hydrothermal nature of granitehosted mineral deposits, it is expected that a fingerprint of the mineralizing fluid may be manifest both petrographically and chemically by the solute chemistry of secondary fluid inclusions on a scale equal to or larger than the mineralized centres. The potential of evaluating this fingerprint to assess metal fertility requires an analytical technique that quantifies the chemistry of such fluidinclusions. A relatively simple approach is to artificially decrepitate fluid inclusions and analyze the resulting decrepitate mounds using a scanning electron microscope (SEM) coupled to an energy dispersive X-ray spectrometer (EDS) [1]. The SEM-EDS methodology described here is applied to a regional-scale study of fluid-inclusions in a large (ca. 7500 km<sup>2</sup>) mineralized (Sn-W-Cu-Zn-U) granitoid intrusion: the 380 Ma peraluminous South Mountain Batholith (SMB) of Nova Scotia. Sample preparation included cutting and grinding granite slabs to 150-200µm thick wafers that are then mounted on standard-sized glass slides for petrographic study. Quartz grains with abundant fluid inclusions are then cut from the wafers and heated to induce decrepitation of inclusions and generate evaporate mounds. The largest and the greatest abundance of mounds occur in grains heated to 500°C (cf. 325° and 400°C). Oven-heating (10°C/min) is appropriate for batch heating, whereas stage-heating

(50°C/min) is suitable for heating single chips and observing decrepitation of inclusions. Comparing raster-mode and point-mode results substantiates mound heterogeneity. Repeat analysis of single inclusions using 5-, 10-, and 30-second run times suggests EDS sensitivity improves with longer run times. Synthesis of standard salt mounds takes into account potential matrix effects associated with X-ray analysis; analysis of standards is used for calibration of EDS results for major solute species in mounds (F-Na-Cl-Ca). Analysis of 4, 8, 16, 32 and 63 mounds in a single sample indicates that 16 analyses provides representative data. Data reduction and display considerations include removal of background signals for quartz, screening data for internal consistency and identification of chemically-distinct fluid inclusion populations in ternary plots of the EDS data. Finally, we apply this methodology to suite of samples from the mineralized SMB. To date, the 485 mound analyses from 63 samples indicate two dominant SMB fluids types: one Na-K and the other F-Na-Ca±K fluid. Trace solutes (Fe, Zn, Sn, Mn and S) occur in some samples.

#### References

[1] D.J. Kontak. (2004) Analysis of Evaporate Mounds as a Complement to Fluid-inclusion Thermometric Data. Canadian Mineralogist, 42, 5, 1315-1329