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# Copper deposition during quartz dissolution by cooling magmatic-hydrothermal fluids: The Bingham porphyry

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#### Abstract

Scanning electron microscope cathodoluminescence imaging is used to map successive generations of fluid inclusions in texturally complex quartz veinlets representing the main stage of ore metal introduction into the porphyry Cu–Au–Mo deposit at Bingham, Utah. Following conventional fluid inclusion microthermometry, laser ablation–inductively coupled plasma–mass spectrometry (LA-ICPMS) is applied to quantify copper and other major and trace-element concentrations in the evolving fluid, with the aim of identifying the ore-forming processes.

Textures visible in cathodoluminescence consistently show that the bulk of vein quartz (Q1), characterized by bright luminescence, crystallized early in the vein history. Cu–Fe-sulfides are precipitated later in these veins, in a microfracture network finally filled with a second generation of dull-luminescing Q2 quartz. Mapping of brine and vapor inclusion assemblages in these successive quartz generations in combination with LA-ICPMS microanalysis shows that the fluids trapped before and after Cu–Fe-sulfide precipitation are very similar with respect to their major and minor-element composition, except for copper. Copper concentrations in inclusions associated with ore formation drop by two orders of magnitude, in a tight pressure–temperature interval between 21 and 14 MPa and 425–350 °C, several hundred degrees below the temperature of fluid exsolution from the magma. Copper deposition occurs within a limited P-T region, in which sulfide solubility shows strong normal temperature dependence while quartz solubility is retrograde. This permits copper sulfide deposition while secondary vein permeability is generated by quartz dissolution. The brittle-to-ductile transition of the quartz–feldspar-rich host rocks

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occurs in the same temperature range, which further enhances vein reactivation and promotes cooling and expansion of fluids ascending across the transition from lithostatic to hydrostatic conditions. © 2005 Elsevier B.V. All rights reserved.

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### 1. Introduction

Porphyry-type ore deposits are centered on intrusions emplaced at depths of a few kilometers and provide the world's major resource of Cu, Mo and Re, and a significant supply of Au [1]. Porphyry stocks intrude above deeper intermediate to felsic magma chambers that are the source of metal-transporting magmatic-hydrothermal fluid focused upward through a dense fracture network in the porphyry [2]. Processes in upper crustal magma chambers are decisive for the generation of a metal charged magmatic hydrothermal fluid (e.g., [3-6]). Focusing of a large ascending fluid flux and the physico-chemical mechanism of metal precipitation in the vein network are prime factors determining the metal enrichment factor, which is hundreds to thousand times average crustal abundance. Several processes have been suggested to trigger sulfide precipitation from magmatichydrothermal fluids, including rapid changes in pressure and/or temperature [7,8], fluid phase separation into coexisting high-salinity brine and low-salinity vapor with partitioning of acid volatiles into the vapor phase [6,9], fluid-rock interaction affecting physico-chemical parameters such as the pH of the fluid [10,11], and dilution of magmatic brines by meteoric water [7,12].

Fluid inclusions provide key insights into mineralizing processes (e.g., [13–15]). The advent of quantitative microanalysis of ore-forming elements in single fluid inclusions [16,17] now allows quantification of the parameters controlling metal precipitation (e.g., [18,19]) and led to a first assessment of fluidchemical processes in the Alumbrera porphyry–Cu– Au deposit [8]. In porphyry deposits, vein relationships and mineral textures are invariably complex, with the result that published fluid inclusion studies typically report very large ranges in temperatures, pressures and fluid salinities [8,12,14,15]. These ranges are probably real and characteristic of such dynamic fluid systems close to the interface between hot magmas and the cold surface of the Earth. However, interpretation in terms of mineral precipitation mechanisms is hampered by the great complexity of fluid inclusion associations without clear relationships between fluid inclusion generations and crystallization stages of ore minerals. Scanning electron microscope cathodoluminescence (SEM-CL) imaging provides a new view of quartz textures in such complex porphyry-hosted quartz–sulfide veins [20–22]. Together with conventional petrography, CL images help to resolve successive generations of fluid inclusion assemblages hosted in quartz and their timing relative to vein quartz and ore mineral formation (e.g., [22–25]).

This paper reports the first detailed study combining SEM-CL-imaging and conventional fluid inclusion microthermometry with quantitative microanalysis of ore-metal concentrations by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICPMS). The results clearly identify the stage of ore-metal precipitation and thus constrain the decisive parameters for the formation of the giant Bingham porphyry Cu–Au(–Mo) deposit.

### 2. Geologic framework

Bingham, located 30 km southwest of Salt Lake City (Utah), is one of the largest Cu–Au(–Mo) orebodies in the world, containing 27.5 Mt of copper, 0.78 Mt of molybdenum 1600 t of gold and 17,700 t of silver [26]. A hundred years of open pit mining and deep drilling provide more than 2 km of vertical exposure through the deposit, which is centered on late Eocene porphyry dikes intruded at ~38 Ma (e.g., [27]) into equigranular monzonite and a thick sequence of Pennsylvanian quartzite and silty limestone (e.g., [28]). The sequence of mineralizing porphyries as currently recognized is [22,29,30] (1) quartz monzonite porphyry, (2) latite porphyry, (3) mafic biotite porphyry (possibly mixed latite and



Fig. 1. Geological map of the Bingham mine showing main lithologies [31], metal zonation and fluid inclusion distribution [22]. The cross section (inset) is tilted today by  $\sim$ 15° to the east, as a result of later Basin and Range tectonics.

minette magmas), (4) quartz latite porphyry breccia and (5) quartz latite porphyry. Copper-gold mineralization associated with potassic alteration occurs in all five intrusions, but the earliest quartz monzonite porphyry intrusion is volumetrically most important and contains the highest ore grade, the highest vein density and the most intense potassic alteration. Later porphyries truncate quartz-sulfide veins in the quartz monzonite porphyry and are markedly less veined, altered and mineralized [22,29]. The copper orebody, as defined by the 0.35% copper grade contour, has the shape of a mushroom cap centered on the quartz monzonite porphyry as its stem. The rim of the orebody extends irregularly downward, into sedimentary rocks in the north, and into equigranular monzonite in the south (Fig. 1). High-grade copper-gold ore (>1% Cu; >1µg/g Au) forms a central body (approximately 100×300 m in cross section, and 1000 m in SW-NE strike length), centered on the quartz monzonite porphyry [31].

The intrusion of each porphyry phase was followed by the formation of (a) barren hairline biotite veinlets, (b) sparse dark micaceous veinlets with biotite-K-feldspar – muscovite  $\pm$  and a lusite  $\pm$  chalcopyrite  $\pm$ bornite halos and (c) abundant and multiple generations of quartz stockwork veins that are intimately associated with both potassic alteration (quartz  $\pm$  Kfeldspar  $\pm$  biotite) and the formation of the coppergold ore [22,29]. Quartz-molybdenite veins (d) formed after the last intrusion was emplaced, postdating Cu-Fe-sulfide introduction [32]. Quartz-molybdenite veins are finally cut by (e) quartz-pyrite veins with sericitic halos [22,29]. Crosscutting relationships between individual stockwork veins (c), even within one porphyry intrusion, show that veins (a) to (c) formed during multiple episodes of fracture opening and mineral precipitation even though all have essentially identical mineralogy. These quartz veins all contain bornite, digenite and chalcopyrite and are in equilibrium with hydrothermal K-feldspar and biotite, present either in the veins or as alteration selvages with disseminated sulfides grains. Early quartz stockwork veins at any one location tend to be undulating and sheeted and are cut and offset by irregular massive, blocky or banded quartz veins containing some K-feldspar as a gangue mineral. The latest quartz stockwork veins are parallel-walled, but still have similar ore grades and contain the same sulfide minerals. Research presented here is based on a more extensive geological, petrographic, SEM-CL and fluid inclusion investigation that focused on the zone of most abundant quartz veining associated with the highest copper–gold grades in the central orebody hosted by quartz monzonite porphyry.

#### 3. Approach and analytical techniques

Following extensive pit mapping, drill core logging and conventional petrographic work [22,29], a fluid inclusion study of more than 60 quartz veins in quartz monzonite porphyry was used to assess the quality and variability of fluid inclusions. The best of these vein samples were prepared as doubly polished 150–600-µm-thick wafers and analysed in detail by SEM-CL to image successive generations of quartz and to correlate these with fluid inclusion assemblages using transmitted light microscopy. This combination of analytical techniques identified a consistent sequence of vein mineral precipitation and a consistent relationship between quartz generations, fluid inclusion assemblages and sulfide deposition.

SEM images were obtained using a CamScan CS44LB instrument. Backscattered electron (BSE) and CL images were taken in sequence under the same instrumental conditions (accelerating voltage of 15 kV, beam current of 10-15 nA, working distance 35 mm, untilted sample adjusted in height to the lower edge of the CL mirror), using an EDAX Phoenix digital image acquisition system. The SEM is equipped with a four-quadrant semiconductor BSE detector (KE Developments Ltd.) and a motor-driven elliptical mirror focusing the CL signal onto a standard photomultiplier detector. The lowest magnification was  $50\times$ , corresponding to an image size of  $\sim 2.2 \times 1.8$  mm. For petrographic and fluid inclusion mapping, larger areas were compiled by digitally overlaying SEM-CL images on normal transmittedlight micrographs. Such composite images were used as a basis to map fluid inclusion assemblages, defined as coevally entrapped groups of inclusions characterized by close spatial association and identical phase proportions at room temperature [33]. Several cycles of petrographic inspection, microthermometry and LA-ICPMS analysis (often using both sides of several wafer chips) were required in order to properly characterize each inclusion assemblage and minimize the loss of inclusions by thermal decrepitation.

Fluid inclusions were measured on a Linkham THMSG 600 heating-freezing stage, calibrated to  $\pm 0.2$  °C for the melting point of CO<sub>2</sub> (-56.6 °C), and the melting point of H<sub>2</sub>O (0.0 °C), and to  $\pm 2.0$  °C for the critical point of pure H<sub>2</sub>O (374.1 °C). The apparent salinity of fluid inclusions, expressed in wt.% NaCl equivalent (wt.% NaCl eq.), was determined from final melting of halite [34] or constrained by clathrate melting [35].

The prototype GeoLas LA-ICPMS system developed at ETH Zürich [36] consists of a 193-nm ArF Excimer laser (Lambda Physik, Germany) combined with an Elan 6100 quadrupole mass spectrometer (Perkin Elmer, Canada). Instrument setup and data reduction procedure for fluid inclusion microanalysis followed that of earlier studies [16,17,37]. Absolute quantification of LA-ICPMS signals is done by time integration of all element intensities, correction for host mineral contributions (in this study Li, Na, K, Sn, Pb and Bi; see [38]), and external calibration of intensity ratios against SRM 610 glass from NIST. Element ratios are recalculated to absolute concentrations for brine inclusions, where the wt.% NaCl equivalent salinity, corrected for contributions by cations other than Na [16], provides an internal standard. For vapor inclusions, where the salinity cannot be determined microthermometrically (CO<sub>2</sub>-clathrate melting but no observation of the homogenization of  $CO_2$  liquid into  $CO_2$  vapor [35]), only element ratios relative to Na are reported.

### 4. Results

### 4.1. Vein petrography and quartz textures from SEM-CL

All quartz-sulfide stockwork veins in the center of the high-grade orebody show two distinct phases of quartz crystallization revealed by contrasting CL light intensity, recording a two-stage history of vein formation (Fig. 2). The first generation of quartz (Q1) is characterized by bright luminescence showing white, light gray and gray color nuances. It forms 90–99 vol.% of the veins (Table 1) and records the initial stockwork veining following hydraulic fracturing of



Fig. 2. Transmitted light (A) and cathodoluminescence (B) images of porphyry–Cu vein quartz sample 211–19 (the contrast between quartz and sulfides enhanced in both images). Only the cathodoluminescence image reveals the complex vein quartz textures, including euhedral growth zoning and dissolution surfaces on Q1 quartz. Fracture-filling Q2 quartz shows fracture-parallel growth zoning. Sulfides are entirely enclosed in Q2 quartz. Abbreviations: qtz=quartz, sulf=Cu–Fe-sulfide.

Table 1		
Characterization of the two quartz types Q1	and Q2 and their	fluid inclusion assemblages

	Q1 quartz	Q2 quartz
Volume of quartz in veins	90–99%, grains (0.5–1 mm), bulk of stockwork veins	1–10%, interstitial and fracture fillings, overgrowing O1
SEM-CL response	bright luminescence (white, light gray and gray nuances)	dull luminescence (gray, dark gray and black nuances)
SEM-CL textures	rare euhedral growth zoning	commonly euhedral growth zoning, partly lining Q1 grain boundaries
	dissolution horizons cutting growth zones	
Relation to Cu-Fe-sulfide deposition	predating	coeval or postdating
Fluid inclusion assemblages	B1 brine and V1 vapor trails and rare clusters assemblages exclusively trapped in Q1	B2 brine and V2 vapor trails and clusters assemblages trapped in Q2 or cutting the Q1/Q2 interface
	fluid inclusions commonly 10-20 µm, rarely up to	fluid inclusions commonly <10 μm,
	50 µm in diameter	vapors up to 40 µm in diameter
	rare boiling trails	rare boiling trails
	secondary aqueous inclusion trails	secondary aqueous inclusion trails
Trace-element concentrations (µg/g, [38])		
Li	2.7–9.0	1.8–3.0
Na	1.3–36	0.6–3.6
Al	63–408	22–64
Р	14–30	14–31
K	2.2–330	1.6–4.4
Ti	65–237	12–39
Fe	<3.2-20	<3.4 to <11
Cu	<0.1-1.0	< 0.1-0.9
Ga	0.1–0.6	0.2–0.4
Ge	0.5–2.5	0.7–2.5
Ag	< 0.05-0.12	<0.07-0.13
Sn	0.8–2.3	0.9–2.1

For concentrations below the limit of detection ( $3\sigma$  criterion), the LOD is given as < value.

the porphyry stock. Local euhedral growth zoning documents crystallization into open space. Some Q1 quartz crystals reveal multiple stages of crystallization and dissolution. These growth features are commonly marked by distinct (rarely oscillatory) variations in CL intensity, but most Q1 grains show relatively homogeneous bright luminescence.

The second-generation quartz (Q2) is volumetrically subordinate but present in all quartz stockwork veins. It shows a dark but often abruptly varying CL response (gray, dark gray and black) and oscillatory growth zoning is common. Q2 occurs in a distinctive microfracture network along Q1 grain boundaries, filling voids that resulted from cracking and partial redissolution of Q1. Transitions in CL response between bright-luminescing Q1 and dull-luminescing Q2 quartz are usually abrupt with truncation of Q1 growth zones. Microfractures filled with Q2 quartz may extend from Q1-dominated veins into the surrounding wall rock, where the Q2 veinlets commonly contain additional K-feldspar. Copper–iron-sulfide grains and gold (composite grains of bornite  $\pm$ digenite  $\pm$  gold, or bornite  $\pm$  chalcopyrite  $\pm$  gold) are invariably mantled by Q2 quartz or in contact with microfractures filled by Q2 quartz. Sulfides were never observed to occur entirely enclosed in pristine Q1 quartz. These textures show that ore metal precipitation occurred after Q1 quartz deposition, and before or during the crystallization of Q2 quartz [22,29].

## 4.2. Fluid inclusion generations and results from microthermometry

Fluid inclusions at Bingham belong to four major types, based on phase proportions at room temperature: brine (B), vapor (V), intermediate density (I) and aqueous inclusions (A). Intermediate-density inclusions contain a large (30-50 vol.%) bubble with or without small opaque or highly refractive transparent crystals, but no halite; they are restricted to the deep part of the Bingham system, several hundred meters beneath the high-grade ore zone sampled here (Fig. 1; [22]). Intermediate-density inclusions are not considered further here, nor the subordinate aqueous inclusions (two phase, 20-30 vol.% liquid at room temperature, apparent salinity= $7.1 \pm 1.6$  wt.% NaCl eq., total homogenization temperature  $T_{\rm h(tot)}$ =318 ± 5 °C), which postdate ore formation (inferred from crosscutting relations with B, V, and I inclusions). Brine and vapor inclusions are associated with the process of stockwork veining and porphyry-Cu-Au mineralization. Their published apparent salinities and total homogenization temperatures show a wide range (e.g., [14,22,39]) and thus warrant a more detailed investigation.

Based on a large collection of quartz stockwork vein samples ([22] and unpublished data) and extensive microthermometry, sample D211-19 from drill hole D211 at a downhole depth of 19 ft (mine coordinates -1353 E/-134.81 N, center of the high-grade orebody) was selected for the fluid-chemical study reported here. Fluid inclusions were strictly classified as assemblages, never as individual inclusions, and all data are reported as averages and error bars of one standard deviation within one assemblage. The timing of fluid inclusion entrapment was related to the formation of Q1 and Q2, as revealed by cathodoluminescence. Special emphasis was put on crosscutting relationships between inclusion assemblages and the O1/O2 interface (Fig. 3E). Petrographic mapping of inclusion assemblages was based on composite CL images and microphotographic overlays from several chips of this 12-mm-wide vein, which contains a relatively large proportion of Q2 quartz. Fig. 3 depicts a small part of the sampled fluid inclusion map.

Two groups of brine and vapor inclusion assemblages were distinguished. Group 1 assemblages are exclusively trapped in Q1 quartz (brine B1 and vapor V1). These assemblages occur as rare clusters, or along trails (most larger inclusions). Group 2 assemblages (brine B2 and vapor V2) either form clusters in Q2 quartz, occur along trails in Q2, or demonstrably cut across the Q1/Q2 interface.

Fluid inclusions of the B1 and B2 assemblages always contain a large halite cube and sometimes also a sylvite daughter; smaller transparent grains (up to five in one inclusion) may include Mg-Ca carbonates, anhydrite and barite (as suggested by transient LA-ICPMS signals). Opaque daughter crystals are a tetrahedral grain of chalcopyrite (more abundant in B1 assemblages), a small red plate of hematite (always present in B2 brines, tends to be larger than hematite in B1 brines) and a rare, unknown phase. B1 brines in group 1 assemblages are irregular or have negative crystal shapes and are commonly between 10 and 40 µm in diameter. B2 brines in group 2 assemblages are isometric and round or have negative crystal shapes and are commonly below 10 µm. Vapor bubble tends to be smaller in B2 (25-40 vol.%) than in B1 brines (30-45 vol.%). Both groups of vapor inclusion assemblages are characterized by inclusions with >75 vol.% bubble and one or two tiny opaque daughter crystals in some instances (chalcopyrite and/or hematite based on shape and color). Vapor inclusions are isometric and round or have negative crystal shapes, and are commonly between 10 and 25 µm, rarely up to 50 µm.

The total homogenization  $(T_{h(tot)})$  of all brine inclusions occurs to the liquid phase, either by vapor disappearance or by final dissolution of halite. In individual assemblages, halite may disappear before or after vapor disappearance, but the temperature difference in these cases is never more than 60 °C. Within one brine assemblage, average salinities have a standard deviation of <5.5 wt.% NaCl eq. and average bubble disappearance temperatures a standard deviation of <55 °C. Total homogenization of B1 brine assemblages occurs at somewhat higher temperatures than in B2 assemblages, but with largely overlapping temperature ranges (90% of all measurements are within the following range: 315 °C<T<sub>h(tot)</sub> $\leq$ 460 °C for B1, n=771; 255 °C $\leq T_{h(tot)}\leq 380$  °C for B2, n=153).  $T_{h(tot)}$  variation in individual assemblages is smaller than the range described by all assemblages of one brine group, thus recording real temperature variability in the sample. The apparent salinities of B1 and B2 brine inclusions largely overlap within a small range (Fig. 4A; average salinity of  $B1=44 \pm 5$  wt.% NaCl eq. n = 723; B2=40 ± 3 wt.% NaCl eq. n = 121).

Low-temperature microthermometry of vapor inclusions showed final melting of CO<sub>2</sub> at  $-56.1 \pm 0.3$  °C, and final melting of CO<sub>2</sub>–clathrate between +3.5 and +7.8 °C, irrespective of host quartz type (Q1 or Q2). Because total homogenization of the CO<sub>2</sub> phase could not be observed during microthermome-



Fig. 3. CL mapping of fluid inclusion generations for sample D211–19. (A) Fluid inclusion groups and mapping legend, (B) sketch of relations between Q1 and Q2 quartz generations used to differentiate two groups of fluid inclusion assemblages. The same vein region is shown in (C) transmitted light, (D) cathodoluminescence (contrast between Q2 and sulfides enhanced), (E) backscattered electron image and (F) interpretative sketch with mapped individual fluid inclusions of various assemblages. For easier comparison of the different images, the contact between the vein-forming quartz type Q1 and the fracture- and vug-filling quartz type Q2 is marked on all pictures with a thin line.



Fig. 4. Total homogenization temperatures ( $T_{h(tot)}$ , °C), salinities (wt.% NaCl eq.), and LA-ICPMS analyses of fluid inclusion assemblages, in absolute concentrations (X, µg/g) for brine assemblages (A) and element concentration ratios relative to Na (X/Na) for vapor assemblages (B). Fluid inclusion assemblages are sorted according to decreasing Cu content (B1, B2 brine assemblages) or Cu/Na ratio (V1, V2 vapor assemblages). Averages of one assemblage (typically 3–12 inclusions) are plotted, with error bars indicating one standard deviation of all individual inclusions in an assemblage.

try (no  $CO_2$  liquid phase discernible even in large inclusions), the salinity of the vapor inclusions is only constrained to be below ~11 wt.% NaCl eq. [35]. Likewise, the small amount of liquid did not allow accurate determination of total homogenization temperatures of the vapor inclusions (see [2]). Four unambiguous boiling trails of B1 and V1 in group 1 inclusions assemblages, revealed total homogenization temperatures (by bubble disappearance in brine) and salinities as follows:  $426 \pm 9 \text{ °C}/47.0 \pm 0.6$  wt.% NaCl eq. (*n*=23),  $385 \pm 5 \text{ °C}/45.8 \pm 0.5$  wt.% NaCl eq. (*n*=1, error indicates uncertainty of mea-



Fig. 5. Copper concentration as a function of total homogenization temperature (each point representing an inclusion assemblage, with  $1\sigma$  error bars) grouped according to the fluid inclusion groups (B1, B2). A boiling assemblage (brine with vapor inclusions on a single trail) is marked with a circle. B1 brine inclusions trapped in Q1 quartz follow a correlation trend parallel to the temperature–solubility curve predicted from experimental data ([41]; congruent chalcopyrite solubility according to Eq. (2), calculated for P=5 MPa and  $aCl^{-}=1m$ ). The steep temperature dependence of the solubility curve is reliable while its absolute position, depending on poorly known composition–activity relationships, remains not well constrained.

surement),  $383 \pm 5$  °C/45.7  $\pm 0.5$  wt.% NaCl eq. (n=8) and  $379 \pm 15$  °C /  $44.4 \pm 0.8$  wt.% NaCl eq. (n=12). These data translate into fluid entrapment pressures of 14-21 MPa (based on the solvus in the binary NaCl-H<sub>2</sub>O system; [40]). Close similarity of brines in boiling trails with apparent salinities and total homogenization temperatures of brine-only inclusion trails is consistent with general fluid entrapment close to liquid-vapor saturation. All homogenization temperatures are therefore taken to approximate entrapment temperatures. Inclusions homogenizing by halite dissolution may require a maximum pressure correction of ~30 °C assuming pressures of 60 MPa (slopes of isochores at conditions defined by boiling trails are  $\sim$ 75 °C/100 MPa [40]). This corresponds to the maximum expected pressure difference, if the boiling trails were trapped at hydrostatic pressures while the halite-homogenizing inclusions were trapped at lithostatic pressure.

# 4.3. Element concentrations in the fluids by LA-ICPMS

Inclusions selected for LA-ICPMS analysis were the largest B1 brines and V1 vapors observed in Q1, and B2 brines and V2 vapors trapped in Q2, to obtain the lowest limits of detection (Fig. 4 and Tables 2 and 3 in the EPSL Online Background Dataset<sup>2</sup>). Selected major elements and ore metals are plotted in Fig. 4, sorted by decreasing Cu concentration (Fig. 4A; brines) or Cu/Na ratio (Fig. 4B; vapors) for each group of inclusion assemblages. Element ratios in the vapor inclusions are less precisely defined due to their overall smaller mass of analyte at given size. Some elements in vapor inclusions are commonly below the limit of detection, and the limited data show considerable scatter that is probably not analytically significant, except for Cu/Na.

The concentrations of most elements in brine inclusions (e.g., B, Na, Mg, K, Ca, Fe, Mn, Zn, Rb, Sr, Ba, Pb and Bi; Fig. 4A and Table 2 in the EPSL Online Background Dataset<sup>2</sup>) and corresponding element ratios in vapor inclusions (e.g., K/Na, Fe/Na, Mn/ Na; Fig. 4B and Table 3 in the EPSL Online Background Dataset<sup>2</sup>) are uniform across all fluid inclusion assemblages (Fig. 4A). Mg and Ba vary slightly, but

<sup>&</sup>lt;sup>2</sup> http://www.elsevier.nl/locate/epsl; mirror site:http://www.elsevier.com/locate/epsl.

Cu varies by more than two orders of magnitude in both inclusion groups. The B1 brine inclusions span the greatest range of Cu contents, with very high average concentrations of 26,000  $\mu$ g/g (2.6 wt.%) in some assemblages down to 400  $\mu$ g/g in others. Spatially associated V1 vapor inclusions have Cu/Na ratios up to 3.4 in some assemblages, probably corresponding to several wt.% Cu in these low-density fluids. Brine inclusions of the later B2 group have intermediate and more constant Cu concentrations, between 8100 and 1450  $\mu$ g/g. V2 inclusions have Cu/Na ratios ranging from 0.43 to ~0.03.

Fig. 5 correlates the copper content of individual fluid inclusion assemblages of the two groups, B1 and B2 assemblages, with total homogenization temperatures, documenting an amazingly systematic trend. B1 fluid inclusions define a distinctive correlation of copper contents decreasing over two orders of magnitude within a small temperature interval (425–350 °C). This inclusion trend is parallel to the chalcopyrite solubility curve calculated by Hezarkhani et al. [41], showing the strong temperature dependence of Cu concentration measured in chloride-bearing liquids. B2 brines have overall lower temperatures but more constant Cu concentrations.

### 5. Interpretation: fluid evolution and Cu–Fe-sulfide deposition

The Cu-Fe-sulfide mineralized quartz veins in the high-grade center of the Bingham porphyry-Cu-Au deposit experienced a complex textural history spanning a large temperature range [14,22,39]. However, fluid compositions documented in this study remained essentially constant with respect to total salinity and the concentrations of all major and trace cations, except for significant and systematic variation in Cu content. Cu concentrations dropped over more than two orders of magnitude and correlate within a narrow temperature interval. We conclude from these and textural observations in many other samples [22] that the main phase of ore formation in the guartz monzonite porphyry was driven by a single source of magmatic-hydrothermal fluid of essentially constant input composition, which ascended through the vein network and precipitated Cu-Fe-sulfide by fluid cooling. Different aliquots of a two-phase mixture of liquid (brine) and vapor were trapped at slightly different times, temperatures and degrees of Cu depletion in the B1 and V1 inclusion assemblages.

Our texturally controlled fluid inclusion data indicate that the high-grade Cu-Au orebody at Bingham formed by bornite and chalcopyrite deposition between 425 and 350 °C at estimated pressures of about 21-14 MPa, corresponding to 1.4-2.1 km paleodepth at cold hydrostatic conditions. These estimated P-T conditions are in the region of retrograde temperature dependence of quartz solubility (e.g., [42]), which explains the textural break in vein evolution by quartz dissolution between the deposition of Q1 and Q2 quartz. Conditions are also near the ductile to brittle transition of quartz-feldspar-rich rocks, where magmatic fluids are most likely to change from lithostatic to hydrostatic pressure (e.g., [42]) and cool as a result of adiabatic expansion. On the sample scale, these P-T changes cause abundant microfracturing and fluid entrapment in otherwise undisturbed earlier Q1 quartz, with the result that nearly all inclusions in the analyzed sample and the great majority of fluid inclusions in other samples from the center of the orebody record temperatures in the vicinity of 400 °C. On the larger scale of the entire porphyry system, steep gradients in temperature, pressure and fluid density in this P-T region exert a positive feedback of vein reactivation and the generation of secondary permeability, further enhancing focused fluid flux and metal advection into the orebody.

The B1 brines are interpreted to postdate Q1 growth and to be trapped during this microfracturing event. Thus, they record the process of copper deposition while no quartz was precipitating. The steep drop in copper concentration by more than two orders of magnitude (Fig. 5) indicates that more than 99% of the original Cu in the incoming fluid was deposited over the small temperature interval between 425 and 350 °C. Incoming fluids may have been a little lower in Cu concentration than the maximum recorded by B1 brine inclusions, because slightly hotter input fluid batches would lead to local dissolution of Cu-Fesulfide grains precipitated by slightly cooler, earlier fluid batches. This may explain the extreme Cu contents of some B1 inclusion assemblages, which are higher than in any other ore fluids we analyzed so far.

B2 brines in Q2 quartz formed after the main mineralizing event. They were trapped during or

after renewed quartz crystallization, at temperatures about 70 °C cooler on average. Fluids belonging to this stage may have been trapped as secondary inclusions in Q1 quartz and in this case would have been classified as B1. However, the clear correlation between copper concentrations and  $T_{h(tot)}$  for B1 fluid inclusion assemblages (Fig. 5) indicates that such misclassification in the assemblages chosen for analysis was not significant. The observation that their copper content is not much lower than that of most B1 brines and shows no correlation with  $T_{h(tot)}$ , is interpreted to reflect local variation in other fluid-chemical parameters, controlled by fluid-mineral equilibria at the pore or microcrack scale. Relatively high Cu concentrations despite low temperatures are expected in essentially stagnant pore fluids in contact with quartz and Cu-Fe-sulfide, if they become depleted in H<sub>2</sub>S due to sulfide precipitation from ore fluids with an initial metal excess, or if their pH falls to low values due to cooling of fluids in isolation from acidneutralizing feldspar.

The correlation between the total homogenization temperature and copper content can be demonstrated with the brine inclusions but not in the coeval vapor inclusions, because  $T_{h(tot)}$  of the latter cannot be measured with useful precision. However, the Cu/Na ratios of vapor inclusions records a similar range (from initial Cu/Na ratios of 3.4 dropping by more than two orders of magnitude to 0.03, Fig. 4B and Table 3 in the EPSL Online Background Dataset<sup>2</sup>), despite overall different metal contents governed by liquid/vapor partitioning [43]. The fluid-compositional data thus imply that both the vapor and the brine contributed to the precipitation of Cu–Fe-sulfides at Bingham.

Temperatures of ore-mineral precipitation defined by texturally controlled inclusion analyses at Bingham confirm the tentative conclusion from the first LA-ICPMS study of fluid compositions from the Bajo de la Alumbrera porphyry–Cu–Au deposit, Argentina [8], where ore deposition occurred at temperatures close to 400 °C, at much lower temperatures than initial quartz veining and magnetite–K-feldspar–biotite alteration. Hezarkhani et al. [41] predicted from thermodynamic calculations that the bulk of chalcopyrite deposition at the Sungun porphyry Cu deposit (Iran) occurred at 360 ± 60 °C. These temperatures are consistent with experimental solubility data (e.g., [44,45]), but lower than temperatures inferred for Au-rich porphyry copper mineralization based on mineral-compositional arguments [46].

Fluid cooling contributes to the precipitation of Cu–Fe-sulfides not only through the temperature dependence of congruent solubility equilibria, such as (e.g., [44,47])

$$\begin{aligned} & 6\text{CuCl}_2^- + 6\text{FeCl}_2 + 11\text{H}_2\text{S}(\text{aq}) + \text{SO}_2(\text{aq}) \\ & = 6\text{CuFeS}_2(\text{s}) + 6\text{Cl}^- + 18\text{HCl} + 2\text{H}_2\text{O} \end{aligned} \tag{1}$$

$$30\text{CuCl}_{2}^{-} + 6\text{FeCl}_{2} + 23\text{H}_{2}\text{S}(\text{aq}) + \text{SO}_{2}(\text{aq})$$
  
= 6Cu<sub>5</sub>FeS<sub>4</sub>(s) + 30Cl<sup>-</sup> + 42HCl + 2H<sub>2</sub>O (2)

but also by the generation of  $H_2S$  by disproportionation of  $SO_2$  upon cooling (e.g., [48]).

$$4SO_2 + 4H_2O = H_2S + 3H_2SO_4$$
(3)

Compared with the overall effect of fluid cooling, other factors were probably of secondary importance in precipitating Cu-Fe-sulfides at Bingham, and probably in other porphyry-type deposits containing bornite and chalcopyrite in ore associated with potassic alteration. K-feldspar-biotite alteration influences ore fluid chemistry in the larger scale hydrothermal system, but it is so pervasive that it could not generate chemical gradients promoting copper deposition at the sharp base of the high-grade orebody at Bingham (Fig. 1). Moreover, published mass-balance estimates [49] indicate that potassic alteration produces rather than consumes HCl and, therefore, does not promote sulfide saturation by acid-producing reactions (Eqs. (1)-(3)). Thus, potassic alteration and sulfide deposition are a common consequence of magmatic fluid cooling, rather than alteration being a chemical driving force for copper deposition. Fluid phase separation certainly had an effect on the large-scale thermal structure of the hydrothermal system, by adiabatic cooling of the ascending ore fluids. It did not directly control Cu-Fe-sulfide precipitation, however, because the sharp base of the high-grade orebody does not coincide with the transition from intermediate-density inclusions at depth to the overlying region where brine and vapor inclusions coexist (Fig. 1)). Likewise, there is no evidence for incursion of meteoric water during or even after B1 fluid introduction.

## 6. Conclusions and implications for porphyry–Cu ore formation

Quantitative data on the fluid-chemical evolution at Bingham demonstrate that fluid cooling across a narrow temperature interval (425–350 °C) is primarily responsible for the formation of this giant porphyrytype ore deposit. This interval is characterized by steep normal temperature dependence of Cu–Fe-solubility but reverse temperature dependence of quartz solubility, the main gangue mineral. Quartz dissolution facilitates advection of metal-bearing fluids along the existing stockwork vein network, where ore metals precipitate in response to fluid cooling in a confined rock volume. The contrasting solubility behavior of quartz and sulfides thus creates ideal conditions for metal enrichment in this particular P-T window.

Our results imply that the total tonnage of Cu eventually contained in a porphyry deposit is primarily determined by the amount of Cu in the starting fluid and the total quantity of magmatic fluid available over the lifetime of the hydrothermal system. Both parameters are ultimately controlled by the dimension of, and processes within, the subjacent magma chamber, acting as the source of ore-forming hydrothermal fluid. Thus, the amount of accumulated ore metal depends on the Cu content of the magma, the degree to which Cu partitions into the exsolving fluid, and the absolute amount of fluid exsolved from a large magma reservoir.

Ore grade, by contrast, strongly depends on metal precipitation mechanisms. The results presented here imply that copper precipitation efficiency is controlled primarily by the thermal structure of the fluid flow system. To enhance the enrichment of high Cu concentrations in a confined high-grade orebody, a large amount of metal-bearing fluid must be cooled while it is flowing through a finite rock mass maintaining an almost steady-state temperature distribution. It is probably no coincidence that the exceptionally highgrade orebody at Bingham also has an exceptionally sharp lower boundary and well-developed ore metal zonation (Fig. 1; [22]). The conspicuously sharp base of the Bingham orebody is likely to represent a copper sulfide saturation horizon that, according to our fluid inclusion data, corresponds to a near-isothermal surface kept in place for considerable time while magmatic fluids ascended through the quartz monzonite porphyry. This requires a steady-state balance between heat advection by the magmatic fluid and heat loss by adiabatic cooling and conduction into the adjacent rocks. The physical mechanisms of cooling a large focused fluid flux is not yet understood but will be a key to the formation of a high-grade porphyry copper deposit.

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### Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2005.02.046.

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