Heterogeneous melt and hypersaline liquid inclusions in shallow porphyry type mineralization as markers of the magmatic-hydrothermal transition (Cerro de Pasco district, Peru)

Bertrand Rottier*, Kalin Kouzmanov*, Anne-Sophie Bouvier**, Lukas P. Baumgartner**, Markus Wälle***[†], Hervé Rezeau*, Ronner Bendezu ****, and Lluís Fontboté*

*Department of Earth Sciences, University of Geneva, 1205 Geneva, Switzerland

**Institute of Mineralogy and Geochemistry, University of Lausanne, 1015 Lausanne, Switzerland

*** Institute of Geochemistry and Petrology, ETH Zürich, 8092 Zürich, Switzerland

**** Volcan Compañía Minera S.A.A., Lima, Peru

[†] present address: Memorial University of Newfoundland, CREAT, CRC and CFI Services (CCCS), Bruneau Centre for Research and Innovation, St. John's, NL, Canada, A1C 5S7

Corresponding author: Bertrand.Rottier@unige.ch

Abstract

Recently identified occurrences of porphyry-style mineralization evidence the link of the world's second largest known epithermal base metal Cerro de Pasco deposit (Peru) to a porphyry system emplaced at depth. They consist of (i) quartz-monzonite dykes and (ii) the south-western part of the large diatreme-dome complex adjacent to the main ore bodies of Cerro de Pasco, and (iii) stockwork of banded quartz-magnetite-chalcopyrite-(pyrite) porphyry-type veinlets crosscutting trachyte porphyritic intrusion cropping out at surface in the central part of the diatreme-dome complex. The latter porphyry-type mineralization observed at the same erosion level as the main epithermal base metal carbonate-replacement ore bodies is the subject of this work. Geological constraints indicate a shallow emplacement level (depth < 1 km, P < 270 bars), implying rather

unusual low-pressure and high-temperature environment for the formation of porphyry-style mineralization.

The banded porphyry-type veinlets record a multiphase history of formation with two successive high-temperature ($>600^{\circ}\text{C}$) stages, followed by a lower-temperature ($<350^{\circ}\text{C}$) stage. More than 90% of the quartz in veinlets precipitates during the first two high-temperature stages. Stage 1 is characterized by the entrapment in hydrothermal quartz of inclusions containing variable proportions of both silicate melt and metal-rich hypersaline (>90 wt % NaCl eq.) liquid, hereafter referred to as heterogeneous silicate melt inclusions (HSMIs). The latter are rarely described in porphyry-type mineralization. We suggest that during stage 1, the inclusions result from heterogeneous entrapment of an evolved hydrous rhyolitic melt mixed with a hypersaline fluid phase at low pressure (270 bars) and high temperature ($>600^{\circ}\text{C}$). The stage 2 is marked by the entrapment of metal- and sulfur-rich hypersaline liquid inclusions, with salinity around 70 wt % NaCl eq, originated from the adiabatic ascent of magmatic hypersaline fluids transferred from deeper parts of the system. The lower-temperature stage 3 is characterized by an important temperature drop from $>600^{\circ}\text{C}$ to $<350^{\circ}\text{C}$ as revealed by microthermometry of aqueous two-phase liquid-vapor (L-V) inclusions. Quartz textures revealed by SEM-CL imaging allow ascribing the sulfide precipitation to the low-temperature mineralization stage 3. *In-situ* SIMS $^{18}\text{O}/^{16}\text{O}$ isotope analyses of quartz across the veinlets are indicative of a magmatic signature of the fluids during the first two stages; while quartz from stage 3 has oxygen isotopic compositions suggestive of minor contribution of meteoric waters to a predominantly magmatic aqueous fluid (~ 10 vol. % of meteoric input), which probably triggered Cu-Fe sulfide precipitation in the stockwork. High metal and sulfur contents of HSMIs and hypersaline liquid inclusions determined by LA-ICP-MS are interpreted to represent the fluid composition prior to the main sulfide precipitation event. The similar Pb-Zn ratio of the bulk ore extracted from the epithermal ore bodies at Cerro de Pasco and the HSMIs and hypersaline liquid inclusions suggest a common source of the fluids associated with the different mineralization styles at Cerro de Pasco.

Keywords: melt inclusions, fluid inclusions, porphyry-epithermal, LA-ICP-MS, SIMS, quartz, SEM-CL.

1 Introduction

Spatial and temporal link between porphyry-type mineralization and epithermal base metal deposits (i.e., Cordilleran polymetallic deposits) is recognized in several telescoped systems where base metal mineralization directly overprints high-temperature porphyry-style mineralization (e.g., Catchpole et al., 2011, 2015; Masterman et al., 2005; Reed et al., 2013; Rusk et al., 2008a). At the world-class (Zn-Pb-Ag-Cu-Bi) Cerro de Pasco Cordilleran deposit a genetic link with a hidden porphyry system at depth has already been evoked by Baumgartner et al. (2008), but no direct evidence reported. Recently, Rottier et al. (2015a) described porphyry-style mineralization in clasts contained in (i) quartz-monzonite dykes and (ii) the large diatreme-dome complex adjacent to the main part of Cerro de Pasco deposit, as well as (iii) porphyry-type stockwork mineralization occurring at surface in the central part of the diatreme. The present study focuses on the latter occurrence where shallow trachyte porphyry is crosscut by a stockwork of banded quartz-magnetite-chalcopyrite-(pyrite) veinlets.

A striking characteristic of this porphyry-style mineralization is the occurrence of inclusions in the hydrothermal quartz consisting of variable proportions of silicate melt and non-silicate chlorine-rich fluid, hereafter referred to as heterogeneous silicate melt inclusions (HSMIs). HSMIs have been observed occasionally in various occurrences in quartz phenocrysts from intrusive rocks, miarolitic cavities and pegmatites (Campos et al., 2002, 2006; Davidson et al., 2005; Davidson and Kamenetsky, 2007; Frezzotti, 1992; Fulignati et al., 2005; Harris et al., 2004; Kamenetsky et al., 2004; Kamenetsky and Kamenetsky, 2010; Lowenstern, 1994; Thomas and Davidson, 2013, 2016; Zajacz et al., 2008). By contrast, HSMIs have been reported in porphyry-type hydrothermal quartz veins only from a few localities: Bajo de la Alumbrera porphyry Cu-Au deposit in Argentina (Harris et al., 2003), Elatsite porphyry Cu-Au deposit in Bulgaria (Stefanova et al., 2014), Deva porphyry Cu-Au deposit in the South Apuseni Mountains, Romania (Ivascanu et al., 2003; Pintea, 1995, 2012), and Biely Vrch shallow porphyry-Au deposit in the Javorie belt, Slovakia (Kodera et al., 2013a, 2013b), and their significance and origin are still controversial and not fully understood.

In the frame of the present study we performed: i) a detailed optical petrography complemented by SEM-CL imaging of quartz and Qemscan quantitative mineralogical and textural definitions, ii) microthermometry and LA-ICP-MS analyses of fluid inclusions, iii) LA-ICP-MS analyses of HSMIs, and iv) *in-situ* SIMS oxygen isotope analyses of hydrothermal quartz. We provide the first description of a shallow porphyry-type mineralization spatially associated with the large Zn-Pb-(Ag-Cu-Bi) epithermal base metal mineralization at Cerro de Pasco and the first detailed description of HSMIs trapped in porphyry-type veinlets. The results allow discussing the origin of the HSMIs trapped in the early stages of formation of the porphyry-type veinlets and their significance as markers of fluid processes that occur at the magmatic-hydrothermal transition. The metal contents of the HSMIs and hypersaline liquid inclusions are placed into the framework of the evolution of the whole mineralizing system at Cerro de Pasco and are interpreted to be equivalent of the parental/original fluid composition before the main low-temperature sulfide precipitation at Cerro de Pasco.

2 Geological setting

The Cerro de Pasco mining district is located 300 km North-East of Lima in the Western Cordillera of Peru. It is part of the mid-Miocene metallogenic belt recognized in Central and Northern Peru (Bendezú and Fontboté, 2009; Bissig et al., 2008; Bissig and Tosdal, 2009; Catchpole et al., 2015; Noble and McKee, 1999). It is the second largest known epithermal base metal ("Cordilleran") deposit after Butte in Montana, USA. Historical production and remaining resources aggregate more than 200 million tons (Mt) at around 7 wt % Zn, 2 wt % Pb, and 3 oz/t Ag in addition to at least 100 Mt at 1.3 % Cu and 1 g/t Au. Furthermore, Cerro de Pasco produced more than 1 billion ounces of Ag during Colonial times (Baumgartner et al., 2008 and references therein).

The Cerro de Pasco mining district is divided in two parts by a regional N15° W-striking reverse fault, locally known as Longitudinal Fault. West of this fault, a large diatreme-dome complex of 2.5 km diameter crosscuts metamorphosed Middle Palaeozoic shales (Excelsior Group), which is the oldest exposed unit in the district, and younger conglomerates and sandstones of the Middle-Late Triassic Mitu Group (Fig. 1; Spikings et al., 2016). The Eastern part of the district consists of a thick sequence

(up to 1000 m) of carbonate rocks belonging to the Late Triassic Chambará Formation, part of the Pucará Group (Angeles 1999; Baumgartner et al. 2008; Rosas et al., 2007). The epithermal base metal mineralization mainly occurs hosted in carbonate rocks along the eastern margin of the diatreme-dome complex (Fig. 1; Baumgartner et al., 2008; Einaudi, 1977). The base metal mineralization is emplaced at shallow level (its upper part < 1 km below the paleo-surface), and was formed by three main successive mineralizing events, as summarized by Rottier et al. (2016): A) pipe-like pyrrhotite-dominated bodies grading outwards into Fe-rich sphalerite (up to 80 vol.%) and galena, B) a large N-S trending funnel-shaped massive pyrite-quartz body, and C) high- to intermediate-sulfidation E-W-trending Cu-Ag-(Au-Zn-Pb) enargite-pyrite veins hosted by the diatreme breccia, and in the eastern part of the deposit large, well-zoned Zn-Pb-(Bi-Ag-Cu) carbonate replacement ore bodies, mainly striking N20° and N60° (Fig. 1).

The diatreme-dome complex was formed by a succession of phreatomagmatic, magmatic and phreatic events (Fig. 1; Baumgartner et al., 2009; Einaudi, 1968; Rogers, 1983). An early phase of explosive activity produced a diatreme-breccia body locally known as Rumiallana Agglomerate, which is the most common lithology in the magmatic complex. The upper part of the diatreme breccia is stratified and includes dacitic accretionary lapilli (0.2–0.5 cm diameter) tuffs showing cross-bedding, interpreted as a base surge deposit and dated by isotope dilution thermal ionization mass spectrometry (ID-TIMS) zircon U-Pb at 15.36 ± 0.03 Ma (Baumgartner et al., 2008, 2009). The lower part of the diatreme, only accessible by drill-holes, consists of a massive non-stratified breccia. Following the phreatomagmatic events, magmatic activity can be summarized as follow: i) dacitic to rhyodacitic lava-dome complexes emplaced along the western margin of the diatreme and dated at 15.40 ± 0.07 Ma (zircon U-Pb ID-TIMS; Baumgartner et al. 2009); ii) a rhyodacitic porphyry stock cropping out in the northern part of the diatreme-dome complex; iii) several small trachyte porphyries (three identified, each less than 10x10 m) cropping out in the central part of the diatreme breccia and crosscut by low-density stockwork porphyry style mineralization, and iv) east-west trending quartz-monzonite porphyry dykes cutting the diatreme breccia and the dacitic to rhyodacitic lava-dome complexes (Fig. 1A) yield ID-TIMS zircon U-Pb dates of 15.35 ± 0.05 Ma and 15.16 ± 0.04 Ma

(Baumgartner et al. 2009; Fig. 1). The last phreatic event at Cerro de Pasco is marked by the emplacement of numerous, 20 cm to 3 m-wide, mainly E-W trending, milled-matrix fluidized breccia dykes, occurring in various parts of the diatreme-dome complex.

Total erosion since the formation of the diatreme-dome complex is estimated to be <1 km on the basis of field relationships and textural characteristics of pyroclastic rocks (e.g., occurrence of lapilli tuff: Baumgartner, 2007; Baumgartner et al., 2008).

3 Porphyry mineralization at Cerro de Pasco

Evidence of three porphyry mineralization types was recently reported at Cerro de Pasco (Rottier et al., 2015a). The two first types consists of hornfels and magmatic clasts crosscut by typical A- and B-type quartz-molybdenite and quartz-chalcopyrite-pyrite-magnetite veins hosted in (i) quartz-monzonite dykes and (ii) the large diatreme breccia. The third type consists of outcropping porphyry-style mineralization hosted by several small trachyte porphyries emplaced in the Rumiallana Agglomerate in the central part of the diatreme-dome complex and is the subject of this research (Fig. 1).

The studied trachyte porphyry represents, based on its major element composition, one of the less evolved magmatic rock analyzed in the Cerro de Pasco mining district (Baumgartner et al., 2008 and additional rock analyses in supplementary material, Table A.1). It crops out at higher elevation than the main carbonate replacement polymetallic bodies (Fig. 1). Its continuation and shape at depth are not known. Two other porphyry bodies displaying similar texture and veining were recently identified by the Geological staff of *Volcan Compañía Minera* at 100 m north of the one reported in this study. Pervasive pyrophyllite-quartz-pyrite alteration grading to illite-smectite-muscovite-pyrite and more externally to chlorite-calcite-pyrite alteration affects the diatreme-breccia in the immediate vicinity to the trachyte porphyry. Figure 1 shows the outline of these alteration zones mapped using Raman spectroscopy, X-ray diffraction, and optical petrography. In the trachyte porphyry itself, plagioclase is altered to sericite and chlorite (mainly along veinlets) and biotite and amphibole to chlorite, epidote and calcite (Figs. 2 and 3).

Both the trachyte porphyry and the surrounding diatreme-breccia up to a distance of around 2-5 m are crosscut by a network of up to 2 cm-thick quartz-magnetite-chalcopyrite-pyrite porphyry-style veinlets with no visible alteration halo over a distance of 2 to 5 m (Figs. 1 and 2). The veinlets are widespread and locally densely distributed with up to 10 veinlets per square meter, they are polydirectional with two main preferential orientations, N-S and E-W. Microscopic observations reveal high chalcopyrite/pyrite ratio with up to 5% chalcopyrite in some veinlets; both sulfides being affected by supergene alteration. Minor amounts of sphalerite, generally as inclusions in chalcopyrite, are observed as well. Pyrite and chalcopyrite are also present as disseminations in the altered trachyte porphyry. Both the trachyte porphyry and the quartz-magnetite-chalcopyrite-(pyrite) banded veinlets are crosscut by E-W trending quartz-monzonite porphyry dykes. Three samples were analyzed for Cu and Au by Volcan Compañía Minera, all display a constant Cu-Au ratio of ~ 10000:1 and the richest mineralized sample graded 0.23 wt% Cu and 0.26 ppm Au.

4 Analytical methods

Ten samples of the trachyte porphyry crosscut by quartz-magnetite-chalcopyrite-pyrite porphyry-style veinlets were examined using transmitted- and reflected-light microscopy. No differences in mineralogy and alteration styles were observed between the ten samples. Five samples with hydrothermal quartz veinlets were selected for a detailed study. Doubly polished 200 μm -thick sections were examined using a standard petrographic microscope to characterize heterogeneous silicate melt inclusions (HSMIs), hypersaline liquid, and aqueous liquid-vapor (L-V) inclusions hosted in quartz. Scanning electron microscopy cathodoluminescence (SEM-CL) was used in order to texturally characterize the different quartz generations in the veinlets and the paragenetic context of the studied HSMIs and fluid inclusions. SEM-CL images were acquired at the University of Lausanne using a CamScan MV2300 SEM and at the University of Geneva using a JEOL JSM7001F SEM, both equipped with panchromatic CL detectors.

Raman microspectroscopy was used to identify solid inclusions trapped in minerals or as daughter phases in fluid inclusions and the composition of the gas phase of fluid inclusions.

Measurements were performed using a confocal LABRAM equipped with a 532.12 nm Nd-YAG Laser coupled with an Olympus BX51 microscope at the University of Geneva. Gas composition was determined using an x100 objective and the following Raman settings: 500 μm confocal aperture, 100 μm slit, and acquisition time of two times 120s. The limit of detection of the method is ~ 0.13 mol% CO_2 (Rosso and Bodnar, 1995).

Microthermometric data of hypersaline liquid and aqueous L-V inclusions were acquired up to temperature of 600°C, using a THMSG 600 Linkam heating–freezing stage mounted on a DMLB Leica microscope calibrated using SYNFLINC standards at -56.6°C , 0.0°C , and 374.1°C (Sterner and Bodnar, 1984). Heating experiments above 600°C were done using a Linkam TS 1500 stage mounted on a DMLB Leica microscope. All experiments were conducted in nitrogen atmosphere to minimize oxidation of the sample. The stage was calibrated using a SYNFLINC standard at 374.1°C , as well as the melting points of AgI at 558°C and NaCl at 801°C . Salinities (wt % NaCl equiv.) were determined based on ice melting or salt melting temperatures using the SoWat software (Driesner, 2007).

Heating experiments on HSMIs trapped in quartz from the porphyry-type veinlets were conducted to produce a homogeneous glass and to observe the phase behaviour of melt inclusions during heating. Quartz chips were heated using the same Linkam TS 1500 stage in nitrogen atmosphere at room pressure. Samples were heated up to 900°C with a heating rate of $50^\circ\text{C}/\text{min}$, and then up to 1150°C with a heating rate of $5^\circ\text{C}/\text{min}$. Samples were cooled to 300°C at a rate of $200^\circ\text{C}/\text{min}$ in order to quench the HSMIs, and to produce a homogeneous glass. Temperatures reported in the paper for the melt inclusions are indicative and do not represent true temperatures of phase transition and homogenization because temperatures recorded during heating experiments with a Linkam stage TS 1500 are strongly influenced by the rate of heating (Student and Bodnar, 1999) and overestimate the homogenization temperature compared to experiments performed under pressure (Student and Bodnar, 2004). After rapid cooling, the quenched HSMIs presented a homogeneous silicate phase containing one or several small globules of salts, opaque crystals and vapour phase of variable size. Heated quartz chips were separated into two groups: one for direct LA-ICP-MS analyses

of the HSMIs and a second one mounted in epoxy, sequentially polished in order to expose on surface the HSMIs, for SEM and electron microprobe analyses.

Electron probe microanalyses (EPMA) were conducted at the University of Lausanne using a Jeol JXA 8200 Superprobe. For analyses of silicate glass, the operating conditions were: accelerating voltage 15 kV, beam current 10 nA, and beam diameter 2 μm . Standards and X-ray emission lines were set up as follows: albite (Na-K α , Al-K α), apatite (F-K α), bytownite (Ca-K α), bornite (Cu-K α), MnTiO₃ (Mn-K α , Ti-K α), olivine (Mg-K α , Fe-K α), orthoclase (Si-K α , K-K α), celestine (S-K α), sphalerite (Zn-K α). Counting times of 10 s on peak and 5 s on background on both sides of the peak were used for Si, Al, and K; 20 s on peak and 10 s on background on both sides of the peak were used for Na, Mg, Ti, Mn, Zn, Fe, Ca and Cu, and 30 s on peak and 15 s on background on both sides of the peak were used for F and S.

For analyses of quartz, the operating conditions were: accelerating voltage 20 kV, beam current 80 nA, and beam diameter 5 μm . Standards and X-ray emission lines were set up as follows: albite (Al-K α), bornite (Cu-K α), and MnTiO₃ (Ti-K α). Counting times of 60 s on peak and 30 s on background on both sides of the peak were used for Ti and Cu, 40s on peak and 20s on background on both sides of the peak were used for Al. Limits of detection were 54 ppm for Al, 74 ppm for Ti and 64 ppm for Cu.

A total of 15 heated HSMIs, 34 hypersaline liquid, and 10 aqueous L-V inclusions were analyzed using a 193 nm ArF Excimer laser with an energy homogenized beam profile coupled with an ELAN 6100 DRC ICP quadrupole mass spectrometer (QMS) at ETH Zurich (Günther et al., 1997, 1998; Heinrich et al., 2003). Table 1 summarizes the analytical conditions, data acquisition parameters, and list of isotopes analysed during laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analytical sessions. Inclusions were ablated using an iris diaphragm for progressive manual increase of the laser beam diameter to limit explosion of the host quartz (Guillong and Heinrich, 2007). LA-ICP-MS transient signals were reduced using Sills software (Guillong et al., 2008). The NIST glass standard SRM 610 was used as an external standard and analyzed two times

bracketing a maximum of 20 unknowns to correct the drift by linear regressions. For aqueous L-V and hypersaline liquid inclusions, Na concentration derived from the microthermometric measurements was used as an internal standard for each ablated fluid inclusion. For hypersaline liquid inclusions, an empirical correction for major dissolved cations other than Na (e.g., K, Fe, Mn, Zn, Cu, and Pb) was applied (Heinrich et al., 2003). Quantification of the HSMIs has been done following the method of Halter et al. (2002). Internal standardization of all melt inclusions analyzed was based on 16.7 wt % Al_2O_3 , derived from EPMA, which is in agreement with the calculated mean Al_2O_3 content obtained from whole rock geochemistry of the volcanic and sub-volcanic rocks of the district (mean = 15.6 ± 0.6 wt % Al_2O_3 , n=13, XRF analyses, supplementary material Table A.1). For host correction (i.e. quartz), 99.5 wt % SiO_2 was assumed as an internal standard.

A total of 41 $^{18}\text{O}/^{16}\text{O}$ isotopic ratio analyses and 12 *in-situ* trace elements analyses (Ti, Al, Fe and Li) were performed on quartz chips placed in indium mounts that included grains of two quartz reference materials (UNIL-Q1 for $\delta^{18}\text{O}$ measurements (Seitz et al., 2016) and BGS-Q1 for trace elements (Audétat et al., 2015)). Measurements were performed at the SwissSIMS ion probe national facility at the University of Lausanne, using a Cameca IMS180-HR. For both sessions, samples were coated with a 40 nm-thick layer of gold. For oxygen isotope measurements, we used a 10kV Cs^+ primary beam, a ~2 nA current, resulting in a ~10 μm beam size. The electron flood gun, with normal incidence, was used to compensate charges. ^{16}O and ^{18}O secondary ions, accelerated at 10kV, were analyzed at a mass resolving power of 2400 and collected on Faraday cups (FCs) multi-collection mode. The data have been obtained during the same session of 12h. FCs are calibrated at the beginning of the session. Mass calibration was performed at the beginning of the session and a nuclear magnetic resonance was used to lock the magnetic field. Details of the analytical settings are described in Seitz et al. (accepted for *Geostandards and Geoanalytical Research*). Each analysis takes less than 4 minutes, including pre-sputtering (30 sec) and automated centering of secondary ions. This setting allowed an average reproducibility better than 0.3‰ (2SD) on UNIL-Q1 reference material at the beginning of the session, and internal error for each analysis lower than 0.3‰ 2σ . A set of 4 analyses of UNIL-Q1 standard, inserted in each mounts, has also been measured every 15-20 analyses for

monitoring the instrument stability, and accuracy by correcting the instrumental mass fractionation, as it can slightly differ from mount to mount. The variation of UNIL-Q1 over the entire session was < 0.3‰ (2SD). The error reported for samples reflected the 2SD bracket between the surrounding standard sessions. Also, a total of 12 spot analyses for trace element (Ti, Al, Fe and Li) were measured at the SwissSIMS using an O⁻ primary beam of 1.1 nA accelerated at 13 kV to bombard the sample surface. Secondary ions were accelerated at 10 kV into the mass spectrometer. ⁷Li⁺, ²⁷Al⁺, ³⁰Si⁺, ⁴⁸Ti⁺ and ⁵⁶Fe⁺ were analyzed on mono-collection mode using the axial electron multiplier (EM). The field aperture was set to 4000 microns and the energy slit to 50 μm. The entrance slit was closed to 61 μm and the exit slit to 405 μm, allowing separating the measured ions from any interference. Before each analysis, a pre-sputtering of 120 seconds using a raster beam of 30 μm was used to clean the sample surface. Automatic calibration on ³⁰Si and centering of field aperture were made before each analysis, just after the pre-sputtering. Measurements were done without any raster, with a 15-20 microns beam. Each analysis consists of 15 cycles of the peak-stepping sequence ⁷Li⁺ (5 sec), ²⁷Al⁺ (3sec), ³⁰Si⁺ (2sec), ⁴⁸Ti⁺ (5sec) and ⁵⁶Fe⁺ (8sec). Reproducibility (in 2SD) was 11% for Li, 7% for Al, 6% for Ti and 11% on Fe on BGS-Q1. Background on the EM was less than 2 counts per hour.

5 Results

5.1 Trachyte porphyry and associated alteration

The trachyte porphyry is mainly composed of phenocrysts (~40 vol.%) of plagioclase, K-feldspar, quartz and biotite within a Si-K-rich matrix (~60 vol.%). The accessory phases mainly consist of apatite, sphene, hornblende, zircon and Fe-oxides.

Albitization halos occur along the quartz veinlets and are illustrated by the Qemscan maps (Fig. 3). Late pervasive alteration resulting in epidote-chlorite-sericite-calcite assemblage mainly replacing biotite and hornblende, the previously formed albite, and to a lesser extent the plagioclase, affects the entire volume of the exposed trachyte porphyry (Fig. 3F and G).

5.2 Vein petrography and SEM-CL quartz textures

The investigated quartz-sulfide veinlets consist of three quartz generations (Fig. 4). The first two quartz generations (Q_{1-2}) are characterized by high CL intensity. They represent more than 90% of the veinlets volume (Fig. 4A) and hosts HSMIs, hypersaline liquid, and, rarely, low-density vapor and aqueous L-V inclusions. The fluid inclusion petrography indicates that quartz Q_{1-2} is formed during two distinct episodes. Most of the quartz grains were formed during the first episode (Q_1) marked by entrapment of HSMIs. It is followed by precipitation of subordinate quartz Q_2 characterized by entrapment of hypersaline liquid inclusions. Quartz Q_2 is mostly intergrown with Q_1 and it overgrows Q_1 grains in rare cases only. No difference in CL light intensity and in most cases neither in texture, between Q_1 and Q_2 is discernible. Hence, we have chosen to join these two early quartz generations under the denomination Q_{1-2} . Quartz Q_{1-2} shows (Fig. 4) roughly-zoned subhedral crystals (Q_{1-2a}), botryoidal (Q_{1-2b}), and subhedral comb-like textures with well-developed oscillatory growth zoning (Q_{1-2c}). Both, Q_{1-2a} and Q_{1-2b} are observed close to the contacts of the veinlets, whereas Q_{1-2c} forms the core of the veinlets. Quartz Q_{1-2a} and Q_{1-2b} are rich in micron-sized magnetite inclusions, small HSMIs, and hypersaline liquid inclusions resulting in the banded texture of the veinlets (Fig. 2B). Botryoidal quartz is commonly observed in shallow porphyry deposits and is interpreted to form from recrystallization of an amorphous silica gel due to rapid fluid decompression (Herrington and Wilkinson, 1993; Koderá et al., 2014; Muntean and Einaudi, 2000; Vila and Sillitoe, 1991). Locally, Q_{1-2a} and Q_{1-2c} grains are overgrown, and in part also resorbed by quartz Q_{1-2d} with similar or lower CL-luminescence (Fig. 4C). Similar textures are documented in porphyry quartz veins (Müller et al., 2010; Penniston-Dorland 2001; Redmond et al., 2004; Rusk et al., 2008b). In one sample, quartz sub-generations Q_{1-2a-d} are crosscut by a quartz vein (Q_{1-2e}), that has similar CL light intensity and texture, and hosts melt and fluid inclusions (Fig. 4C). The different textures indicate that the different Q_{1-2} generations were formed during successive hydrothermal episodes. Despite textural differences, all Q_{1-2} sub-generations display high CL intensity and host the same types of fluid and melt inclusions and therefore in the following will not be differentiated. None of the Q_{1-2} sub-generations has been

observed to contain sulfide inclusions or to be in direct contact with sulfide minerals; therefore Q_{1-2} is considered to be pre-sulfide.

The next quartz generation Q_3 is volumetrically minor and it was observed in all studied samples in microfractures crosscutting Q_{1-2} and, subordinately, in voids resulting from the dissolution of Q_{1-2} (Fig. 4A, B and D). Quartz Q_3 hosts only aqueous L-V and low-density vapor inclusions; HSMIs and hypersaline liquid inclusions are not observed. The contact between quartz generations Q_{1-2} and Q_3 is marked by an abrupt change in CL intensity, Q_3 showing low CL intensity with black, dark gray, and gray well-formed oscillatory growth zones (Fig. 4A, B and D).

Chalcopyrite, pyrite, and rare sphalerite grains are systematically intergrown with Q_3 suggesting that sulfides postdate Q_{1-2} and precipitate contemporaneously with or after Q_3 . The veinlets are locally reopened and filled with calcite, epidote, and chlorite, i.e., the same mineral assemblage pervasively altering the host trachyte porphyry (Fig. 3A).

5.3 In-situ SIMS oxygen isotope analyses of quartz

In-situ SIMS oxygen isotope analyses were performed on quartz Q_{1-2} and Q_3 from two samples (supplementary material, Table A2). The two quartz generations display significantly different oxygen isotope composition: $\delta^{18}O_{Q_{1-2}} = +10.2\text{‰}$ ($n=30$, $2\sigma=\pm 0.5$) and $\delta^{18}O_{Q_3} = +12.8\text{‰}$ ($n=10$, $2\sigma=\pm 1.8$). The $\delta^{18}O$ values throughout the different Q_{1-2} textures are nearly homogeneous within error (2σ on UNIL-Q1 reference material is $\pm 0.3\text{‰}$), whereas $\delta^{18}O_{Q_3}$ values are more scattered and an increase toward the center of the veinlets from 10.4 to 13.3‰ is recognized (Fig. 5A, C).

5.4 SIMS and LA-ICP-MS trace element analyses in quartz

Lithium, Al, Ti, and Fe contents were analyzed by SIMS on 6 spots in Q_{1-2} and 6 spots in Q_3 (Fig. 5, Table 2). In both quartz generations, Al content is similar ($Q_{1-2} = 333\text{-}958$ ppm, $Q_3 = 345\text{-}1100$ ppm), whereas that of Li is slightly higher in Q_3 ($Q_{1-2} = 4\text{-}20$ ppm, $Q_3 = 4\text{-}64$ ppm). Iron content is low in Q_{1-2} and Q_3 , ranging from 3 to 16 ppm, with the exception of two values in botryoidal quartz Q_{1-2b} (136 and 144 ppm). Titanium content is significantly higher in Q_{1-2} than in Q_3 (Fig. 5, B, C), with the

highest values recorded in the botryoidal quartz (Q_{1-2} = 126-358 ppm, Q_3 = 2-9 ppm). Titanium is a CL activator (e.g., Rusk et al., 2008b), thus observed differences in Ti content may explain the differences

A total of 68 LA-ICP-MS trace element analyses of quartz hosting HSMIs, hypersaline liquid and aqueous L-V inclusions (Table 3) were obtained. The LA-ICP-MS results confirm the higher Li and lower Ti content in Q_3 measured by SIMS. No major differences in trace element content between the two quartz generations have been observed except for Sn, which is systematically lower in Q_3 .

5.5 Petrography and microthermometry of HSMIs and fluid inclusions

The studied quartz-hosted inclusions belong to the following four major types: i) heterogeneous silicate melt inclusions (HSMIs), ii) hypersaline liquid inclusions, iii) aqueous L-V inclusions, and iv) low-density vapor inclusions. Detailed mapping of melt and fluid inclusions revealed that HSMIs and hypersaline liquid inclusions are exclusively hosted in Q_{1-2} , whereas aqueous L-V and low-density vapor inclusions occur as primary fluid inclusion assemblages (FIAs; Goldstein and Reynolds, 1994) in Q_3 and as secondary trails in Q_{1-2} .

The HSMIs are small, mostly below 2 μm , some up to 20 μm in size and therefore difficult to recognize at room temperature. They form masses of several finely crystallized transparent minerals and a deformed vapor bubble (Fig. 6.A, C and E). HSMIs are primary, exclusively trapped in the core of Q_{1-2} grains that frequently has a hexagonal shape (Fig. 6). Rare secondary HSMI trails crosscut the quartz. During heating experiments, the progressive melting of different minerals is observed. At around 900°C, two distinct liquid phases appear. At 1150°C, all former solids are molten and the two distinct liquid phases are still present. Following rapid cooling, HSMIs quench into a silicate glass including one or several small globules crowded with salt crystals, opaque minerals, and a vapor bubble. If the globules are heated again, the salt phases melt between 280° and 350°C forming a chloride melt, and an unidentified opaque crystals melt at temperature above 500°C (Fig. 7); above 800°C, the inclusions melt completely. The salts and the chloride melt react and change color from pale green to reddish-brown under the green laser light of the Raman, making impossible the

identification of the different phases. Raman analyses of the vapor phase do not reveal presence of CO₂ nor of other gases (e.g., CH₄, N₂...).

Most hypersaline liquid inclusions are between 5 and 25 µm in size. They form rare primary assemblages and often pseudo-secondary and secondary trails in Q₁₋₂, but are never observed in Q₃. They crosscut primary HSMIs and seldom are spatially associated with the silicate melt inclusions; therefore they are interpreted to postdate the HSMIs entrapment. The hypersaline liquid inclusions contain a dense aggregate of transparent crystals, one or two unknown opaque crystals, and often a hematite flake (Fig. 8A, B and C). They contain also deformed vapor bubbles that fill 25 to 40 vol. % of the inclusions, whereas a liquid phase makes less than 10 vol. % of the inclusion, frequently much less. The transparent crystals include: (1) pale-green weakly anisotropic rounded crystals building up to 30 vol. % of the inclusion, tentatively identified as Fe-chloride species although uncertainty remains because of their strong reaction under the Raman monochromatic light; (2) small cubic to rounded daughter crystals, possibly KCl; (3) large cubic daughter crystals interpreted as NaCl, and (4) green birefringent rectangular crystals, determined as anhydrite by Raman, that fill up to 10 vol. % of the fluid inclusion. Raman analyses of the vapor phase reveal the presence of CO₂ with no H₂O. Microthermometry results of these hypersaline liquid inclusions can be summarized as follows: (1) The pale-green weakly anisotropic rounded crystals (Fe-chloride ?) melt between 268° and 323°C; when cooling below 120°C, they reprecipitate as an aggregate of tiny irregular grains. (2) Melting temperature of the possible KCl crystals mainly occurs between 294° and 320°C, just after melting of the first solid; exceptionally temperatures up to 380°C were also recorded. (3) NaCl melting temperature occurs between 552° to 620°C. (4) Anhydrite is the last solid to melt; in one assemblage melting temperatures ranged between 625° to 765°C. Owing to stretching and decrepitation, total homogenization temperatures could only be measured for one hypersaline liquid inclusion assemblage with vapor disappearance between 660° and >800°C. These temperatures could be affected by modification of density related to the α-β quartz transition (Bodnar 2003), and should be taken with caution. Opaque minerals decreased in size during heating, rarely reaching complete dissolution. The common presence of anhydrite and hematite in the hypersaline liquid inclusions could indicate H₂

diffusion out of the inclusions (Mavrogenes and Bodnar 1994). Salinities of these inclusions, determined from halite final melting using the equation of Bodnar and Vityk (1994), range between 68 and 77 wt % NaCl eq. (Table 4).

The aqueous L-V inclusions observed in Q_3 as primary and secondary FIAs and rarely as secondary FIAs in Q_{1-2} are irregularly shaped and generally small, between 5 and 30 μm in size (Fig. 8D, E and F). The vapor phase occupies between 20 and 25 vol. % of the inclusion cavities and no CO_2 was detected by Raman spectroscopy. A total of 8 FIAs each including 5 to 14 individual fluid inclusions were measured (Fig. 9, Table 4) yielding average homogenization temperatures (T_h) between 272° and 329°C and ice melting temperatures ($T_{m_{ice}}$) between -22.6° and -0.3°C, corresponding to salinities between 24.12 and 0.46 wt % NaCl eq. (Bodnar and Vityk, 1994). Since no detectable liquid phase is present at room temperature, no microthermometric measurements could be performed in the low-density vapor inclusions.

5.6 LA-ICP-MS analyses of fluid inclusions

5.6.1 Hypersaline liquid inclusions

A total of 34 hypersaline liquid inclusions from 6 different FIAs were analyzed by LA-ICP-MS. Average element concentrations and standard deviations for each FIA are summarized in Table 5. The reproducibility of element concentrations within FIAs is good ($1\sigma < 25\%$ of the mean value of the FIA) for Na, K, Rb, and Cs, acceptable ($1\sigma < 35\%$ of the mean value of the FIA) for Pb, Mn, and Zn, and relatively poor ($1\sigma = 35\text{--}80\%$ of the mean value of the FIA) for S, Ca, Cu, Sr, Mo, Ag, and Ba. Poor reproducibility for some elements can be explained partly by inhomogeneous entrapment of some opaque and transparent solids in the hypersaline liquid inclusions during their formation (Fig. 10). For instance, variations of S, Ca, Sr, and Ba contents might be mainly linked to entrapment of anhydrite crystals and of Cu, S, Mo, Ag, and W - to trapped opaque minerals. Variations may also be related to post-entrapment modifications, including diffusion. Post-entrapment diffusion of Cu and Ag through the host quartz has been well documented by Kamenetsky and Danyushevsky (2005), Li et al. (2009) and Lerchbaumer and Audétat (2012). Abundances of Na, K, and Fe of around 45%, 35 %, and 20%

($\pm 5\%$), respectively, correspond to common compositions for porphyry brines (Fig. 10A; Kouzmanov and Pokrovski, 2012). Metal contents are elevated with Mn and Zn ranging from 5000 to 25000 ppm, Pb from 1000 to 7000 ppm, Mo mainly from 250 to 1000 ppm, W from 13 to 370 ppm, and Ag from 10 to 142 ppm (Table 5). Copper concentrations are heterogeneous with a group with values between 5000 and 60000 ppm and a second group between 13 and 1000 ppm. Sulfur content varies between 9000 to 57000 ppm. The positive correlations of S with Cu and Ca (not shown) suggest that part of the sulfur is present as Cu-sulfide solid inclusions and as anhydrite. Several elements, including B, Al, Ti, As, Sn, and Sb were not accurately detected due to low signal/background ratio and/or their high concentration in the host quartz.

Rubidium and Cs contents in the fluid inclusions can be used as a proxy for the degree of differentiation of the melt from which hydrothermal fluids are exsolved (Audétat and Pettke, 2003). The ranges of Cs and Rb contents measured in the hypersaline liquid inclusions may reflect a progressively increasing differentiation of the melt from which they are exsolved. Positive correlations of K, Pb, Mn, Mo, Zn, and W with Rb and Cs possibly reflect enrichment of these elements in the melt during magmatic differentiation and subsequently in the exsolved fluids (Fig. 10).

5.6.2 Aqueous L-V inclusions

Twenty-two aqueous L-V inclusions were selected for LA-ICP-MS analyses. Due to their relatively small size and/or their low salinity, only 10 analyses of fluid inclusions from 4 FIAs are considered to be analytically representative although the data present low reproducibility within each FIA. Concentrations of Cu (192-1231 ppm), Zn (683-861 ppm), Ag (1-3 ppm), Pb (11-446 ppm), and Mo (2-83 ppm) are moderate to low. Cesium and Rb contents are low, with 4-20 ppm and 8-33 ppm, respectively, compared to the relatively high Sr concentrations ranging from 82 to 205 ppm. Lithium, B, Al, S, Ca, Ti, As, Sn and Sb have concentrations below the detection limit.

5.7 Composition of heterogeneous silicate melt inclusions (HSMIs)

5.7.1 Characterization HSMIs after heating using back-scattered electron imaging

Prior to EPMA, quartz chips heated up to 1150°C were polished until HSMIs were exposed. Polished HSMIs were classified into four different types based on back-scattered electron (BSE) images. Type 1 is the most common and corresponds to a homogeneous silicate glass with one or several lighter circular spots (Figs. 11A and D). These lighter spots correspond to globules crowded with salt and opaque crystals observed using the petrographic microscope. EDS analyses of these globules reveal elevated concentrations for Cu and Cl and occasionally weak signals for S and Ag. Type 2 inclusions correspond to homogeneous silicate melt with numerous tiny (< 100 nm) white spots dominantly formed by Cu and Cl according to the EDS analyses performed (Fig. 11B). Type 3 inclusions represent homogeneous silicate melt inclusions (Figs. 11A and E). Type 4 inclusions are HSMIs with some remnant silicate crystals (Fig. 11C).

5.7.2 EPMA

A total of 60 EPMA were performed including 41 on silicate glass from HSMIs of types 1, 2 and 3, and 19 on Cu- and Cl-rich globules from HSMIs of type 1. Since HSMIs are mostly less than 2 µm in size, i.e., a similar volume than that excited by the electron beam, it is challenging to get accurate silicate glass-only compositions (supplementary material, Table A.3). The main contamination sources during analyses of the silicate phase were (1) contamination by small Cu-rich globules, and (2) contamination by the host quartz. The latter can be due to partial melting of the host quartz boundary during the heating experiments, or to partial excitation of the host quartz by the electron beam.

The trend observed on the Al₂O₃ vs. SiO₂ plot in Figure 12 can be interpreted as reflecting different degrees of contamination of the melt inclusion analyses by the host quartz. It can be assumed that the analysis showing the highest Al₂O₃ value corresponds to the less contaminated composition. The chemical composition revealed by this analyses is rhyolitic (73.04 wt % SiO₂, 16.73 wt % Al₂O₃, 6.96 wt % K₂O, 1.99 wt % Na₂O, 1.67 wt % FeO, 0.4 wt % TiO₂, 0.25 wt % CaO, <0.1 wt % MgO). It

has SiO₂ content of 73 wt % that is geologically meaningful and its composition is coherent with the evolution trend outlined by the compositions of least altered surrounding magmatic rocks from the Cerro de Pasco district (Fig. 12; supplementary material, Table A.1), we therefore consider the obtained composition as representative for the composition of the silicate melt during entrapment of the HSMIs.

The analyses of Cu- and Cl-rich globules are also contaminated by the surrounding silicate glasses and the host quartz as shown by the data provided in the supplementary material, Table A.3. The quantitative EPMA and qualitative EDS measurements reveal positively correlated high Cu (up to 40 wt %) and Cl (up to 19 wt %) concentrations. Sulfur content is commonly below 1.25 wt % with the exception of one measurement giving a value at 6.4 wt %.

5.7.3 LA-ICP-MS analyses

The LA-ICP-MS data on heated HSMIs were treated using as an internal standard the Al₂O₃ content of 16.7 wt % obtained from EPMA for the sample considered to be the most representative for the composition of the silicate melt (see above), value which is also consistent with the average content of 15.72 ± 0.46 wt % Al₂O₃ obtained from whole rock geochemistry (n=13, XRF analyses; electronic supplementary material, table A.1) of rocks ranging from dacitic to rhyolitic composition from the Cerro de Pasco mining district. The LA-ICP-MS results have been summarized in Table 6 and plotted versus Zn in Figure 13, using the affinity of this element to chlorine as a proxy for the abundance of chlorine-rich globules in the analyzed HSMIs. For most elements, a large compositional spread is observed. To a large extent it is due to the coexistence in the HSMI of different proportions of silicate glass and hypersaline globules. The different elements can be classified as a function of their behavior versus Zn. Manganese, Fe, Mo, W, and Pb strongly correlate (linear correlation coefficient $r > 0.9$) with Zn, indicating that they are mostly hosted in the chlorine-rich globules (Fig. 13). Moderate positive correlations ($0.9 > r > 0.7$) between K, Ca, Mg, Rb, Sr, La, Ce and Zn suggest that they are also subordinately hosted in the silicate phase (Fig. 13). By contrast, Na, Ba, Cs, Cu, Ag, and Au show no linear correlations with Zn indicating that they are mostly hosted in the silicate phase (Fig. 13).

Analyses of HSMIs prior to heating experiments are difficult because without heating it is almost impossible (i) to recognize HSMIs, (ii) to identify properly individual versus a group of HSMIs, and (iii) to identify small solid inclusions ($<1\mu\text{m}$) hosted in quartz close to or attached to them. Nevertheless, four analyses were conducted on non-heated spots that are thought to represent HSMIs (supplementary material, Table A.4). Analyses reveal high FeO contents, up to 19 wt %, probably due to contamination by small magnetite inclusions; therefore analyses could not be considered as representative. Notwithstanding these limitations, it was recognized that Cu and Ag contents were constantly 1 to 2 orders of magnitude lower than those in heated HSMIs.

5.8 Cation diffusion through quartz

As highlighted by several studies, quartz-hosted fluid and melt inclusions can, after entrapment, diffusively lose or gain some elements including H, He, Li, Na, Cu, and Ag (Kamenetsky and Danyushevsky, 2005; Lerchbaumer and Audétat, 2012; Li et al., 2009; Mavrogenes and Bodnar, 1994; Zajacz et al., 2008, 2009). To test if this diffusion phenomenon applies to the studied HSMIs, profile of Cu concentrations of two quartz grains were acquired by EPMA and subsequently imaged by X-ray Cu concentration maps. The Cu content of a grain that was heated at 1150°C at room pressure under nitrogen atmosphere, ranged between below detection limit (64 ppm) and 291 ppm (Fig. 14).

In contrast, an unheated quartz grain yielded constantly Cu contents below detection limit. The Cu concentration map shows a strong positive correlation between Cu and Al in the heated quartz, suggesting increased Cu diffusion in quartz growth zones and sectors with lattice defects generated by Al^{3+} incorporation into the structure (Fig. 14B and C). LA-ICP-MS analyses of quartz crystals hosting HSMIs and hypersaline liquid inclusions having been heated at 1150°C and below 600°C , respectively, show a strong enrichment in Cu, Ag, Na, Rb and Li in quartz heated at 1150°C compared to unheated quartz (Fig. 15).

6 Discussion

6.1 Origin of HSMIs in porphyry veins: Supercritical melt versus heterogeneous entrapment

In contrast with the porphyry environment, where, as mentioned above, they have been rarely recognized, heterogeneous melt inclusions consisting of coexisting silicate phase and water-rich phase have been well documented in pegmatites and aplites associated with S-type granites (e.g., Thomas and Davidson, 2013, 2016; Veksler et al., 2002). In pegmatites, HSMIs are interpreted to result from entrapment of “supercritical melt” containing up to 33 wt % H₂O (Thomas and Davidson, 2013). Such heterogeneous melt inclusions are strongly enriched, up to several weight percent, in B, F, Cs, Rb and P (Thomas and Davidson 2016, and references therein); elements acting as fluxing agents in the melt and thus increasing the miscibility gap between silicate melt and water, allowing the formation of such water-rich melts at the magmatic-hydrothermal transition (Veksler, 2004).

In contrast, the HSMIs in early stage porphyry stockwork quartz at Cerro de Pasco do not show a significant enrichment in incompatible elements such as B, F, Cs and Rb (below 500 ppm, Figs. 12 and 13; Table 6). These results discard the hypothesis that the studied HSMIs are the entrapment product of a single "supercritical melt" and favor the heterogeneous entrapment of two fluids including a silicate melt and a chlorine-rich fluid. Heterogeneous entrapment has already been proposed by several authors to explain presence of HSMIs in magmatic quartz phenocrysts and miarolitic cavities (Campos et al., 2002, 2006; Davidson et al., 2005; Davidson and Kamenetsky, 2007; Frezzotti, 1992; Fulignati et al., 2005; Harris et al., 2004; Kamenetsky et al., 2004; Kamenetsky and Kamenetsky, 2010; Lowenstern, 1994; Zajacz et al., 2008) and in quartz from porphyry quartz veins (Harris et al., 2003; Pintea, 1995 and 2012). At Cerro de Pasco, a heterogeneous entrapment scenario is supported by (1) an extremely variable melt/globule ratio in the HSMIs (Figs. 6H and I), (2) the positive correlation of elements compatible with the chlorine-rich fluid phase in the HSMIs (e.g., K, Fe, Ca, Mn, Pb, Sr, Rb) outlining mixing trends between two hypothetical end members - an evolved silicate melt and a magmatic fluid (Fig. 13). Since in the studied HSMIs, the presence of globules does not

allow determining the exact trace element composition of the silicate phase, the melt inclusions with the lowest Zn content (<1000 ppm) have been taken as the best available proxy for the composition of the silicate phase (Table 6, Fig. 13), whereas hypersaline liquid inclusions are used as a proxy for the magmatic fluid end-member.

Two different scenarios can explain the heterogeneous entrapment of a silicate phase and a hypersaline fluid. First, residual melt and hypersaline fluids could be transported as a heterogeneous mixture of two immiscible fluids toward shallow levels and then trapped together. This model implies ascent of both liquids having contrasting densities (e.g., 2.6 g/cm³ for the melt and <1.5 g/cm³ for the hypersaline fluid; Driesner 2007) and viscosity along narrow structures in the shallow portion of a porphyry system, which may be not realistic considering their contrasting physical properties. An alternative, more plausible, model is the ascent of a hydrous evolved melt as a single phase to shallow upper crustal levels, which subsequently exsolves an aqueous fluid at P-T conditions below the miscibility field of a vapor phase and a hypersaline fluid (Fig. 16). The evolved melt and the newly formed hypersaline fluids are then trapped together to form the HSMIs, while the low-density vapor phase tends to escape the site of exsolution by density contrast. This exsolution below the miscibility field of vapor and hypersaline liquid requires anomalously high-T for a given pressure; such hot environment is ideally provided by shallow porphyry intrusions like the trachyte porphyry subject of the present study. This model implies a genetic link between the silicate phase and the hypersaline fluids trapped as globules in the latter; the existence of such link is supported by similar Cs and Rb content in the analyzed HSMIs, independently from their melt/globule ratio (Cs and Rb being elements with fluid/melt partition coefficient close to 1: Zajacz et al., 2008).

Our hypothesis could be also applied to the formation of abundant primary HSMIs with similar characteristics to those at Cerro de Pasco, described in porphyry quartz veins at Deva (Pintea, 1995 and 2012, Ivascanu et al. 2003) and Bajo de la Alumbrera (Harris et al. 2003) porphyry Cu-Au systems. By contrast, our hypothesis probably fails to be applied to the melt inclusions described by Stefanova et al. (2014) in quartz from porphyry veins at Elatsite, since they are volumetrically minor, secondary, and only few of them contain globules of chlorine-rich fluid. Stefanova et al. (2014)

propose that the Elatsite silicate melt inclusions correspond to droplets of residual melts transported by the hydrothermal fluids.

6.2 Fluid evolution

The presence of simultaneously trapped HSMIs and hypersaline liquid inclusions in quartz Q_{1-2} indicates high temperatures of formation ($>600^{\circ}\text{C}$) consistent with the few obtained total homogenization temperatures of both inclusion types (Table 4). Taking into account that the maximum erosion does not exceed 1 km after the trachyte porphyry emplacement (Baumgartner 2007; Baumgartner et al., 2008), the maximum lithostatic pressure for the formation of the porphyry-type mineralization can be estimated at 270 bars.

Titanium incorporation in quartz is temperature and pressure dependent (Huang and Audétat, 2012; Rusk et al., 2008b; Thomas et al., 2010; Wark and Watson, 2006), and also depends on the quartz growth rate (Huang and Audétat, 2012). However, the latter parameter appeared to be strongly variable in the studied hydrothermal quartz veinlets as suggested by the variety of textures revealed by SEM-CL. We recognize that the application of the Ti-in-quartz thermometer is problematic and therefore temperatures calculated using the Ti contents in quartz (Table 2 and 3) and the equation of Huang and Audétat (2012) at $P=0.27$ kbar and $\alpha_{\text{TiO}_2}=1$, can only be used as indicative of high temperature quartz Q_{1-2} precipitation ($T > 600^{\circ}\text{C}$) and lower temperature quartz Q_3 precipitation ($T < 450^{\circ}\text{C}$).

Early quartz Q_{1-2} hosting the HSMIs and the hypersaline liquid inclusions is formed during two consecutive stages. Stage 1 corresponds to magmatic-hydrothermal transition conditions whereby the HSMIs reflect injection of a hot and evolved silicate melt to shallow crustal levels (i.e., <1 km $\approx$ 270 bar under lithostatic pressure). It implies that the surrounding environment is hot enough to prevent complete solidification of the melt. During its ascent, the melt decompresses by conserving its high temperature ($>600^{\circ}\text{C}$) triggering separation of a chlorine-rich phase with salinity $>90\%$ wt % NaCl eq. and a low-salinity and low-density vapor phase (Fig. 16; Fournier, 1999; Driesner and Heinrich 2007; Weis et al., 2012). Rapid quartz precipitation following the decompression and phase

separation (Fournier 1999) allows heterogeneous entrapment of the silicate phase and the chlorine-rich fluid.

Stage 2 corresponds to a hydrothermal stage without silicate melt injection in the shallow environment, in parallel to the thermal retraction of the magmatic-hydrothermal system. Assuming a magmatic temperature for the melt ($\approx 750^{\circ}\text{C}$), a pressure >700 bars is necessary (Driesner and Heinrich, 2007) to separate a brine (green "B2" in Figure 16), with salinity around 70 wt % NaCl eq. as measured in the hypersaline liquid inclusions (Fig. 9, Table 4). The high temperatures registered by microthermometry and the high Ti content in Q_{1-2} suggest that the hypersaline liquid trapped in Q_{1-2} is expelled toward shallower levels with a minimum loss of heat (i.e., almost adiabatically). During its decompression, the ascending fluid reaches halite saturation in the H_2O -NaCl system at around 390 bars (Fig. 16; Driesner and Heinrich, 2007), i.e. before arriving to a pressure of <270 bar ($<1\text{ km}$), as assumed for the formation of the studied porphyry-type mineralization. In a more realistic complex system H_2O -NaCl-KCl-FeCl-(ZnCl)-(CuCl)-(MnCl)-(PbCl), the phase that would first crystallize is a NaCl-KCl solid solution (Robelin et al., 2004; Kodera et al., 2014). Therefore, it is suggested that small amounts of NaCl-KCl solid solution have crystallized and been lost by the fluid during its ascent. This provides an explanation for the trend observed in the Na-K-Fe diagram toward more Fe-rich compositions of HSMIs inclusions, up to 55 wt % Fe (Fig. 10A). The measured hypersaline liquid inclusions are not so enriched in Fe as the ones reported by Kodera et al. (2014) at the Biely Vrch shallow porphyry (up to 70% wt % Fe; Fig 10A), where important NaCl-KCl precipitation is thought to have occurred during fluid ascent.

The high-temperature vapor inclusions (green and red V in Fig. 16) that could have been trapped with the HSMIs and the hypersaline liquid inclusions are not observed. Direct exsolution of hypersaline liquid by magma is often argued to explain a lack of vapor inclusions (Cline and Bodnar, 1991; Cline and Vanko, 1995; Ulrich et al., 2002; Webster, 2004), a process that would require a high Cl/ H_2O ratio of the melt (>0.35 considering a latite composition, Webster, 2004), implying an anhydrous or an extremely Cl-rich magma (Webster, 2004). Such a high Cl/ H_2O ratio is not compatible with the typical water content in arc magmas (> 4.5 wt %; e.g., Grove et al., 2003). We

prefer to explain the absence of vapor inclusions by fast ascent and decoupling of the low density vapor phase ($<0.2 \text{ g/cm}^3$ at 270 bar, Driesner, 2007) from the dense hypersaline liquid and the associated silicate phase in such a shallow environment.

Presence of aqueous L-V fluid inclusions recorded in Q_3 indicates temperature drop to $<350^\circ\text{C}$. The time gap between formation of Q_{1-2} and Q_3 is not known. Minimum entrapment pressures of the aqueous L-V inclusions, calculated using SoWat software (Driesner, 2007; Driesner and Heinrich 2007), range from 48 to 126 bars (Table 4). Considering the FIAs with the highest $P_{\min}$ of entrapment, minimum emplacement depth of 475 m under lithostatic conditions, and of 1750 m under hot hydrostatic conditions is required. Based on the depth of formation of $<1 \text{ km}$ as indicated by field evidence (Baumgartner 2007; Baumgartner et al., 2008), it can be concluded that quartz Q_3 precipitated under lithostatic or supra-hydrostatic regime. Calculated entrapment temperatures, using the SoWat software (Driesner, 2007; Driesner and Heinrich 2007) and considering a pressure of 270 bars, are between 287° and 346°C . The observed large salinity range (0.46 to 24.11 wt % NaCl eq.) could result from local boiling and/or a mixing of magmatic fluid with minor hot meteoric water, as suggested by oxygen stable isotope analyses discussed below.

6.3 Origin of the fluid and ore precipitation

Oxygen isotopic signatures of the mineralizing fluids in equilibrium with quartz generations Q_{1-2} and Q_3 were calculated using the *in-situ* (SIMS) oxygen isotope analyses of quartz (mean values of $\delta^{18}\text{O}_{Q_{1-2}} = 10.2\text{‰}$ and $\delta^{18}\text{O}_{Q_2} = 12.8\text{‰}$) and precipitation temperatures of 650°C for Q_{1-2} and 315°C for Q_3 (the mean entrapment temperature assuming a pressure of 270 bars of aqueous L-V inclusions, Fig. 5C). Applying the equation of Matsuhisa et al. (1979), fluid in equilibrium with Q_{1-2} and Q_3 , would have compositions of $\delta^{18}\text{O}_{\text{fluid}Q_{1-2}} = 8.9\text{‰}$ ($n=30$, $2\sigma=0.4$) and $\delta^{18}\text{O}_{\text{fluid}Q_3} = 6.5\text{‰}$ ($n=10$, $2\sigma=1.8$), respectively (Fig. 5C). The calculated $\delta^{18}\text{O}_{\text{fluid}}$ in equilibrium with Q_{1-2} could be interpreted, considering the presence of melt inclusions in this quartz generation, to represent the magmatic oxygen isotope signature. The drop of 2.4‰ of $\delta^{18}\text{O}_{\text{fluid}}$ between Q_{1-2} and Q_3 may be attributed to input of around 11% of meteoric water (considering $\delta^{18}\text{O}$ of $-13 \pm 1 \text{‰}$ for local meteoric water during mineralization: Baumgartner et al., 2008). The above calculations of oxygen isotopic composition of

fluid in equilibrium with quartz Q_{1-2} do not consider the potential influence of high-salinity (>70 wt% NaCl eq.) of the fluid on isotope fractionation. Hu and Clayton (2003) have shown, at pressures > 5 kbar and temperatures >750°C, that the oxygen isotope fractionation factor in highly saline fluids could decrease up to 0.7‰ compared to the fractionation factor in low-salinity fluids. In contrast, Zhang et al. (1989) did not detect any difference of the fractionation factor at atmospheric pressure depending on the salinity. Even if a fractionation decrease in the range proposed by Hu and Clayton, (2003) was considered, the influence on the proportion of meteoric water input for the present study would be marginal (up to 14% instead of 11%).

The textural relationship between Cu-bearing minerals and quartz suggests that sulfides co-precipitate with or post-date Q_3 (Fig. 4). Assuming that the fluid from which Q_3 precipitated represents the ore-forming fluid, it can be concluded that sulfides precipitated from a moderate temperature (<350°C) magmatic-dominated fluid mixed with minor contribution of meteoric waters. LA-ICP-MS analyses of aqueous L-V inclusions reveal a low to moderate metal content of this fluid (Cu= 92-1231 ppm, Zn= 683-861 ppm, Ag= 1-3ppm and Pb=1 -446 ppm), compared to fluids associated with Q_{1-2} (Figs.10 and 13). Similar precipitation of Cu-Fe sulfides spatially associated with late quartz generations (commonly with lower CL intensity) has been reported from other porphyry systems (Klemm et al., 2007; Landtwing et al., 2005, 2010; Müller et al., 2010; Redmond et al., 2004), suggesting decoupling between the high-temperature events (>500°C) responsible for most of the quartz precipitation and the lower-temperature events (<450°C) linked to sulfide precipitation. By contrast, Harris et al. (2003) and Rusk et al. (2008a) proposed that metal precipitation is associated with high-temperature quartz at Bajo de la Alumbrera and Butte porphyry deposits, respectively.

6.4 Cu and Ag diffusion through quartz

The reported Cu and Ag diffusion through quartz into the HSMIs explains their extreme enrichment in these two metals (respectively up to 20 wt % Cu and up 1 wt % Ag). Diffusion during heating experiment was fast and efficient at experimental conditions of 1150°C and 1 atm during heating runs of < 90 minutes (Fig 14). The good correlation between Al and Cu distribution (Fig. 14), suggests that Cu is incorporated into the quartz structure by replacement of monovalent cations, likely

H⁺, present in an interstitial position as charge compensation for Al³⁺ (Götze et al., 2004). Source of the copper is probably the chalcopyrite present in the veinlets. In the present study, the high Cu contents measured in quartz and their good correlation with Al, point directly to copper diffusion without need of comparing analyses of fluid or melt inclusions before and after heating as done in the previous studies by Kamenetsky and Danyushevsky (2005), Zajacz et al. (2008, 2009), Li et al. (2009), and Lerchbaumer and Audétat (2012).

6.5 Implications for ore formation processes at Cerro de Pasco

The banded quartz-magnetite-chalcopyrite-(pyrite) veining affecting the trachyte porphyry is the first described porphyry-type mineralization spatially associated with the world's second largest epithermal base metal Cerro de Pasco deposit. The epithermal base metal mineralization is attributed to be formed by dilution of high-salinity magmatic fluids stored at depth (Baumgartner et al. 2008; Rottier et al., 2015b). Even if there is a temporal gap between formation of the porphyry-type veinlets and base metal epithermal mineralization, study of high-temperature fluids trapped in the veinlets provides information on the parental fluid composition likely exsolved from an underlying active magmatic system. The studied HSMIs and hypersaline liquid inclusions are unusually enriched in sulfur and metals (including Zn, Pb, Mo and W; Cu concentrations cannot be considered because of post entrapment diffusion). The absence of sulfides associated with Q₁₋₂ is easily explained by the high temperature and salinity of the mineralizing fluids resulting in high metal solubility that prevents sulfide precipitation. Therefore metal ratios recorded by HSMIs and hypersaline liquid inclusions are not affected by sulfide precipitation and are direct indicators of the composition of the ore-related magmatic system. The Zn/(Pb+Zn) ratio of the bulk ore extracted from the epithermal base metal deposit ~0.78 is similar to the ratio measured in the HSMIs and the hypersaline liquid inclusions yielding ~0.82 ($\sigma=0.03$) and ~0.80 ($\sigma=0.06$), respectively. This similarity points to a unique source at depth for the magma at the origin of the epithermal mineralization and the HSMIs and the hypersaline liquid inclusions (Fig.17).

7 Summary and conclusions

Detailed petrography combined with analyses of HSMIs, hypersaline liquid, and aqueous L-V inclusions and their host banded quartz veins from shallow porphyry type mineralization cropping out at the present-day surface allow to trace fluid processes at the magmatic-hydrothermal transition at Cerro de Pasco, one of the largest Cordilleran base metal deposits on Earth, in which a link with a porphyry system had been proposed but not yet evidenced.

Early quartz Q_{1-2} from banded quartz-magnetite-chalcopyrite-(pyrite) porphyry-type veinlets records two high-temperature stages ($>600^{\circ}\text{C}$) in the magmatic-hydrothermal evolution (Fig. 18). Stage 1 is characterized by the entrapment of heterogeneous inclusions containing variable proportions of evolved silicate melts and hypersaline liquid whereas during stage 2 only magmatic hypersaline liquid inclusions are trapped. Precipitation of quartz Q_3 records a low-temperature stage 3 ($<350^{\circ}\text{C}$) associated with the precipitation of a chalcopyrite-pyrite-sphalerite-(pyrite) assemblage possibly favored by mixing of minor meteoric water with magmatic-dominated fluids, as indicated by the *in-situ* SIMS $^{18}\text{O}/^{16}\text{O}$ isotope analyses.

The entrapment of HSMIs is not common in classical porphyry Cu-Mo deposits. It requires anomalously high temperature for a given pressure to allow phase exsolution below the miscibility field of vapor and hypersaline liquid. At Cerro de Pasco, this is facilitated by the shallow emplacement of the trachyte porphyry, indicating that temperatures $>700^{\circ}\text{C}$ at less than 1 km depth were reached. Our results lead to a better understanding of the significance and origin of the HSMIs. We show that primary HSMIs are abundant in early Q_{1-2} and are formed by heterogeneous entrapment of an evolved silicate melt and hypersaline liquid (salinity around 90 wt % NaCl equiv., Fig. 16). The trapped phases are interpreted to be the result of exsolution at low pressure (270 bars) and high temperature ($>600^{\circ}\text{C}$) from a hydrous evolved rhyolitic melt ascending to shallow levels. Vapor that, under these conditions should have also exsolved is thought to have escaped and was not trapped in the early Q_{1-2} .

SEM-CL imaging of the studied veins reveals that sulfide precipitation occurs during or after the precipitation of quartz Q_3 . High sulfur and metal contents of HSMIs and hypersaline liquid inclusions

are interpreted to reflect the fluid composition before the main sulfide precipitation, and, therefore, their metal ratios can be used as tracers of the magmatic body from which they are exsolved at depth. The similar Pb-Zn ratio of the bulk ore extracted from the epithermal ore bodies at Cerro de Pasco and from the HSMIs and hypersaline liquid inclusions suggest a common source of the fluids responsible for the different mineralization styles at Cerro de Pasco.

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9 References

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10 Figure captions:

Figure 1: Geological map and cross-section of the diatreme-dome complex. The different epithermal mineralization styles at Cerro de Pasco were compiled from field observations and previous work of Rogers (1983), Baumgartner et al. (2008) and the Volcan's geological staff. A) Location of the Cerro de Pasco district. B) Geological map, black arrows show location of small trachyte porphyries C) Zoom of one of the trachyte porphyry outcrops.

Figure 2: A) Outcrop of the trachyte porphyry intruding the diatreme breccia. B) Quartz-magnetite-chalcopyrite-(pyrite) veinlet in the trachyte porphyry. C) Quartz-magnetite-chalcopyrite-(pyrite) veinlets in the diatreme breccia. D) Polished slab showing a quartz-monzonite dyke crosscutting the trachyte porphyry and the quartz-magnetite-chalcopyrite-(pyrite) veinlets (arrows). E) Transmitted light microphotograph of a banded quartz-magnetite-chalcopyrite-(pyrite) veinlet crosscutting the trachyte porphyry. The dark bands close to the veins walls visible also in B, C, and D correspond to the botryoidal quartz bearing micrometric magnetite inclusions.

Figure 3: A) QEMSCAN map of a trachyte porphyry sample crosscut by quartz-magnetite-chalcopyrite-(pyrite) veinlets, one of them showing albite in-fill; insets indicate the position of photomicrographs F and G. Distribution maps of albite and quartz (B), chlorite, epidote, calcite, and quartz (C), X-ray elemental map of Na (D), and Ca (E). In E the intensity of the green color corresponds to variable Ca-content in plagioclase grains and yellow color indicates presence of calcite, apatite, epidote, and sphene. F) Transmitted light photomicrograph of amphibole and biotite phenocrysts replaced by chlorite and calcite (//N). G) Transmitted light photomicrograph (xN) of plagioclase phenocrysts replaced by sericite and/or albite. Abbreviations: Ab- albite, Ap- apatite, Chl- chlorite, Cc- calcite, Ep- epidote, Qz- quartz, Mag- magnetite, Le - leucoxene, Ser- sericite, Spn- sphene.

Figure 4: A) SEM-CL images of an entire quartz veinlet showing different quartz textures and generations (sample CP-14-BR-305); B and C) Zoom of the SEM-CL image A; D) SEM-CL images of a veinlet (sample CP-14-BR-305) the white arrows pointing to quartz Q_{1-2d} overgrowing and partly overprinting Q_{1-2a} and Q_{1-2c} .

Figure 5: A) SEM-CL image of a quartz-magnetite-chalcopyrite-(pyrite) veinlet with location (red spots) and results of SIMS oxygen isotope analyses and with location and number of SIMS trace element analyses (blue spots). B) Zoom of the SEM-CL image showing the contrasting Ti contents between quartz generations Q_{1-2} and Q_3 and the location of the profile plotted in C. C) Plot, along the profile shown in B, of $\delta^{18}O$ of quartz determined by SIMS analyses, and of calculated $\delta^{18}O$ of fluid in

equilibrium with quartz, using the equation of Matsuhisa et al. (1979) at 650°C for quartz Q_{1-2} and at 315°C for quartz Q_3 (see text for discussion). Titanium content in the two quartz generations determined by SIMS is also plotted.

Figure 6: A) Transmitted light photomicrograph of primary not heated HSMIs in a quartz crystal core (Q_{1-2}). B) Corresponding SEM-CL image, showing a well-developed oscillatory growth zoning (quartz sub-generation Q_{1-2c} overgrown by quartz sub-generation Q_{1-2d}); most HSMIs are located in the high CL intensity core. Examples of hexagonal-like (Q_{1-2}) cores (C and D) and not hexagonal (E) with abundant primary not heated HSMIs (transmitted light photomicrographs). F) The same quartz Q_{1-2} core than in (E) after heating at 1150°C; the HSMIs display now silicate glass and globules crowded with salt and opaque crystals. H-I) Zoom of HSMIs after heating at 1150°C showing a silicate phase and one or several globules with abundant salt and opaque crystals.

Figure 7: Step heating of an HSMI at 22°C (A), 200°C (B), 250°C (C), 350°C (D), 450°C (E), and 550°C (F). The black bar corresponds to 10 μ m.

Figure 8: Transmitted light photomicrographs of different fluid inclusion types in Q_{1-2} and Q_3 : A) Primary hypersaline liquid inclusions hosted in Q_{1-2} . B-C) Secondary hypersaline liquid inclusions hosted in Q_{1-2} . D-F) aqueous L-V inclusions hosted in Q_3 .

Figure 9: Homogenization temperature vs. salinity diagram for the hypersaline liquid and aqueous L-V FIAs; the black arrow right to the hypersaline liquid FIAs indicates that homogenization temperatures were not reached and are superior to 600°C.

Figure 10: Composition (LA-ICP-MS microanalysis) of hypersaline liquid inclusions in Q_{1-2} . Each point is a single analysis, the different colors corresponding to different FIAs. A) Mass variation of major cations (Na, K and Fe) of the hypersaline liquid inclusions in a ternary Na-K-Fe diagram. Crystallization of NaCl-KCl solid solution during ascent of the hypersaline fluid may explain the evolution marked by the blue arrow (see text). Published compositions of hypersaline fluids from Cu $\pm$ Au $\pm$ Mo porphyry deposits (grey circle; compiled by Kouzmanov and Pokrovski, 2012) and compositions of hypersaline fluids from the Biely Vrch deposit (grey diamonds; Kodera et al., 2014)

are also plotted for comparison. B-H) Concentration of selected elements versus Rb in the hypersaline liquid inclusions.

Figure 11: BSE images of HSMIs heated at 1150°C and then exposed at surface by polishing: A) HSMIs of type 1 and 3; B) HSMIs of type 2; C) HSMI of Type 4; D) HSMI of type 1; E) HSMIs of type 3.

Figure 12: Al_2O_3 vs SiO_2 content of HSMIs heated at 1150°C obtained by EPMA and whole rock composition (XRF analyses) of magmatic rocks from the Cerro de Pasco district (n=13, supplementary material, Table A.1).

Figure 13: Concentrations of selected elements versus Zn obtained by LA-ICP-MS analyses of single HSMIs and hypersaline liquid inclusions.

Figure 14: EPMA of quartz: A) Location of EPMA spots on a SEM-CL image of Q_{1-2} hosting HSMIs. B) and C) Elemental Cu-K α and Al-K α maps. D) Plot of Al and Cu concentrations obtained by EPMA, LOD of Cu = 64 ppm.

Figure 15: Trace element concentrations determined by LA-ICP-MS microanalyses of Q_{1-2} heated at 1150°C (in red), and of Q_{1-2} heated at <600°C (in blue).

Figure 16: Pressure-composition cross section of the H_2O -NaCl phase diagram (modified from Driesner and Heinrich, 2007) illustrating the fluid pathways for the high-temperature events at Cerro de Pasco. Stage 1 corresponds to magmatic-hydrothermal transition conditions, and the HSMIs reflect injection of a hot and evolved silicate melt to shallow levels. During its ascent, the melt decompresses by conserving its high temperature (>600°C) triggering separation of a chlorine rich phase "red B" with salinity > 90% wt % NaCl eq. and a low-salinity and low-density vapor phase "red V". During Stage 2, the hydrothermal fluid has to have exsolved at greater pressure. Assuming a magmatic temperature for the melt ($\approx 750^\circ\text{C}$), a pressure of above 700 bars is necessary (Driesner and Heinrich 2007) to separate a brine (green "B"), with salinity around 70 wt % NaCl eq. as it has been measured in the hypersaline liquid inclusions (Fig. 9, Table 4).

Figure 17: LA-ICP-MS microanalyses of HSMIs, hypersaline liquid and aqueous L-V inclusions plotted in a Cu-Zn-Pb ternary diagram.

Figure 18: Schematic representation of the mineralization stages distinguished in the quartz-magnetite-chalcopyrite-(pyrite) veinlets hosted by the shallow trachyte porphyry at Cerro de Pasco. As explained in the text, Q_1 and Q_2 are not easily discernible, and in most cases both quartz generations have been merged under the common denomination Q_{1-2} . The stage 2 quartz overgrowth is exaggerated for the scope of clarity.

11 Table

Table 1 : LA-ICP-MS machine and data acquisition parameters

<i>Excimer 193 nm ArF laser Compex 110I</i>	Fluid and Hypersaline inclusions hosted in Quartz	HSMIs hosted in Quartz
Energy density	~20 J/cm ²	~20 J/cm ²
Repetition rate	10 Hz	10 Hz
Crater sizes	15-60 µm	15-40 µm
Ablation cell	In-house built glass chamber with anti-reflection coated silica glass window	In-house built glass chamber with anti-reflection coated silica glass window
Cell He gas flow	1.1 l/min He	1.1 l/min He
Cell H gas flow	5 ml/min H ₂	5 ml/min H ₂
<i>Data acquisition parameters</i>		
Readings per replicate	400	400
Points per peak	1 per mass	1 per mass
Oxide production rate	tuned to <0.5 % ThO	tuned to <0.5 % ThO
Dwell time per isotope	40 ms fo Fe, 30 ms for Ag and Ca 10 ms for the others	10 ms for all isotopes
Isotopes analyzed (fluid inclusions program)	⁷ Li, ¹¹ B, ²³ Na, ²⁷ Al, ²⁹ Si, ³⁴ S, ³⁹ K, ⁴⁴ Ca, ⁴⁹ Ti, ⁵⁵ Mn, ⁵⁷ Fe, ⁶⁵ Cu, ⁶⁶ Zn, ⁷⁵ As, ⁸⁵ Rb, ⁸⁸ Sr, ⁹⁸ Mo, ¹⁰⁷ Ag, ¹¹⁸ Sn, ¹²¹ Sb, ¹³³ Cs, ¹³⁷ Ba, ¹⁸⁴ W, ¹⁹⁷ Au, ²⁰⁸ Pb	⁷ Li, ¹¹ B, ²³ Na, ²⁵ Mg, ²⁷ Al, ²⁹ Si, ³⁴ S, ³⁹ K, ⁴⁴ Ca, ⁴⁹ Ti, ⁵⁵ Mn, ⁵⁷ Fe, ⁶⁵ Cu, ⁶⁶ Zn, ⁷⁵ As, ⁸⁵ Rb, ⁸⁸ Sr, ⁸⁹ Y, ⁹⁰ Zr, ⁹³ Nb, ⁹⁸ Mo, ¹⁰⁷ Ag, ¹¹⁸ Sn, ¹²¹ Sb, ¹³³ Cs, ¹³⁷ Ba, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁷³ Yb, ¹⁸⁴ W, ¹⁹⁷ Au, ²⁰⁸ Pb

Table 2: SIMS trace element results of quartz generations Q₁₋₂ and Q₃.

Analysis #	Quartz generation	Li ppm	1 σ %*	Al ppm	1 σ %*	Ti ppm	1 σ %*	Fe ppm	1 σ %*
4	Q ₁₋₂	12.2	6	958	4.3	193	1.3	9.1	7.3
5	Q ₁₋₂	5.7	10	514	12.3	156	2	15.8	2.9
6	Q ₁₋₂	6.3	6.6	523	11.4	358	1.7	145	2.5
7	Q ₁₋₂	4.1	8.4	333	12.8	224	0.54	137	1.5
10	Q ₁₋₂	20.5	7	627	6.3	126	1	6.2	6.8
11	Q ₁₋₂	7.5	6.8	746	3.7	144	1	7.5	9.6
	Mean	9.4		617		200		53.4	
	Min	4.1		333		126		6.2	
	Max	20.5		958		358		145	
12	Q ₃	23.7	3.3	1100	5.1	7.6	4.8	4.1	17.4
8	Q ₃	20.8	8.6	439	9.5	3	15.4	5	12.7
9	Q ₃	64.2	2.5	956	3.9	9.2	3.9	16.3	1.3
1	Q ₃	nd		348	0.67	4.7	0.56	14.4	0.47
2	Q ₃	6.1	10	345	10.7	2.4	17.3	4.5	17.7
3	Q ₃	4	12	348	9.2	2.9	12.8	3.5	17.3
	Mean	23.8		589		5		7.9	
	Min	4		345		2.4		3.5	
	Max	64.2		1100		9.2		16.3	

(*)Internal error (error on the different cycle of an analysis); nd: not detected

Table 3: Summary of trace element compositions of Q₁₋₂ and Q₃ determined by LA-ICP-MS analyses.

Quartz generation	Li (ppm)	Na (ppm)	Al (ppm)	K (ppm)	Ti (ppm)	Fe (ppm)	Rb (ppm)	Sr (ppm)	Sn (ppm)
Q ₁₋₂ (n=64)	2.9 - 43.3	0.5 - 257	22.6 - 1570	53.9 - 318	107 - 318	14 - 1422	0.1 - 5.7	0.01 - 2.1	23 - 50
	17 ± 9.9	41.3 ± 63.1	340 ± 206	190 ± 59.5	201 ± 51	223 ± 263	1/1.2	0.46 ± 0.61	26.2 ± 6.4
Q ₃ (n=4)	33.4 - 54.1	8.9 - 24.1	607 - 960	nd	2.9 - 13.3	nd	nd	0.17 - 0.31	21.8 - 25.4
	47.8 ± 9.8	15.3 ± 6.9	844 ± 164		6.9 ± 4.7			0.24 ± 0.1	23.3 ± 1.5

nd: not detected

Table 4: Homogenization temperature and salinity determined by microthermometric measurements of 6 hypersaline liquid inclusion assemblages in Q₁₋₂ and 8 aqueous L-V inclusion assemblages in Q₁₋₂ and Q₃.

FIA	FI type	n	Salinity (wt% NaCl eq.)	1 σ	Th (°C)	1 σ	P* (bar)
CP-14-BR-305''-E-1	Hypersaline	9	70.9	1.5	680->800		
CP-14-BR-305''-D-1	Hypersaline	9	72.2	2.1	> 600		
CP-14-BR-305''-F-1	Hypersaline	6	70	2.2	> 600		
CP-14-BR-305'-2-3	Hypersaline	21	73.2	2.1	> 600		
CP-14-BR-305'-2-4	Hypersaline	11	71.2	1.9	> 600		
CP-14-BR-305'-2-5	Hypersaline	4	72.5	1.8	> 600		
CP-14-BR-305'-4-1	L-V	8	0.46	0.28	308	9	96
CP-14-BR-305'-4-2	L-V	10	0.66	0.22	297	17	82
CP-14-BR-305'-3-1	L-V	7	1.64	0.17	329	12	126
CP-14-BR-305'-3-2	L-V	14	6.07	0.27	281	8	63
CP-14-BR-305'-2-1	L-V	9	24.09	1.0	272	6	48
CP-14-BR-305'-2-2	L-V	6	6.78	0.49	311	12	96
CP-14-BR-305-A-2	L-V	9	1.99	0.17	292	5	76
CP-14-BR-305-A-3	L-V	5	11.42	0.07	300	8	80

*Average minimum pressures of the FIA calculated using the SoWat software (Driesner, 2007; Driesner and Heinrich 2007)

Table 5: Composition of 6 hypersaline liquid inclusion assemblages in Q₁₋₂ and 4 aqueous L-V inclusion assemblages in Q₁₋₂ and Q₃ obtained by LA-ICP-MS analysis

FIA	type	n	Li (ppm)		Na (ppm)		S (ppm)		K (ppm)		Ca (ppm)		Mn (ppm)		Fe (ppm)		Cu (ppm)		Zn (ppm)	
			Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ
305'-S-1	Hypersaline	3	nd		186035	11322	15329		127553	30367	48679	28576	9903	8058	77030	10760	499	687	4646	1874
305'''-D-1	Hypersaline	7	138	62	161828	9620	39868	12487	142482	17304	50258	14655	14149	1952	88710	12425	26507	18264	12540	5474
305'''-F-1	Hypersaline	6	307	64	152904	19706	21027	12364	151700	15949	36614	10048	14457	1614	109123	46624	9184	6910	16515	2003
305'''-E-1	Hypersaline	6	nd		171916	10328	26073	12550	131103	20527	45417	27915	14510	4787	83197	25478	15144	8596	12656	1373
305'-2-3	Hypersaline	7	nd		168538	20495	19485	10825	135624	24140	56095	30556	13198	5183	77487	35449	230	243	10549	8131
305'-2-4	Hypersaline	5	nd		175869	18047	9401		124252	9627	44790	25257	9795	1695	99831	45234	524	155	13675	4787
305b-3-1	L-V	3	nd		6176	0	nd		2833		nd		565		7155	9097	1231		861	270
305'-4-2	L-V	5	nd		7435	6713	nd		nd		nd		93		1372		192	233	683	317
305'-3-2	L-V	1	nd		23643		nd		nd		nd		nd		nd		nd		nd	
305'-4-1	L-V	1	nd		4131		nd		nd		nd		nd		nd		nd		nd	
			Rb (ppm)		Sr (ppm)		Mo (ppm)		Ag (ppm)		Cs (ppm)		Ba (ppm)		W (ppm)		Au (ppm)		Pb (ppm)	
			Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ	Mean	1 σ
			513	486	1066	697	577	205	37	1	33	33	1266	1454	109	99	3.5		2272	482
			1191	265	793	275	611	247	58	22	89	14	298	110	172	73	0.6	0.2	3314	1042
			1402	144	818	263	510	215	65	39	156	10	756	105	86	18	1.4	0.9	4057	1350
			1101	143	1946	927	941	572	54	25	113	4	888	448	258	83	1.8	0.8	2980	532
			943	631	1326	888	458	351	64	59	52	35	834	634	100	109	1.4		2282	1587
			696	59	916	517	362	86	55	8	37	9	465	288	45	24	0.9	1	2751	413
			33	4	90	54	83	86	nd		5	1	20	5	20	8	nd		98	93
			8	8	86	115	22	19	1		7	8	23	10	34	1	0.2	0.03	11	6
			24		207		2		3		20		nd		nd		1.5		nd	
			17		82		7		nd		4		nd		nd		nd		446	

nd: not detected

Table 6: Summary of the HSMIs compositions in Q₁₋₂ obtained by LA-ICP-MS analysis.

	Zn < 1000ppm			All the data		
	n	Mean	1 σ	n	Mean	1 σ
K ₂ O (%)	6	7.0	1.1	14	9.0	2.7
Na ₂ O (%)	6	2.8	1.3	14	3.7	2.1
MgO (%)	5	0.08	0.04	12	0.11	0.04
CaO (%)	4	0.6	0.27	10	1.2	0.81
FeO (%)	6	1.6	0.7	13	2.2	1
Mn (ppm)	6	686	201	14	1930	1357
Zn (ppm)	5	554	157	13	1557	1011
Cu (ppm)	6	33494	19976	14	64580	57719
Rb (ppm)	6	576	46.5	14	659	133
Sr (ppm)	6	94.9	30.9	14	179	142
Mo (ppm)	6	26.1	20.6	14	78.1	54.5
Ag (ppm)	6	696	645	14	1874	2792
Cs (ppm)	6	48.6	10.8	14	56.1	16.9
Ba (ppm)	6	85.5	52.6	14	143	139
W (ppm)	6	4.1	2.6	14	15.1	13.8
Au (ppm)	4	0.27	0.13	8	0.26	0.09
Pb (ppm)	6	110	53.6	14	317	258
Mg (ppm)	5	471	210	12	682	267
Y (ppm)	6	5.4	1.8	14	6.2	3.1
Zr (ppm)	6	149	84.9	13	153	77.6
Nb (ppm)	6	59.6	52.1	13	55	37.4
La (ppm)	6	16.3	5.4	14	36.9	24.7
Ce (ppm)	6	37.1	7.3	14	74.1	43.3
Yb (ppm)	4	0.93	0.56	10	1.1	0.72

Figure 1:

Figure 2:

Figure 3:

Figure 1 consists of three panels (A, B, C) showing back-scattered electron (BSE) micrographs of garnet and clinopyroxene in sample 1000. Panel A shows a garnet (Q₁₋₂a) and clinopyroxene (Cpy) contact with host rock. Panel B shows a garnet (Q₁₋₂c) and clinopyroxene (Cpy) contact with host rock. Panel C shows a garnet (Q₁₋₂a) and clinopyroxene (Cpy) contact with host rock. A 200 μm scale bar is provided.

Figure 5:

Figure 6:

Figure 7:

Figure 8:

Figure 9:

Figure 10:

Figure 11:

Figure 12:

Figure 13:

Figure 14:

Figure 15:

Figure 16:

Figure 17:

Figure 18: