



# Abstract Volume 6<sup>th</sup> Swiss Geoscience Meeting

Lugano, 21<sup>st</sup> – 23<sup>rd</sup> November 2008



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Geosciences  
Platform of the Swiss Academy of Sciences

**SUPSI**

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Robert Moritz, Thomas Wagner

*Swiss Society for Mineralogy and Petrology (SSMP)*

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## 7.1

### Low temperature fluid phase relations of granitic solutions and implications for crustal mass transport.

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Aqueous fluids transport and precipitate dissolved silicate components in natural hydrothermal processes throughout the earth's crust. To understand the solubility of significant mineral assemblages over large ranges of P-T, we have employed the diamond-trap technique to investigate aqueous fluids in equilibrium with K-feldspar, muscovite and quartz (KMQ) from 0.5-2.5 GPa and 600-700 °C. Fluids were found to be highly peralkaline ( $K_2O/Al_2O_3$  up to 9, by weight) despite relatively high concentrations of dissolved aluminum (>0.04 mAl at 1 GPa, 700°C) in these fluids, compared to corundum ± kyanite solubility in the absence of alkalis [1].

Over the P-conditions investigated, measured fluid compositions have K:Si=1:3, which is higher than HKF\* aqueous speciation calculations predict (extrapolated to the investigated PT-conditions, following [2]).

Our KMQ solubility data indicate K-Si species are significantly more abundant than aluminous 'feldspar-like' complexes [3]. Further experiments, involving synthesis of quartz-hosted fluid inclusions, were conducted to investigate fluid/melt immiscibility and bracket the wet melting reaction quartz + muscovite + K-feldspar + V = L. Inclusion petrography and microthermometry indicate that the occurrence of (supercritical) melt-fluid miscibility in simplified granitic systems is sensitive to the compositional evolution of the fluid and might actually be encountered upon cooling (and not heating) of the system.

Our experimental results reveal retrograde solubility patterns governing the evolution of residual granitic solutions that may be linked to the possible occurrence of continuous solubility between fluid and melt in peralkaline granitic systems, as Bowen postulated 80 years ago [4]. Moreover, the results indicate paths leading to enhanced mass mobilization in natural fluids at low-temperatures.

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## 7.2

### Mineralogy and Fluid inclusions investigations of carbonate hosted Pb-Zn-Ba-(Cu) deposits in Jebel Ajered, Central Tunisia.

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Carbonate-hosted Pb-Zn-Ba-(Cu) epigenetic deposits in Jebel Ajered, is located in the Central Tunisia (300Km from Tunis). The deposits are hosted by Upper Aptian carbonate Unconformity. The potential reserve estimated of 1.2Mt grading 8% Zn, 4% Pb and 2% Ba.

This study presents the results of a geological, mineralogical, and geochemical investigation of the carbonate-hosted Pb-Zn deposits.

This mineralization is hosted by hydraulic breccias related to extensive dolomitized and silicified limestone, collapse cavities and karsts generated with dissolution of host rock (Fig. 1-A, 1-C, 1-F and 1-D). These mineralizations have different shapes ranging from mineralized breccias to stratabound and concordant with host rocks and fault-related. (Bouhlel et al., 1988 and Bejaoui et al., 2006 and 2007)

The metalliferous mineral association is formed by galena, sphalerite, pyrite, chalcocopyrite, goethite and covellite. Minerals non-metalliferous are; dolomite, quartz and Barite.

In this study we measured inclusions in sphalerite and in quartz from Jebel Ajered. Two-phase inclusions were observed in studied minerals. They consist of vapor and aqueous solution of NaCl with small amount of  $MgCl_2$  and  $CaCl_2$  (Fig. 1).

Inclusions in sphalerite consist of vapor and aqueous solution of NaCl with small amount of  $MgCl_2$  and  $CaCl_2$ . They are located in growth surface and their size is less than  $100\mu m$ . Melting temperature of ice ( $T_{mi}$ ) varies from  $-11^\circ C$  to  $-14.5^\circ C$ . Homogenization temperature ( $T_h$ ) varies from  $125^\circ C$  to  $140^\circ C$ . Calculated salinity varies from 15 to 18 wt. % NaCl equiv. and densities vary between  $1,07 g/cm^3$  and  $1,12 g/cm^3$ .

Homogenization temperature in quartz1 (Fig. 1-B and 1-D), gangue of sphalerite varies from  $128^\circ C$  and  $147^\circ C$ . Salinity range from 15 to 19 wt.% NaCl. Fluid inclusions in quartz cogenetic with barite consist of vapour and aqueous solution of NaCl with small amount of  $MgCl_2$  and  $CaCl_2$ . Eutectic temperature ( $T_e$ ) varies from  $-40^\circ C$  to  $-22^\circ C$ . Their size is less than  $80\mu m$ .  $T_{mi}$  varies from  $-19^\circ C$  to  $-15^\circ C$  (Fig. 2). Inclusions were homogenized on liquid in temperature from  $155^\circ C$  to  $171^\circ C$ . Salinity varies from 18 to 21wt. % NaCl equiv. We can observe decreasing salinity with the gradual decreasing temperature ( $T_h$ ) from quartz cogenetic with barite to sphalerite. These features of mineralogical and fluid inclusions study suggest a possible contribution of basinal brines mineralizing fluids in ore formation. The Ajered stratabound ore deposits are similar to Mississippi valley type deposits. Isotopic and trace elements are in progress.

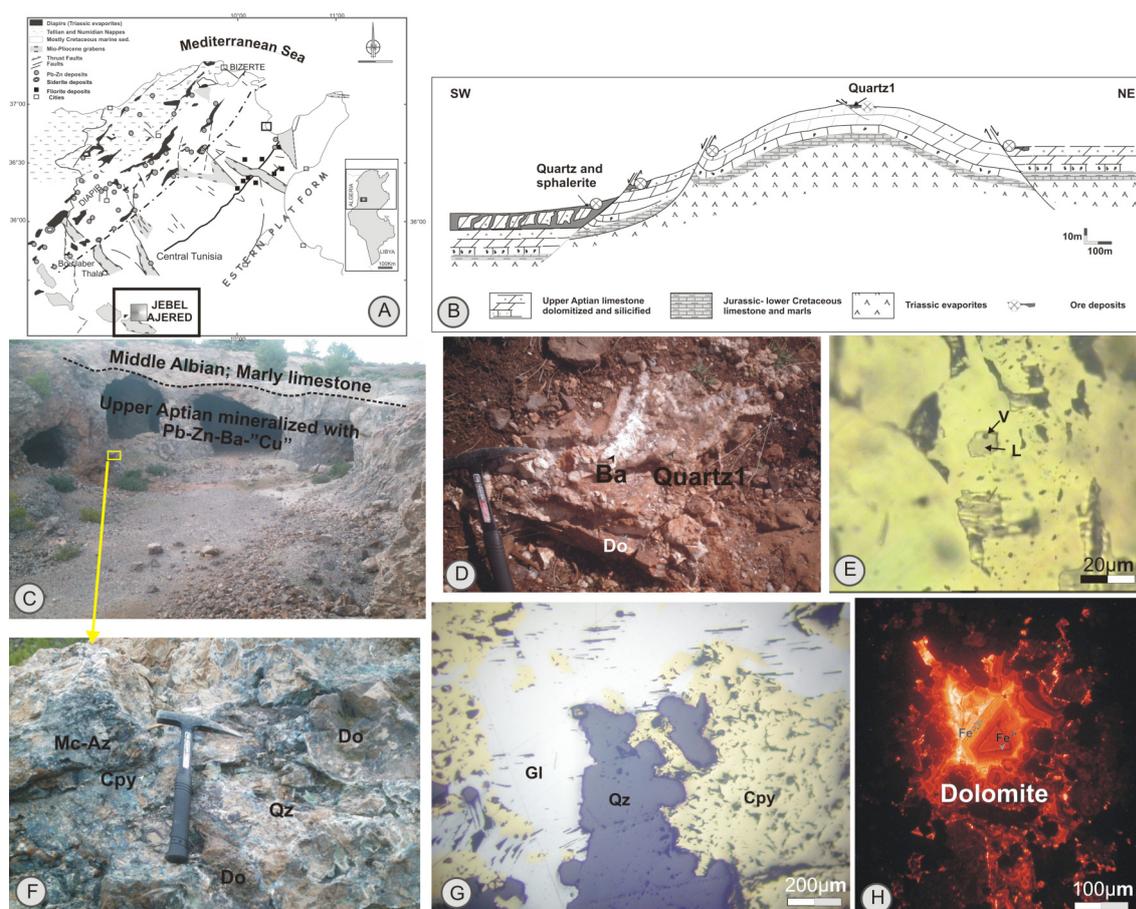


Fig. 1. A: Localization of study area in Tunisian structural map, B: distribution of ore bodies in cross section, C: Ajered old mine where ore deposits are located, D: Geodic quartz collapsed with barite. E: primary aqueous fluid inclusions in sphalerite, F: Hydraulic breccias mineralized with chalcocopyrite and galena, G: coarse-grained quartz associated with chalcocopyrite and galena, H: Cathodoluminescence photomicrograph of dolomite, in contrast to the dolomite crystals, this cement shows a bright orange color with well developed zoning with different iron content. (Do; dolomite, Ba: Barite, Cpy: Chalcocopyrite, Qz: Quartz, Mc-Az: Malachite and azurite, Gl: Galena, V: Vapor, L: Liquid).

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## 7.3

# Miocene magmatism and related porphyry and polymetallic mineralization in the Morococha district, central Peru

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The Morococha mining district in central Peru displays a complex magmatic and hydrothermal history where several intrusive events and spatially associated mineralization and alteration styles are recognized. At least nine main intrusions form several magmatic clusters and four ore body types: porphyry mineralization, massive pyrite-quartz bodies, polymetallic replacement bodies, and polymetallic veins crossing the entire district, have been distinguished. Porphyry mineralization and alteration are restricted to the vicinity of certain intrusions, whereas replacement bodies and polymetallic veins do not seem to show any spatial relationship to a particular intrusion. The geology of the district consists of Permian continental volcanic rocks and red beds, Triassic-Jurassic sedimentary carbonate, volcanic rocks and basalts, Late Cretaceous siliciclastic and carbonate rocks, cut by several Miocene intrusions. The oldest intrusion (14.1 Ma; Kouzmanov et al., 2008) covers a large area in the western part of the district. The mineralization, however, is related to the emplacement of younger Miocene intrusions (7-9 Ma; Beuchat, 2003, Kouzmanov et al., 2008). The polymetallic mineralization postdates both intrusive events.

Porphyry style alteration and mineralization was recognized in three areas: (1) the Toromocho porphyry Cu-Mo deposit in the central part of the district; (2) the Codiciada Cu-Mo porphyry in the north-eastern part, and (3) the Ticlio Cu-Au porphyry in the westernmost area. Only the latter two are included in this study. Other mineralization styles, partly in the epithermal range, in the Morococha district include (a) endo- and exoskarns; (b) pyrite-quartz bodies; (c) replacement polymetallic bodies, and (d) polymetallic veins.

The *Codiciada Cu-Mo porphyry system* comprises an igneous suite of microdiorite, porphyritic microdiorite, quartz-feldspar porphyry, and amphibole-biotite porphyry intrusions. The petrochemical analyses of intrusions in the Codiciada area display negative Nb, Ta, and Ti anomalies indicating a magmatic arc setting. Chondrite-normalized REE patterns show weak negative Eu anomalies suggesting minor plagioclase fractionation, probably at shallow crustal levels. Strong LREE fractionation (high Ce/Yb ratios) and associated intra-HREE fractionation (e.g. Dy/Yb) suggest a combination of hornblende and garnet fractionation in the magma source. The rocks consistently display Sr contents >600-700 ppm and Y contents <18 ppm allowing their classification as adakite-like (Richards and Kerrich, 2007). This is consistent with initial evolution of the magma at the base of a thickened continental crust. The alteration styles in this system consist of pervasive Na-Ca, selective pervasive potassic and phyllic alterations, as well as silicification. Porphyry style veinlets are quartz-pyrite-chalcopyrite±pyrrhotite, quartz-molybdenite and quartz-pyrite-sericite in composition. Molybdenite, chalcopyrite and pyrite, occur in much lower quantities, disseminated in the altered rock.

The *Ticlio Cu-Au porphyry* is a single granodiorite intrusion showing a pronounced zonation pattern with respect to mineralization and alteration. Its central part is characterized by the occurrence of high-density quartz-magnetite±K-feldspar stockwork. The zone rimming the core shows strong K-feldspar alteration with low-density magnetite and quartz-magnetite veining. This zone hosts small amounts of chalcopyrite and bornite as disseminations and in veinlets. Native Au is observed as small inclusions in chalcopyrite. The peripheral parts of the system show weak biotite, K-feldspar and actinolite alteration, as well as weak chalcopyrite and pyrite mineralization. The most distal part of the porphyry system is characterized by weak propylitic alteration.

In the Morococha district steeply dipping (N 110° E to N 150° E) porphyry quartz-molybdenite and quartz veinlets have been observed at several locations. This suggests a possible structural relationship with the emplacement of quartz-feldspar porphyry dykes with the same trend found in the Codiciada area. The late porphyry-stage pyrite-quartz-sericite veinlets cut the quartz-molybdenite veins. These veinlets show, a not well defined N 70° E orientation and dip from 80° to 90° NW-SE.

The epithermal polymetallic veins in the district are fault-controlled and belong to two main systems: (a) normal dextral or sinistral faults striking N60-80, and (b) normal dextral faults striking N20-30. Field evidence suggests that the N60-80 system predates the N20-30 one. Both systems are enriched in base-metals, whereas the N60-80 has higher contents in quartz and pyrite. Polymetallic mineral association can be found as well in some re-opened N 70° E trending pyrite-quartz-sericite porphyry veinlets.

Both, the Ticlio (Cu-Au) and the Codiciada (Cu-Mo) porphyry systems in the Morococha district are genetically related to Late-Miocene subvolcanic intrusions with similar petrochemical characteristics; however they show different alteration and

mineralization styles, suggesting different depth of emplacement and/or different P-T-X conditions of ore-formation. The Ticlio porphyry is most probably more deeply eroded than the Codiciada system. Both porphyries are crosscut by the lately formed polymetallic veins.

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## 7.4

### Paragenesis and preliminary fluid inclusion data of porphyry-related base metal mineralisation styles in the Miocene Morococha district, central Peru

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The Morococha district, located in the western Cordillera of the Central Peruvian Andes, is characterised by barren and Cu-Mo porphyry bodies of Miocene age, ranging from 14.1 – 7.7 My (Beuchat, 2003; Kouzmanov et al., 2008), intruded into volcanic and sedimentary rocks. Good outcrop conditions and superimposing of different hydrothermal mineralisation styles make Morococha an ideal location for the study of a porphyry-related hydrothermal mineralisation system. In Morococha, mineralisation processes from porphyry-dominated (Bendezú et al., 2008) to near-surface epithermal environment can be studied in detail (Fig. 1).

Following main mineralisation styles post-date porphyry ore formation in the Morococha district: (a) massive magnetite-serpentine exoskarns and diopside-garnet endoskarns, partly hydrated to epidote, amphibole and chlorite, often bearing polymetallic mineralisation; these are found where mainly Jurassic dolomitic carbonates of the Pucará Group are in contact with porphyry intrusions; (b) massive pyrite-quartz bodies with phyllic alteration halos found in the fringe areas of certain intrusives and/or as replacement of previously formed breccia zones such as in the base of the Pucará Group just overlying Permian volcanics; (c) polymetallic manto-type bodies occurring mainly as a replacement of tectonic and dissolution breccias within the Pucará Group, overthrust-related breccias, and skarnified beds of particular horizons of limestones within the lower units of the Pucará Group. In composition, the replacement bodies range from magnetite, chalcopyrite, sphalerite, and galena-bearing pyrrhotite- and pyrite-dominated bodies to quartz-carbonate-sulphosalts bodies; (d) steeply dipping epithermal Zn-Pb-Ag-Cu-bearing veins with phyllic alteration halos hosted by NNE to ENE trending fractures and cutting the previous ore styles. Zn-Pb-Ag-Cu-bearing veins cross-cut at district scale/district-wide the intrusive bodies, the surrounding sediments, as well as the skarn and pyrite-quartz bodies. They are well distinguished into two stages within the vein. A (i) quartz-pyrite-rich stage with arsenopyrite, Fe-rich sphalerite and pyrite with inclusions of pyrrhotite, galena, chalcopyrite, and minor amounts of Bi-Ag-sulphosalts, stannite, scheelite, and bismuthinite, is followed by a base metal stage (ii), rich in Cu-sulphosalts, sphalerite, galena and Mn-carbonates, including economically important Ag-bearing minerals of the fahlore group. The Mn-rich carbonate zones have abundant quartz and rhodochrosite, and in minor quantities rhodonite, pyrite, fahlore and alabandite with inclusions of native Te and Ag-tellurides. Copper values in the polymetallic veins increase from Zn-Pb-rich veins in external parts of the district towards the central parts of the district, as the importance of sphalerite, galena and Mn-bearing minerals decreases, while that of chalcopyrite, tennantite, enargite, and Cu-Sn-bearing sulphides increases, indicating a higher sulphidation-state in the central part of the Morococha district.

First fluid inclusions data from quartz crystals of the pyrite-quartz stage from a polymetallic vein cutting the Potosí Miocene microdiorite show intermediate salinities of up to 13 wt% eq. NaCl and homogenisation temperatures of up to 380°C. A maximum hydrostatic pressure of 210 bar for the earliest precipitation of the crystals has been calculated. These results are consistent with magmatic ore-forming fluids at mesothermal to epithermal conditions. Towards younger growth zones of the quartz crystals, salinities and homogenisation temperatures decrease down to about 1 wt% eq. NaCl and 265°C, respectively, a trend ascribed to increasing influence of mixing with meteoric fluids.

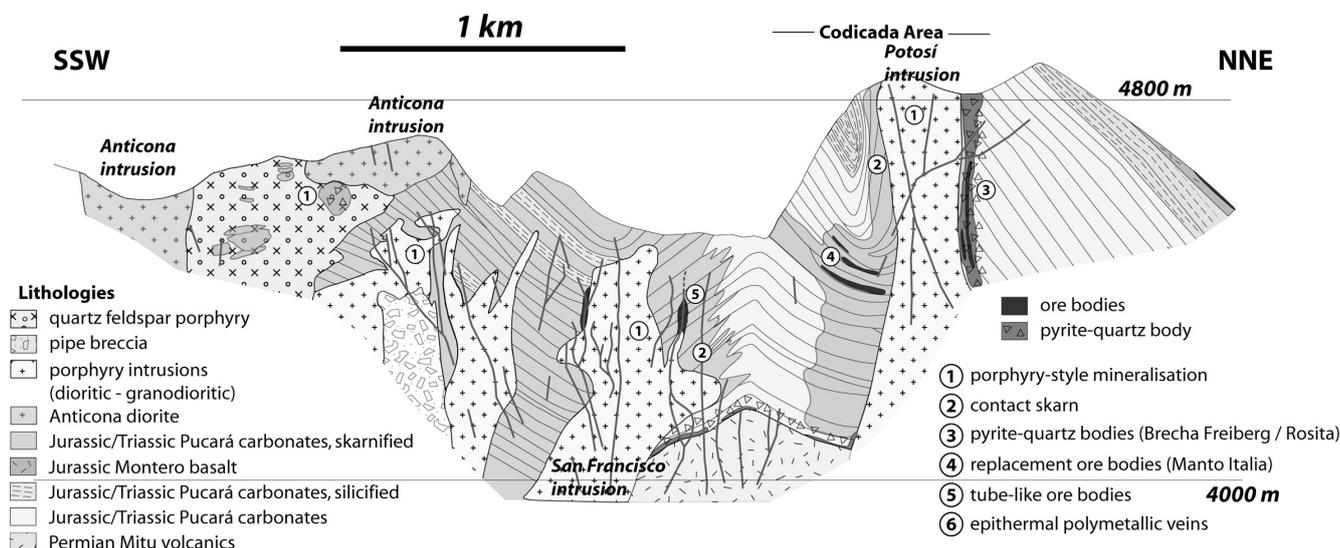


Figure 1: Schematic cross-section through the Morococha district including lithologies and mineralisation styles (vertically exaggerated, southern section modified after León, 2006 based on geological maps from the Cerro de Pasco Copper Corporation; northern section modified after geological maps from Pan American Silver Corp.).

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## 7.5

### Formation of sphalerite mineralisations and cadmium enrichments in the Hauptrogenstein formation (Upper Bajocian) of Jura Mountains (Switzerland): geological, geochemical and isotopic (O, C, S) evidence

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Disseminated sphalerite (ZnS) mineralisations occur in carbonates of Triassic and Jurassic ages in the Jura Mountains (Holenweg, 1967; Hofmann, 1989 and 1993). The cadmium content in sphalerite crystals reaches values of 6000 mg/kg (Graeser, 1971). Cadmium concentrations of up to 21.4 mg/kg was also observed in carbonates of Bajocian and Oxfordian ages (Prudente, 1999; Benitez-Vasquez, 1999; Veuve, 2000; Dubois et al., 2002; Rambeau, 2006), which exceed the mean marine carbonate value of 0.03 mg/kg (Gong et al., 1977; Tuchschnid, 1995). These elevated cadmium contents in the rock substratum lead to cadmium enrichments in the corresponding soils of up to 16 mg/kg, which largely exceed the Swiss official tolerance guideline values for non-polluted soils fixed at 0.8 mg/kg.

In order to develop a predictive tool to identify Cd-enriched soils related to Jurassic rock substrata we need to reconstruct the pathways along which Cd was transferred and concentrated inside the carbonate rock and construct the model of Cd incorporation. Previous research (Veuve, 2000; Rambeau, 2006) established a model of syngene and early diagenetic enrichment in Cd of shallow-water carbonate rocks in Jura mountains with organic matter as a vector of Cd transport.

We propose a model of formation of Cd-bearing sphalerite mineralisations and cadmium incorporation into the Jurassic

rocks during periods of tectonic and hydrothermal activity in the region. Basement rocks are inferred to be the source of zinc and cadmium, amongst other elements, and fluid flow controlled by the permeability of the different formations of Jurassic carbonates the principal vector of Cd transfer.

To test our model we study the samples of shallow-marine oolitic carbonates of Bajocian age (Hauptrogenstein formation) including sphalerite crystals sampled by H. Holenweg in Auenstein (AG, Jura Mountains). Optical thin-section microscopy, XRD and ICP-MS and sulphur, carbon and oxygen isotope geochemistry analyses are presently performed on these samples to clarify the conditions of sphalerite mineralisation and Cd distribution inside the rock.

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## 7.6

### Phosphorites-Hosted Zinc and Lead in the Sekarna Ore Deposit (Central Tunisia)

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The Sekarna Zn-Pb deposit is located in Central Tunisia, at the north-eastern edge of the Rohia graben. The deposit is composed with sulfide and non-sulfide zinc-lead ore bodies. Mineralization form two major ore types: (1) Disseminated Zn-Pb sulfides forming lenses in sedimentary phosphorite layers, and (2) cavity-filling zinc oxides ore (calamine-type ore) cross-cutting Upper Cretaceous and Lower Eocene limestone.

In this abstract we focus on the sulfide Zn ore body of Saint Pierre, which is hosted in a sedimentary phosphorites unit, 5 meter in thickness, Lower Eocene in age. Mineralizations occur as stratiform lenses sphalerite-rich, with minor galena, Fe-sulfides and barite. The sulphide mineralization occurs as replacement of carbonate cements of phosphorite pellets and post-date four diagenetic events that are: phosphatogenesis, glauconitization, compaction and silicification.

Microthermometric analyses of fluid inclusions in sphalerite give a homogenization temperature in the range of 80° to 130°C. The final ice melting temperatures were in the range of -22°C to -11°C corresponding to salinities of 15 to 24-weight % NaCl eq. This fluid is typical of basinal brines.

The sulphur isotope compositions of sphalerite have homogeneous  $\delta^{34}\text{S}$  values forming a narrow range between -11.2 ‰ and -9.3 ‰, mean at -10.22 ‰. The sulphur isotope compositions of galena have homogeneous  $\delta^{34}\text{S}$  values forming a narrow range between -16 ‰ and -12.3 ‰, mean at -13.85 ‰.

Barite from Sekarna deposit has  $\delta^{34}\text{S}$  values between 24.9 ‰ and 25.3 ‰, mean at 25.1 ‰. Barite is enriched of about 4 ‰ when compared to the Tertiary sea water.

Fluid inclusion homogenization temperature and sulphur isotopes indicate that the reduced sulphur in sulfides was derived through reduction of marine sulphate by bacterial sulphate-reduction process using organic matter from phosphorite source rocks.

In terms of global classifications of mineral deposits, mineralization in the Sekarna shares some characteristics of both Mississippi Valley Type (MVT) deposits and Sedimentary Exhalative (SEDEX) deposits. The features of the Sekarna deposit that are akin to MVT deposits are: Simple mineralogy, replacement of carbonates, fluid inclusions characteristics (low to moderate homogenisation temperatures and high salinities). The features of the Sekarna deposit that are akin to Sedex type are: disseminated sulfide textures, hosted within specific phosphorites beds, organic-rich.

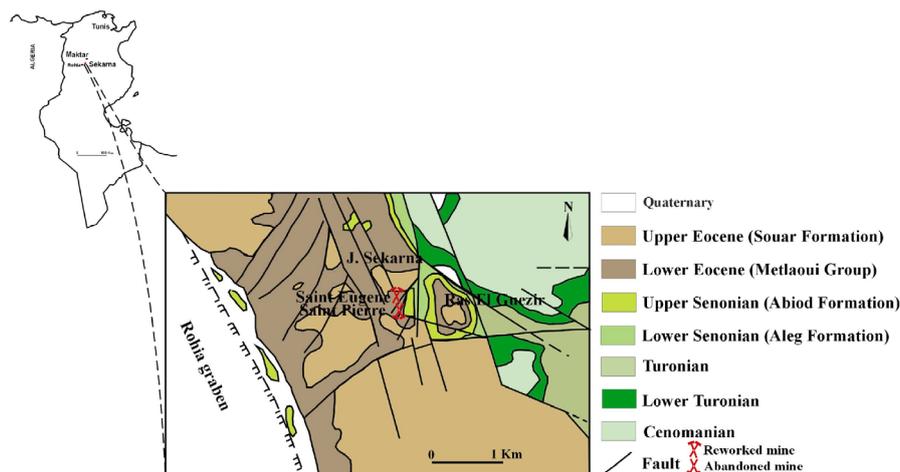


Figure 1. Location and geological map of the Sekarna area, showing the main Zn-Pb deposits. (modified from Zaïer 1999)

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## 7.7

### Numerical modelling of fluid flow in submarine hydrothermal systems

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Fluid flow through submarine hydrothermal systems transports a major part of the Earth's heat to its surface and greatly impacts the chemistry of the crust and overlying ocean. Associated high-temperature "black smokers" are manifestations of active ore-forming systems and can be regarded as modern analogues of massive sulphide deposits whose ancient equivalents have been exploited as world-class mines onshore.

The physics of these systems is complex because seawater can phase-separate, either via boiling or condensation, into a low-salinity vapour and a high-salinity brine. In order to model the sub-seafloor hydrology with numerical transport simulation techniques, a new pressure-enthalpy-salinity scheme has been developed which includes the full phase relations of the NaCl-H<sub>2</sub>O system up to 1000 °C and 5000 bars and accurately captures boiling, condensation, and salt precipitation. Simulations with homogeneous permeability representing mid-ocean ridge systems show that many of the key-observations at black smoker systems can be explained by the non-linear dependence of the fluid properties on temperature, pressure, and salinity (Coumou 2008).

Research cruises dedicated to seafloor hydrothermal activity along the intra-oceanic Kermadec arc have systematically surveyed and sampled numerous hydrothermal plumes. Venting ranges from relatively high temperature ( $\approx 300^{\circ}\text{C}$ ), metal-rich fluids to lower temperature, gas-rich and metal-poor fluids. In contrast to black smoker systems at mid-ocean ridges, some vent sites found at arc-related hydrothermal systems show evidence for significant contributions from magmatic sources (e.g., de Ronde et al. 2005).

We will develop a new numerical model, based on observations in currently active arc-related systems, to assess the influence of first-order physical parameters, seafloor topography, and the contribution of magmatic fluids to fluid flow patterns, thermal structure, and phase-separation (Figure 1). We aim to predict the optimal conditions for which metal-rich magmatic vapour may cool and contract to an aqueous liquid, which in turn is likely to generate particularly Cu- and Au-rich mineralization on the seafloor.

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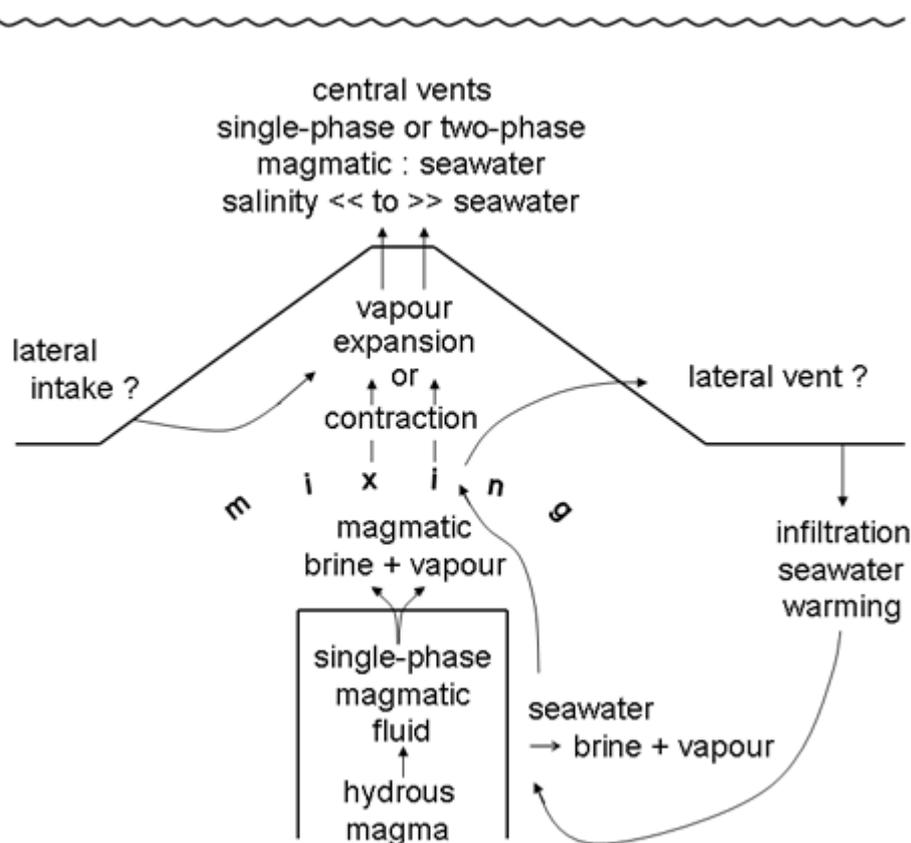


Figure 1. Schematic concept of hydrothermal fluid processes that may occur inside a submarine volcano underlain by a magmatic intrusion. Saline, single-phase fluids exsolved by crystallizing magma may separate into magmatic brine and vapour, selectively carrying certain ore metals and volatile components. The size of the magmatic heat and fluid sources, water depth, large-scale rock permeability and the intrinsic properties of the salt-water fluid system are likely key controls on the dynamic fluid evolution in space and time.

## 7.8

### Maureen unconformity-related U-Mo-F deposit, Georgetown, QLD, Australia

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Maureen deposit is situated about 290 km south-west of Cairns and 35 km by north-north-west of Georgetown. The general lithofacies can be subdivided into a Proterozoic metamorphic complex (Bain et al., 1978; Oversby et al., 1975), namely the Robert River Subgroup which is unconformably underlying the Maureen Volcanic Group of Carboniferous age, which in turn unconformably underlays the Mesozoic Gilbert River Formation. The Maureen Volcanic Group is subdivided into the basal Fiery Creek Formation, which is hosting the U-Mo-F mineralisation, the Lower Volcanic Unit and the Upper Volcanic Unit (Bain and Withnall, 1980; O'Rourke, 1975).

The deposit has a calculated grade of 0.12 %  $U_3O_8$ , 13.1 %  $CaF_2$  and 0.07 % molybdenum. The geological setting of Maureen deposit shows characteristics of unconformity-type uranium deposits. Uranium is supposed to be transported in the hexavalent state in oxidized basinal fluids. Along deeply rooted fractures and faults reduced basement fluids rise. Where mixing between these two fluids occurs uranium is reduced and precipitates. The aim of this study is to identify the transporting fluid of uranium and other relevant ore forming components and to find evidence for mixing of reduced and oxidized fluids.

The precipitation of U, Mo and F was spatially related to the intersection of steeply dipping faults with the Precambrian – Palaeozoic unconformity and occurred preferentially in coarse grained and pebbly sandstone or conglomerate beds of the Fiery Creek Formation. Mineralised zones appear as elongated narrow bodies showing a close relationship to EW oriented structures. Mineral contours of U, Mo and fluorite are shown in Figure 2 along an EW cross section through the Southern mineralisation zone. Typical alteration assemblages include fluorite, dickite, chamosite and disseminated pyrite. In low to intermediate mineralized samples muscovite shows enrichment in Mg where it occurs in contact with chlorite. Such mineral assemblages show characteristics of hydrothermal deposits where the mineralizing fluids have compositions that are drastically different from the country rock assemblages (Komninou and Sverjensky, 1995). During early mineralisation, fluorite matrix replacement stays within narrow zones surrounding fractures. With progressive mineralisation grain replacement, veining and finally chemical brecciation dominate. Sulfide-rich mineral assemblages located in deeper parts of the deposit near the unconformity represent the reduced end member of the system, whereas assemblages containing anatase, trögerite and other oxides are supposed to represent the oxidized end member. Further constraints on mixing of oxidized basinal fluid with reduced basement fluids were obtained from fluid inclusion analysis. Figure 2 illustrates the result of LA-ICP-MS analysis and microthermometry on a fluid inclusion sample from Maureen deposit.

This study combined field observations with fluid inclusion analysis and mineral geochemistry providing important insights into transport and precipitation processes of unconformity-related uranium deposits.

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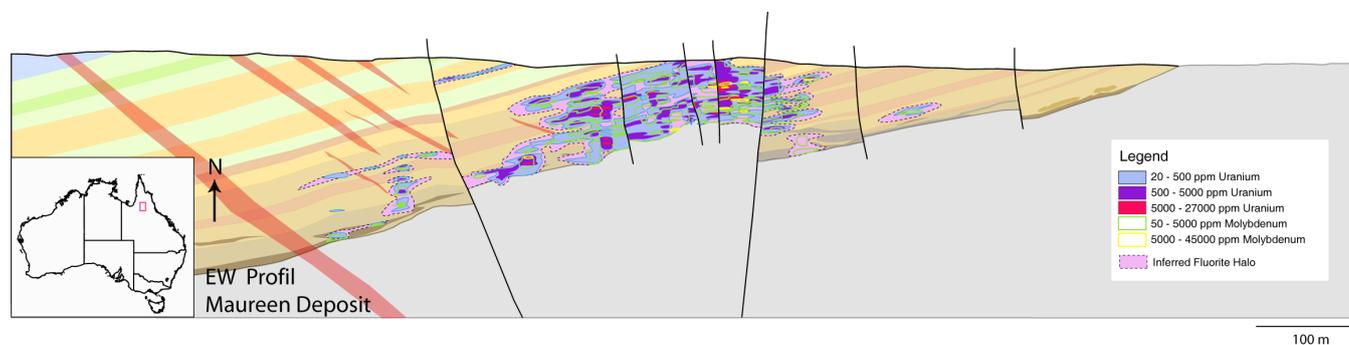


Figure 1. EW cross-section through the Southern mineralisation at Maureen deposit. Mineral contouring based on drill hole data provided by Mega Georgetown showing the distribution of U, Mo and Fluorite. The contour lines of U, Mo and F overlap, but differ in their extents. Fluorite forms an extensive halo surrounding high grade ore bodies.

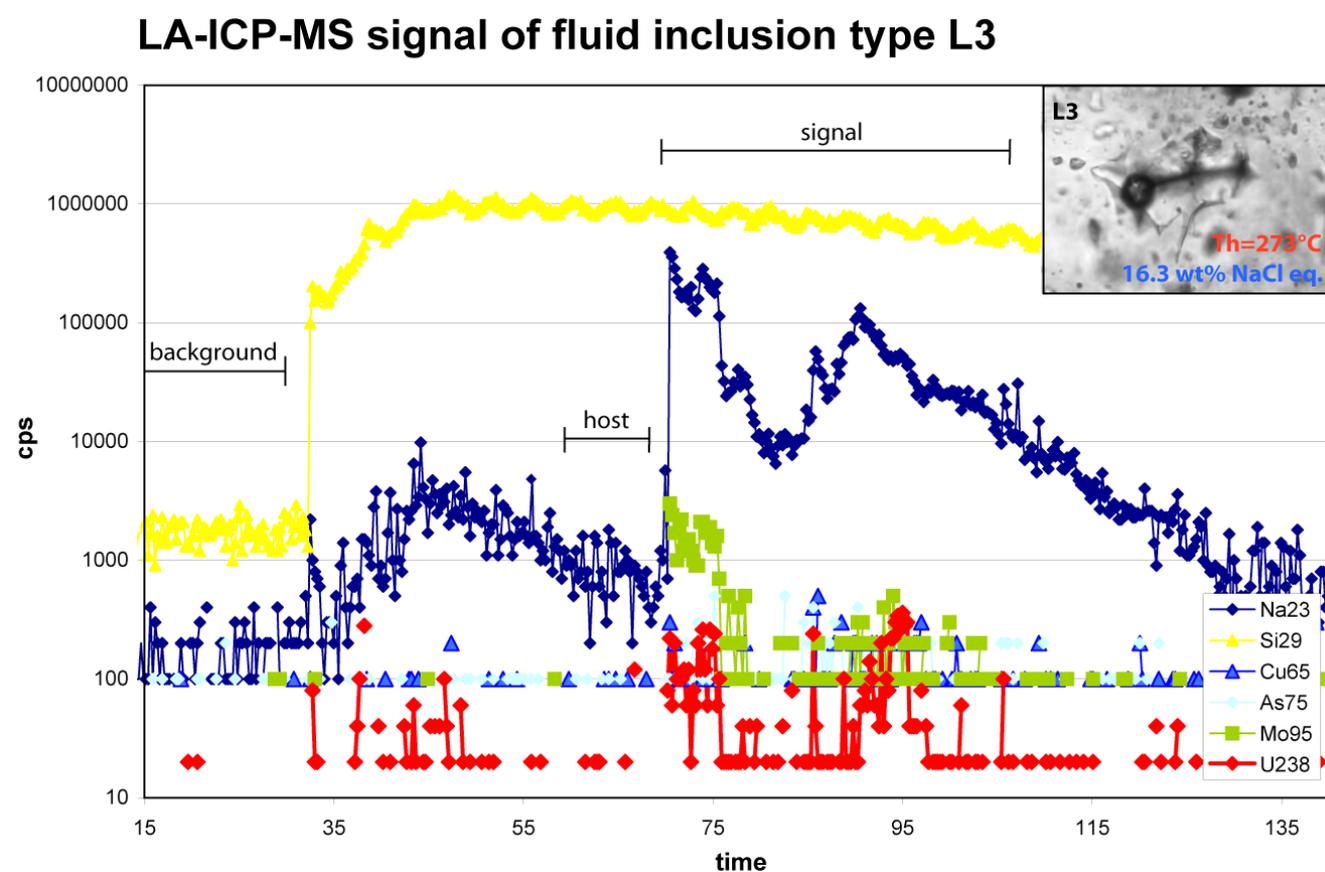


Figure 2. LA-ICP-MS signal of a saline 2 phase fluid inclusion (L3-type) showing corresponding peaks for U, Mo, As, Cu and Na. The uranium concentration is 11 ppm and Mo has a much higher concentration of 702 ppm, which is very unusual.

## 7.9

### Olivine-Ti-clinohumite veins and their relation to partial dehydration of high pressure serpentinites

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A major question concerning the dehydration of subducted ultramafic (UM) rocks is whether they have the potential to leave a chemical fingerprint on the mantle wedge above them. Fluids released by UM rocks at high P and T are not directly accessible. However, they can be traced by studying the chemistry of serpentinites that were subducted to depths of serpentine dehydration. In the present study we explore peak-metamorphic veining in high pressure (HP) serpentinites of the Erro-Tobbio Unit (ET), Ligurian Alps, Italy, in order to learn about the chemical composition of the fluid released by these rocks during partial dehydration.

The ET Unit represents ultramafic mantle (UM) that was hydrated on the Tethys ocean floor. The UM rocks were then subducted to depths of 65-80 km at around 550-600°C and developed olivine (Ol) + Ti-clinohumite (Ti-Cl) + antigorite (Atg) + clinopyroxene (Cpx) + magnetite (Mag) peak mineral assemblage. The same minerals dominate adjacent HP veins, but their proportions are different. The ET HP serpentinites went through partial dehydration to form Ol + Atg from brucite (Brc) + low-T serpentine polymorph (Srp) (Scambelluri et al., 2001). Olivine has abundant polyphase (serpentine ± magnetite ± methane) inclusions in wall rocks as well as in the veins, and is often accompanied by inclusion-rich Ti-Cl. The abundance and appearance of these inclusions and the presence of methane indicate that these polyphase inclusions represent fluid inclusions modified by post-entrapment modification(s) during exhumation. Trace element analysis of these inclusions reveals subtle but significant differences in dehydration fluid chemistry, which can be linked to different mineral proportions and water/rock ratios during fluid release and migration.

Fluid in the ET rocks was partly channelized and migrated as attested by the veins. Vein bulk rock trace element concentrations show enrichment in Ti, Ba, Nb, Li, HREE and Cu relative to the wall rocks, accompanied by depletion in Cr. Based on trace element distribution in Srp of recent ocean-floor serpentinites decomposition of Brc + Srp produces relatively dilute fluids. This requires high net fluid flux to produce HFSE-rich veins. However, disequilibrium in and around fluid conduits may enhance reactions and trace element uptake from the fluid. High concentration of certain trace elements in vein Cpx (e.g. Sr 191-202 µg/g) and Ol (e.g. Li 9.8-35.5 µg/g) are therefore not necessarily indicative of significant addition of these elements from an external source. Our study emphasizes the importance of mineral stability and trace element chemistry in influencing bulk rock and fluid geochemical evolution.

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## 7.10

### Trace element uptake into quartz cement – a function of temperature or fluid characteristics?

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In the Interior Oman Sedimentary Basin (Fig. 1) siliciclastic sediments of the Permo-Carboniferous Haushi Group were deposited under both glacial (Al Khlata Formation) and temperate to semi-arid (Gharif Formation) conditions. Due to a varied subsidence, these sediments today cover depths ranging from surface outcrop in the SE to almost 5000 m in the NW. Burial is maximal in the NW part of the basin, whereas in the SE uplift of up to 2000 m is indicated from basin modeling results. Basin-wide authigenic quartz cementation began concurrent with the Late Cretaceous obduction of the Oman Mountains,

and thus, independent of burial depth or temperature (Juhász-Bodnar, 1999). Crystallization temperatures vary between 85 and 150°C. Pressure solution is the major source of silica since no other cogenetic reactions occurred which could release silica.

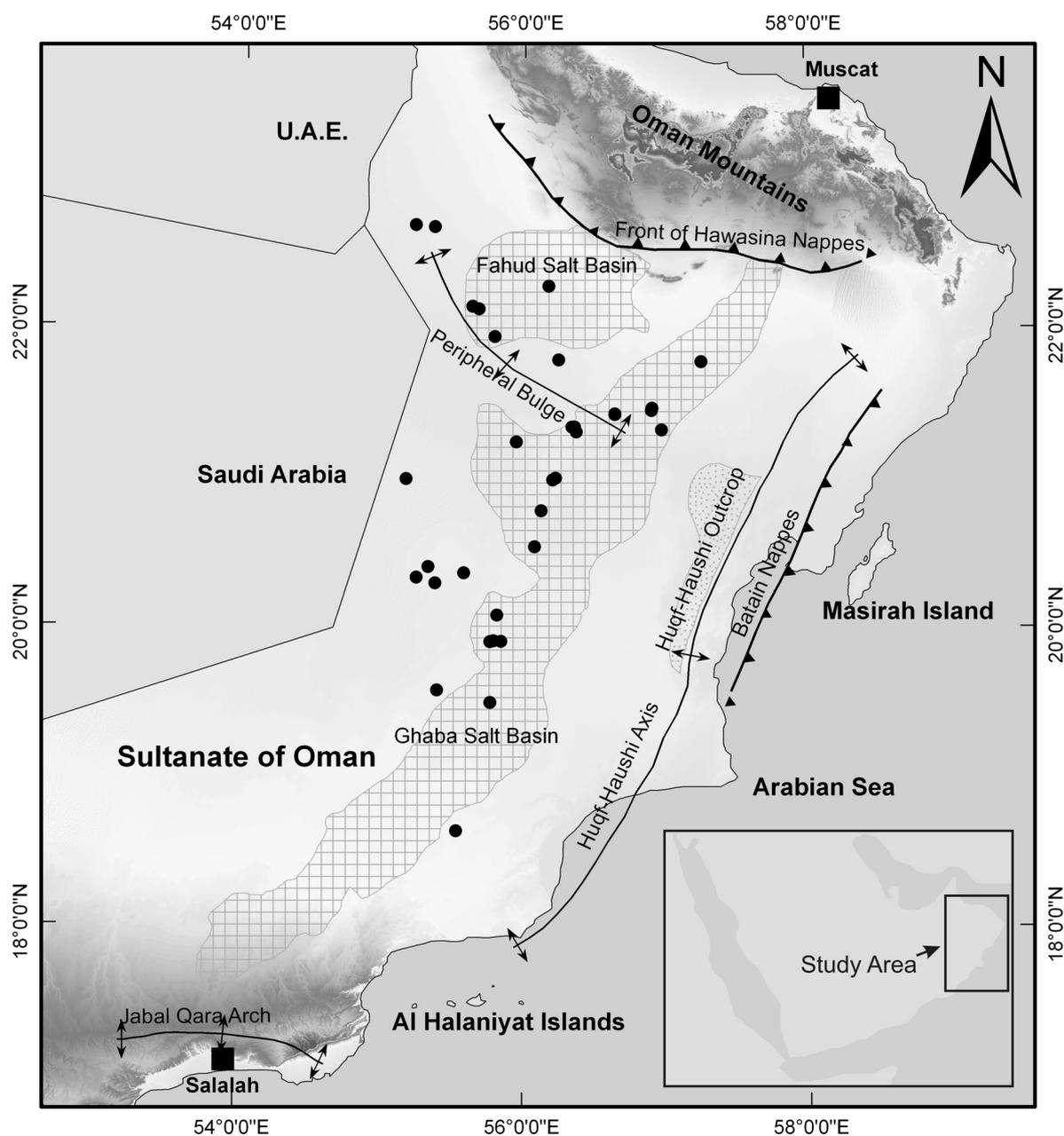


Fig. 1: Map of the sampling area. Well locations are marked by black dots.

LA-ICPMS and SIMS analyses of authigenic quartz reveal Al and charge balancing Li as the predominant impurities ranging from 60 to 1700  $\mu\text{g/g}$  and 0.5 to 60  $\mu\text{g/g}$ , respectively. Li and Al are correlated with an atomic ratio of 0.11 ( $R^2=0.94$ ) in the Al Khlata Formation and 0.14 ( $R^2=0.80$ ) in the Gharif Formation. SIMS analyses indicate a positive correlation between H and Al. Na is below 10  $\mu\text{g/g}$  and not correlated with any other trace element. Be, B, K, Ti and Fe are below the element-specific limits of detection of ca. 0.5  $\mu\text{g/g}$  (using a 32  $\mu\text{m}$  spot for analysis).

The mean Al concentration is independent of the stratigraphy and crystallization temperature but the Al concentration varies by a factor of 3 on a regional scale. Additionally, the measured Li/Al ratio is higher than published values for quartz cement formed between 80 and 120°C (Demars et al., 1996), but is lower than ratios in hydrothermal vein quartz formed at temperatures between 200 and 300°C (Perny et al., 1992).

The low Al/Li atomic ratio and the absence of significant other cations required for charge balancing Al in quartz implies the presence of additional positive charged ions such as  $\text{H}^+$ , which was only semi-quantitatively determined by SIMS. In addition, the highly variable concentrations of Al and Li and hence H, at constant atomic ratios indicate a regionally and temporally variable pH-value. This variability suggests that pH-value is not buffered internally (Landtwing and Pettke, 2005) but externally by processes such as organic matter maturation and/or hydrocarbon migration.

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## 7.11

PVTx properties of H<sub>2</sub>O-NaCl fluids using Brillouin scattering spectroscopy

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Saline-rich aqueous fluids play a very important role in a wide range of geological events in the Earth's crust and mantle. These processes include, for example, metamorphic reactions, the magma production in the mantle wedge beneath active volcanoes at subduction zones, the transport of chemical components in several geological settings, the alteration of the seafloor and the formation of ore deposits. Mixtures in the H<sub>2</sub>O-NaCl binary system are a good proxy for these saline-rich aqueous fluids. Essential for quantitative modelling of phase equilibria related to such geological processes is the knowledge of the thermodynamic properties of these fluids at geologically relevant pressure and temperature conditions. Despite the important role of these geological fluids, very few experimental data on aqueous saline-rich fluids other than pure H<sub>2</sub>O are available at pressures higher than 0.1-0.5 GPa. For instance, the equations of state (EoS) for H<sub>2</sub>O-NaCl are restricted to 0.5 GPa. Therefore, the interpretation of subduction-related fluid processes and other fluid-mediated geological events requires the extrapolation of thermodynamic properties through over an order of magnitude in pressure.

In this contribution we present the PVTx properties of H<sub>2</sub>O-NaCl binary mixtures with different NaCl concentrations up to high P-T conditions, calculated from sound velocity measurements in the external heated membrane diamond anvil cell using Brillouin scattering spectroscopy.

Brillouin scattering spectroscopy allows the direct measurement of sound velocities of compressional waves ( $V_p$ ) propagating in the fluid and hence, the evaluation of the equation of state  $\rho(P,T)$ . The obtained sound velocities and densities are compared with available data in the literature.

The results are combined with previous experimental and theoretical EoS to provide the thermodynamical properties of the most relevant aqueous systems involved in geological fluid-mediated processes in the Earth's crust and mantle.

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## 7.12

# Low-Salinity fluids at the Bajo de la Alumbrera porphyry Cu-Au deposit, Argentina

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New evidence from several major porphyry copper and epithermal deposits concerning the role of low-salinity fluids has been published. In contrast to earlier interpretations, the parental magmatic fluid is considered to have an intermediate density and salinity. Several metals including copper and gold are mainly transported by a vapor-like fluid, not by a high-salinity brine. This vapor can then contract and carry significant amounts of metal to the low-temperature epithermal regime.

The Bajo de la Alumbrera porphyry copper-gold deposit in north western Argentina is well studied in terms of geology, alteration geochemistry and fluid characteristics, but low-salinity fluids are not documented extensively. In this study, samples particularly from the earliest and latest veins have been taken, to test these new findings at Alumbrera. The aim of the study was not a complete reassessment of the fluid evolution but to fill gaps of previous studies. The mean to investigate fluid characteristics are inclusions in vein minerals, whose salinities and temperatures are measured by microthermometry, and which are then chemically analyzed using LA-ICP-MS.

A very copper-rich, intermediate-density fluid with high homogenization temperatures, as well as high-density vapor inclusions, have been found and analyzed, surprisingly not in the earliest but in a texturally late vein. Nevertheless, similarities to the original magmatic fluids from other deposits indicate that also at Alumbrera the parental fluid was not a high-salinity brine, as inferred by previous studies, but a fluid with intermediate density and salinity.

In late veins, aqueous fluids have been investigated which could easily be the ore fluids for an epithermal deposit, as for example the nearby Farallón Negro deposit. The analytical method has been adapted to measure gold with very low detection limits, and indeed, gold has been detected with a high confidence in those very low-salinity fluids.

In addition to that, attempts to characterize the fluid belonging to relatively late pyrite-chalcopyrite veins occurring in many deposits but never investigated properly have been made, but compositional results are sparse. However, microthermometry indicates aqueous fluids with low salinity being the type of fluid responsible for those veins. Few boiling assemblages have also been analyzed, showing that in a phase separation copper, sulfur and gold partition preferentially into the vapor phase, confirming observations on other deposits. The transition from the vapor-like fluid to an aqueous liquid, called contraction, which is assumed to be responsible for high gold concentrations in ore fluid for epithermal deposits, has not been found in fluid inclusions.

The results presented here are not sufficient to document the whole fluid evolution of the Bajo de la Alumbrera deposit, more samples and analyses would be necessary. Nevertheless, evidence has been found that the new models can be applied to Alumbrera as well and low-salinity fluids indeed are responsible for many processes forming porphyry copper deposits.

## 7.13

# The Pb-Zn-Sr-Ba deposits in Northern Tunisia: trace elements, rare earth elements and Sr geochemical evidence for their origin

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Several Pb-Zn-Sr-Ba deposits are known in the North of Tunisia (Figure 1). Although, several works have been interested in their genetic conditions (Rouvier et al. 1985; Orgeval, 1994; Sheppard et al., 1996; Souissi et al., 2007), the source of metals is yet to be debated.

According to the geological context, the Triassic series may be divided into three dominating facies (i) a megabreccia made of micritic black dolostones with variegated clays and altered basalt fragments (Jalta mine in the Nappes Zone). (ii) a thick bedded dolomitic series, interlayered with thin marly layers (Bechateur quarry in the Nappe Zone), (iii) a chaotic mixture of gypsum, variegated clays and lenticular bodies or isolated blocks of black micritic dolostones that crop out along major faults (J. Ressay in the Tunisian Dorsale) or as diapirs (Boukhil, Lakhouat, Fej Lahdoum, Kebbouch, Guern Halfaya, Fej Hassene, Doghra in the Dome zone).

The mineralizations (stratiform bodies, cavity fillings, karsts, disseminations, veins, stockworks) may be hosted in the Triassic carbonated series (Jalta mine, Guern Halfaya, Jebel Ghozlane), but mainly in the younger carbonated units mechanically in contact with the Triassic: the Upper Jurassic (J. Ressay), The Upper Cretaceous (Boukhil, Lakhouat, Fej Lahdoum, Kebbouch, Guern Halfaya, Fej Hassene, Doghra), the Eocene (Boukhil) and the Mio-Pliocene (Jalta mine, Jebel Ghozlane).

The Geochemical investigation is based on metallic trace elements (MTE), rare earth elements and Sr isotopes analysis. The MTE geochemistry, conducted on the different Triassic lithologic facies, shows that, apart from the barren series of the Bechateur quarry area, strong anomalies in these elements are recorded either in clays (Pb, Zn, Cd) or carbonates (Pb, Zn, Cd, Cr, Co, Cu). REE and Sr isotopes analyses have been conducted on celestite samples and their carbonated (dolomite, calcite) hosts collected along the Triassic-Upper Cretaceous contact. The results show that the total REE contents are too high in the carbonates with respect to those in the celestite samples. In addition to that, the REE spectra of the two mineral species are quite different from each other: carbonates are characterized by nearly flat spectra, the LREE being slightly more concentrated than the HREE, while celestites are characterized by negative Ce and Er anomalies along with strong positive Eu anomalies. Such a result shows that the mineralizing fluids may be assimilated to deep basinal brines which have been equilibrated with detrital sedimentary series or rock units rich in feldspars (Taylor and McLennan, 1985). On another respect, Sr isotopes analyses conducted on the Triassic rocks (dolomite:  $0,708152 \pm 8$  to  $0,708908 \pm 9$ , gypsum:  $0,708090 \pm 9$ ) and on celestite samples ( $0,708706 \pm 9$  to  $0,710225 \pm 9$ ) show that  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are anomalous with respect to the Triassic (0,70690 to 0,70794), Jurassic (0,70677 to 0,70778) or Cretaceous (0,7071 to 0,7077) sea water. Orgeval (1994) and Sheppard et al. (1996) supposed that fluids enriched in  $^{87}\text{Sr}$  have been, continually, in contact with the Triassic diapirs.

Taking into account the positive anomalies of the MTE in the Triassic rocks, part of these elements could be sourced from these units. However, the geological contexts (diapirs or major faults deeply rooted in the basement, both associated to positive geothermal gradients), the REE and the Sr isotopes data as well as the presence of a Pb-(Zn-Ba) mineralization hosted in the Permian "Upper Dolostones" in the South of Tunisia, strongly support the hypothesis that all the elements should be deeply sourced. So, the Paleozoic series (siliciclastics or primary ore deposits) seem to be favourite potential sources.

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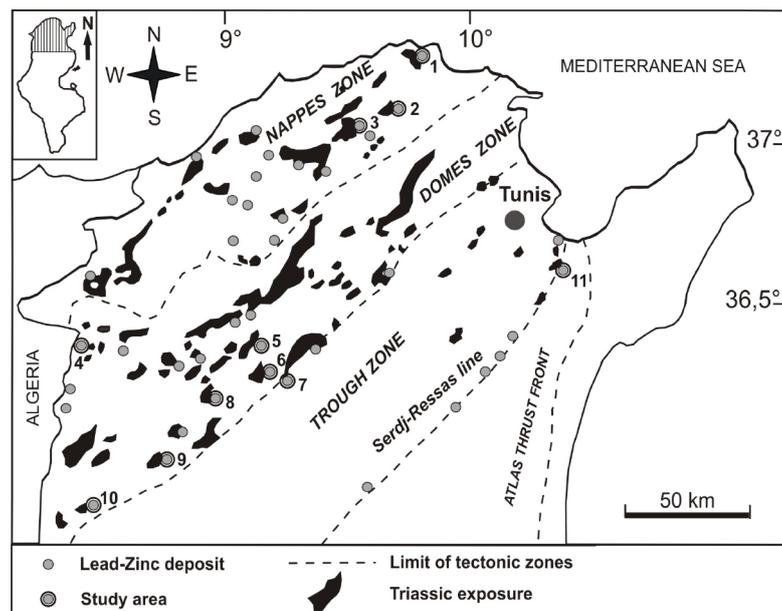


Figure 1. The Triassic exposures and Pb-Zn deposits in Northern Tunisia

1 Bechateur; 2 Jebel Ichkeul; 3 Jalta; 4 Fej Hassense; 5 Fej Lahdoum; 6 Boukhil; 7 Lakhouat; 8 Kebbouch; 9 Doghra; 10 Guern Halfaya; 11 Jebel Ressas.

## 7.14

### The Mississippi Valley type fluorite ore of Jebel Stah (North-Eastern Tunisia) II: contribution of the REE and Sr isotopes geochemistry to the genetic model

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Several F-(Ba-Pb-Zn) belong to the fluorite district of Zaghouan (FDZ) in the north-east of Tunisia. They are associated to Lower Liassic and Upper Jurassic carbonate formations (Oust and Ressas formations, respectively). Unconformities (paleoreliefs, hard grounds, phosphatic condensed layers, karstification, sedimentary gaps) separate them from the overlying sedimentary cover. These formations run along a major fault considered to be a major tectonic lineament which cuts the basement and its sedimentary cover, trending in the atlasic (NE-SW) direction. Chaotic masses of the Triassic (evaporates, clays and dolostones) crop out frequently along this fault (Fig. 1).

The mineralizations occur either as stratoid bodies along the unconformity surfaces or located at the top of the Oust (Stah, Kohol) or the Ressas formations (Zriba-Guebli, Mecella). They may be also associated to a fracture network which cuts the carbonated formations and their marly-calcareous cover (H. Jedidi, J. Oust, Sidi Taya).

Souissi et al. (1997, 1998) have pointed out the epigenetic character of the mineralization of J. Stah, which is rattached to the MVT group of deposits dominated by fluorite. The deposition has resulted from the hydrothermal ( $135 \pm 20$  Wt % NaCl equiv.) circulation of a Na-Ca-Cl brine ( $20 \pm 1$  Wt % NaCl equiv.) in depth. Subsequent circulations are responsible of the remobilisation in deeper conditions of the fluorite ( $185 \pm 20^\circ\text{C}$ ,  $10 \pm 1$  Wt % NaCl equiv.) followed by the deposition of the massive

quartz within fractures ( $225 \pm 20^\circ\text{C}$ ,  $5,5 \pm 1$  Wt % NaCl equiv.). This study is conducted to provide the genetic model with new arguments in the light of REE and Sr isotopes geochemistry.

The results of the REE geochemistry allow to conclude that the epigenetic dolomites and the finely crystallized fluorite replacing the carbonated matrix (laminated karst deposits and dark layers of the banded ore) exhibit similar REE spectra showing a slight enrichment in LREE with respect to the HREE along with weak cerium and europium anomalies. The coarse crystalline petrographic types of fluorite (open space fillings, veins, geodes) and the associated calcite are characterized by REE spectra showing a depletion in the LREE and a weak negative Eu anomaly. Such a geochemical character allows to conclude that fluorites, in this case, have crystallized from the residual fraction of the same ore fluid.

Strontium isotopes analysis, conducted on different fluorite ore samples show that all the strontium isotope ratios fall in the narrow range  $0,708154 \pm 8$  to  $0,708333 \pm 8$ . So, one can deduce that fluoride has been carried by a basinal fluid which is more radiogenic than both of the Triassic ( $0,70690$  to  $0,70794$ ) and the Jurassic ( $0,70677$  to  $0,70778$ ) sea water (Burke et al., 1982; Koepnick et al., 1990). The migration of this fluid could have been released by a hydraulic fracturing during a post Jurassic major extensional phase. It is noteworthy, however, that several intra-paleozoic fluorite ores hosted in sedimentary series to which magmatic events may be associated are documented all around the Mediterranean basin: in France (the Tarn, the Pyrénées atlantiques, the Cordesse), in Spain (the Asturian province, the Valle De Tena in the Huesca Province) and in Italia (the Sarrabus area of Sardinia). This kind of deposits exists also elsewhere in the world: in England (the North Pennine ore field and the Derbyshire Province, in Canada (the Saint Lawrence deposits of Southern Newfoundland and in the Mississippi Valley, USA (Southern Illinois-Western Kentucky and Sweetwater-Tennessee). For this reason, the authors strongly support the idea that the basinal brines trapped in the underlying Paleozoic sedimentary column, which is rich in siliciclastics, could account for the radiogenic  $87\text{Sr}/86\text{Sr}$  signature recorded for the fluorite ore of Jebel Stah. Fluoride should come from the lixiviation of primary deposits hosted in this series.

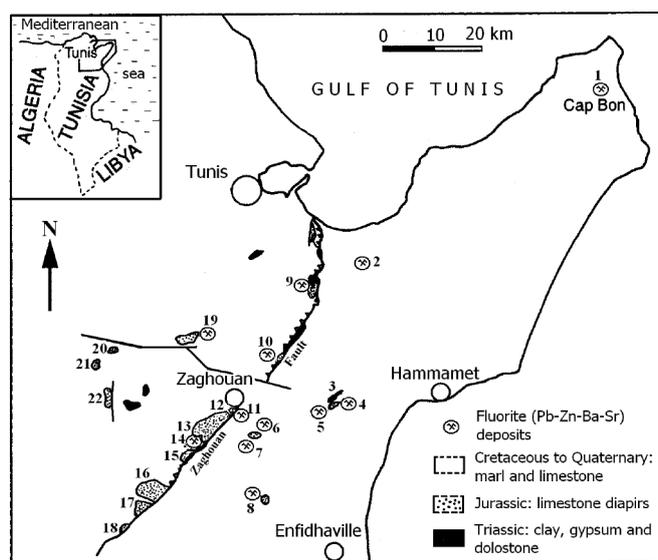


Fig. 1: Location map of the Jurassic diapirs in north-eastern Tunisia and the associated F-(Pb-Zn-Ba) deposits. 1 Oued M'tak, 2 J. Mokta, 3 Ore deposit running along the side of the Triassic outcrop of Hammam Jedidi, 4 J. Azreg, 5 J. el Hammam, 6 Hammam Zriba, 7 J. Guebli, 8 J. M'dekker, 9 J. Ressas, 10 J. Messella, 11 Sidi Taya, 12 Poste Optique, 13 J. Stah, 14 J. Kohol, 15 J. el Azeiz, 16 J. Bent Saidane, 17 J. Fkirine, 18 J. Zaress, 19 J. Oust, 20 J. Aziz, 21 J. Bou Kornine, 22 J. Rouas.

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## 7.15

### Towards a quantitative process model of a porphyry Cu-Mo-Au deposit at the example of Bingham, Utah.

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Porphyry copper deposits form from magmatic hydrothermal systems. Dissolved metals are transported in both, vapour and liquid phases and precipitated by rapid changes in temperature and pressure. The driving forces for fluid flow in these systems are fluid density variations generated by the thermal energy released by a magmatic intrusion. In our previous generic models (Driesner and Geiger, 2007) we have been able to predict zones, where temperature and/or pressure change over a short distance, therefore leading to precipitation of metals in a limited volume. The second prerequisite for ore concentration is the amount of fluid passing through this volume. The time scale of these processes may vary between a few 10'000 or several 100'000 years.

Landtwing (2004) demonstrated from fluid inclusion data that ore deposition in Bingham took place at temperatures between 350 and 425°C and pressures between 14 and 21 MPa (about 1.4-2.1 km paleodepth assuming hydrostatic conditions). She concluded from textural observations that vein and ore formation was driven by a single source of magmatic-hydrothermal fluid originating from a porphyry quartz monzonite. The overpressure from the boiling fluid also induced hydrofracturing, creating the initial pathways for the fluid. Because the ore deposition temperature was in the field of quartz dissolution by vapour, she explained the observed two quartz generations in the veins (one before, one after Cu deposition) by the generation of secondary permeability by quartz dissolution. Ore precipitation from a vapour phase took place in a temporal narrow phase of increased permeability. These findings concur with the results from Heinrich et al. (1999), who identified a vapour-like fluid responsible for Cu and Au transport.

Furrer (2006) proved with compositional analysis that the fluids are not convecting around the intrusion, due to missing evidence of fluid dilution. Therefore the fluid originates from the intrusion and is not modified by fluid mixing at the depths determined by Landtwing (2004).

With the availability of these data and our in house finite element code (CSMP++), which is able to model mass conservative hydrothermal saline multiphase fluid flow (Driesner and Geiger, 2007), we will test the predictions from the generic models using the Bingham deposit as a field example. Being supplied with detailed 3D mine data by Kennecott Copper Exploration including ore grades and lithology, we are now capable to set up a model of the ore body, reconstruct the palaeoenvironment and compute the flow paths, the likely ore deposition areas and porosities generated by hydrofracturing. These porosities must correlate with vein density data measured by Grün (2007). From the calculated P-T conditions we can predict ore precipitation zones, which must correlate with the observed field data.

If simulated values are in agreement with observed data, conclusions about the duration of ore forming hydrothermal systems and predictions about the estimated size of unexplored porphyries can be made. As a further step, we are considering extending the model area to batholite scale and try to explain why nearby intrusions a barren, while in bingham a world class deposit has formed.

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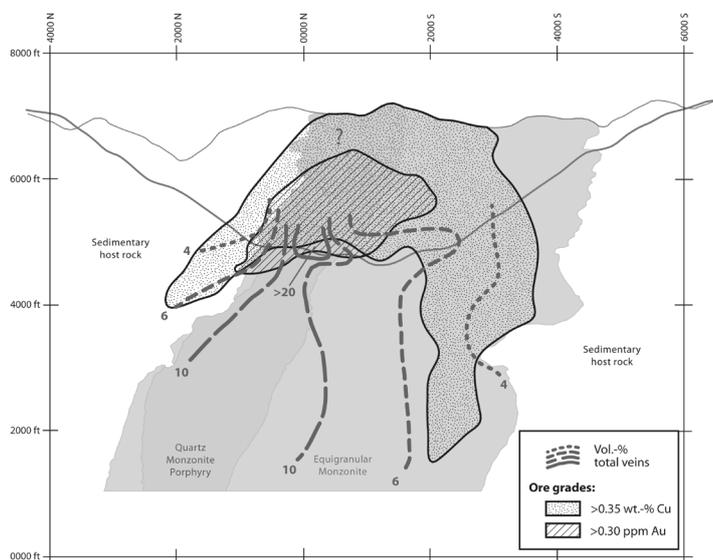


Figure 1: Vein density and Cu as well as Au ore grades in Bingham after Grün (2007)

## 7.16

### Fluid chemical characterisation of the Pataz, Marsa and Parcoy mineralized districts in the Peruvian Eastern Cordillera

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During the Carboniferous a widely extended plutonism occurred on the north-western coast of the South-American terrain which is represented today by a large number of granodioritic-monzogranitic intrusions along the Peruvian Eastern Cordillera. These granitoid intrusions contain structurally controlled, shear zone hosted vein type deposits, with several distinct stages of quartz-pyrite-galena-sphalerite-arsenopyrite-gold mineralization. The strike directions of the mineralized veins are corresponding with the main fault directions from  $\approx N100^\circ$  to  $\approx N165^\circ$  of the area (Haerberlin et al., 2002). Pataz, Marsa and Parcoy mining districts enclose two main contemporaneous auriferous vein systems, which can be distinguished by their dip directions: (a) steeply dipping ( $\approx 45^\circ$ - $60^\circ$  to the E), (b) subhorizontal ( $\approx 10^\circ$ - $15^\circ$  to the E) veins.

New fluid inclusion analysis is being carried out on the three quartz stages of the subhorizontal veins of Pataz, Marsa and Parcoy mining districts (Jimena, Glorita 2, Valeria, Michauara, Rosa Orquidea and Sambuca veins). The result will be compared to previous microthermometric measurements on the steeply dipping vein system of Pataz mineralization (La Lima 2, Choloque) (Haerberlin, 2002). The variability in the sulphide mineral precipitation capacity of the fluid system is represented by a significant decrease in the salinity, from the primary, coarse pyrite (up to 5mm in diameter) bearing, barren quartz stage, through the gold bearing sulphide mineralization to the late stage quartz-carbonate veining. The O isotope analysis based on extended sampling following lateral and vertical dimensions are devoted to show any possible meteoric fluid input into the circulating (magmatic)-hydrothermal system.

There are several different theories on the formation of the Pataz mineralized bodies. Previous investigation interpreted these auriferous vein systems as orogenic gold deposits however there is still an open debate about any possible magmatic link. This study is addressing the issue on the chemical properties of the fluids involved in the formation of the gold deposits and their relationships with any possible contemporaneous magmatic event.

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