Contrasting hydrological processes of meteoric water incursion during magmatic-hydrothermal ore deposition: an oxygen isotope study by ion microprobe

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Meteoric water convection has long been recognized as an efficient means to cool magmatic intrusions in the Earth's upper crust. This interplay between magmatic and hydrothermal activity thus exerts a primary control on the structure and evolution of volcanic, geothermal and ore-forming systems. Incursion of meteoric water into magmatic-hydrothermal systems has been linked to tin ore deposition in granitic plutons. In contrast, evidence from porphyry copper ore deposits suggests that crystallizing subvolcanic magma bodies are only affected by meteoric water incursion in peripheral zones and during late post-ore stages. We apply high-resolution secondary ion mass spectrometry (SIMS) to analyze oxygen isotope ratios of individual growth zones in vein quartz crystals, imaged by cathodo-luminescence microscopy (SEM-CL). Existing microthermometric information from fluid inclusions enables calculation of the

oxygen isotope composition of the fluid from which the quartz precipitated, constraining the relative timing of meteoric water input into these two different settings. Our results confirm that incursion of meteoric water directly contributes to cooling of shallow granitic plutons and plays a key role in concurrent tin mineralization. By contrast, data from two porphyry copper deposits suggest that downward circulating meteoric water is counteracted by up-flowing hot magmatic fluids. Our data show that porphyry copper ore deposition occurs close to a magmatic – meteoric water interface, rather than in a purely magmatic fluid plume, confirming recent hydrological modelling. On a larger scale, the expulsion of magmatic fluids against the meteoric water interface can shield plutons from rapid convective cooling, which may aid the build-up of large magma chambers required for porphyry copper ore formation.

Keywords: ore deposits, hydrothermal systems, magmatic processes, oxygen isotopes, meteoric water convection

1. Introduction

The depth ranges and timescales of the intrusion of magmatic bodies into the Earth's crust prohibit direct monitoring and quantification. Geological studies of extinct and exposed fossil intrusions indicate that differences in pluton assembly (Annen et al., 2015), magma injection rates and volumes (Caricchi et al., 2014) and duration of magmatic activity (Michel et al., 2008; von Quadt et al., 2011; Bachmann et al., 2012) can result in different magmatic and associated hydrothermal systems, such as the formation of upper crustal plutons or large volcanic eruptions (Caricchi et al., 2014). The formation of giant magmatic-hydrothermal ore deposits, including porphyry copper deposits, requires large magma reservoirs (Dilles, 1987;

Cline and Bodnar, 1991; Steinberger et al., 2013), but it remains unclear whether pluton-sized volumes of magma are emplaced rapidly (Dilles, 1987; Glazner et al., 2004), or whether plutons are amalgamated from several smaller magma bodies that intruded episodically into the crust (Halter et al., 2005; Michel et al., 2008). Rate and mode of magma injection determine how long a pluton takes to crystallize, together with the rate of heat loss from the magma reservoir. In the permeable upper crust, meteoric water convection contributes significantly to pluton cooling (Cathles, 1977; Hayba and Ingebritsen, 1997; Gerdes et al., 1998) and is therefore expected to influence the lifetime, physical make-up and petrological evolution of upper-crustal magma reservoirs (Spera and Bohron, 2001; Miller et al., 2007; Schaltegger et al., 2009). The role of meteoric water in hydrothermal ore formation has been variably interpreted as a main agent for metal transport and ore deposition (Sheppard et al., 1971; Taylor, 1971; Taylor, 1974; Cathles, 1977), as a diluent for metal-rich magmatic saline liquids triggering chemical precipitation of ore minerals (Eastoe, 1978; Dilles, 1987; Sun and Eadington, 1987), or as a dominantly physical agent for cooling magmatic ore fluids (Sillitoe, 1973; Henley and McNabb, 1978; Burnham and Ohmoto, 1980; Hedenquist and Lowenstern, 1994).

Quartz veins in mineral deposits record the compositions of fluids during the thermal history of a magmatic-hydrothermal system. At the Yankee Lode tin deposit (Mole Granite, Australia; Audétat et al., 1998), fluid pressures determined from co-existing vapor and saline liquid inclusions constrain the paleo-depth to 2.5 ± 1 km and document a transition from an early magmatic regime at lithostatic fluid pressure to a cooler hydrostatic environment. This change led to incursion of meteoric water and cassiterite precipitation as the result of mixing between the meteoric water and ascending hot, saline metal-bearing magmatic liquid, as indicated by fluid inclusion LA-ICP MS trace element analyses (Audétat et al., 1998; Audétat

et al., 2008). Regional-scale oxygen isotope measurements of hydrothermal quartz from deposits distributed around the Mole Granite, using conventional analyses, show an evolution from early magmatic fluids in pegmatitic veins within the roof of the granite ($\delta^{18}\text{O} = \sim 9\text{‰}$), through mixing with meteoric water in the tin stage, to purely meteoric waters ($\delta^{18}\text{O} = \sim -15\text{‰}$) during the late stage base metal mineralization in distal veins hosted by sedimentary wall rocks (Sun and Eadington, 1987).

Porphyry Cu systems often form at similar depths to Sn deposits (~2-3 km) but their roots are voluminous plutons located at depths of 5 km or more (Sillitoe, 2010). Due to the complexity of copper ore deposition and superimposed and overprinting alteration events, the mechanism of metal precipitation from the mineralizing fluids remains a matter of discussion (Sheppard et al., 1971; Gustafson and Hunt, 1975; Eastoe, 1978; Hemley et al., 1992; Hedenquist and Lowenstern, 1994; Redmond et al., 2004; Landtwing et al., 2005; Sillitoe, 2010; Heinrich and
86 Candela, 2014; Blundy et al., 2015). The currently prevailing theory favors precipitation of
87 ore minerals from magmatic fluids expelled from cooling upper crustal magma chambers (Richards, 2011). In this model, meteoric water incursion only affects peripheral and post-ore alterations, whereas main-stage mineralization and associated potassic alteration is thought to be dominated by magmatic fluids (Gustafson and Hunt, 1975; Bowman et al., 1987; Sillitoe, 2010). Based on stable oxygen and hydrogen isotope analyses of alteration minerals from porphyry copper deposits, meteoric water incursion affects sericitic, argillic and propylitic alterations (Sheppard et al., 1971; Taylor, 1974; Bowman et al., 1987; Hedenquist and Lowenstern, 1994; Taylor, 1997; Sillitoe, 2010). A significant meteoric water component in the early quartz-K-feldspar-biotite-chalcopyrite precipitating fluid has been inferred for the Butte porphyry copper deposit and a few Tertiary deposits intruded into flat-lying, permeable volcanic host rocks (Sheppard et al., 1971; Sheppard and Taylor, 1974; Taylor, 1974). Also,

petrographic evidence from the Far Southeast porphyry copper deposit (Philippines) shows that Cu sulfide mineralization can be associated with the transition from potassic to sericitic alteration (Hedenquist et al., 1998). Oxygen and hydrogen isotope analyses of white mica and biotite from the Far Southeast and the El Salvador (Chile) porphyry copper deposits indicate admixing of 10-20 % of meteoric water to a dominantly magmatic-hydrothermal fluid associated with copper precipitation (Watanabe and Hedenquist, 2001).

Fluid inclusion studies (Landtwing et al., 2010; Stefanova et al., 2014) following textural mapping of quartz vein samples by Scanning Electron Microscopy Cathodo-Luminescence (SEM-CL) indicate that copper precipitated after deposition of most vein quartz at temperatures of 450 – 350°C (Rusk and Reed, 2002; Redmond et al., 2004; Landtwing et al., 2005). Such low temperatures cannot be attained by adiabatic cooling of magmatic fluids exsolved from a magma chamber and require an external cooling agent (Henley and McNabb, 1978; Fournier, 1999). Numerical simulations suggest that cooling is controlled by heat loss of a magmatic fluid plume to convecting meteoric water. Copper sulfides precipitate at this interface, which is characterized by a sharp drop in fluid pressure and temperature (Weis et al., 2012). The simulation results are in line with previous interpretations of the evolution from a central potassic to the outer and partly later sericitic alteration zone, corresponding to the transition from a lithostatically pressured magmatic fluid regime to a hydrostatically pressured fluid mixture dominated by meteoric water (Gustafson and Hunt, 1975).

119 Microtextural and fluid inclusion studies at porphyry copper deposits show that sulfide
120 precipitation during the main ore-stage is commonly characterized by a lack of quartz
121 precipitation and quartz re-dissolution (Rusk and Reed, 2002; Redmond et al., 2004;

Landtwing et al., 2005; Stefanova et al., 2014). Retrograde quartz solubility occurs in a region of low pressure just above the critical temperature of pure water (Kennedy, 1950), whereas at higher pressure or in single-phase fluids of higher salinity quartz solubility increases monotonously with temperature (Fournier, 1983). An empirical fit of experimental quartz solubility in the $\text{H}_2\text{O} - \text{NaCl} - \text{SiO}_2$ system over a wide range of density, salinity and pressure (Akinfiev and Diamond, 2009) provides a basis for evaluating bulk quartz solubility in vapor and liquid mixtures, to interpret micro-textural observation of quartz precipitation and dissolution. In the present study, we map texturally-controlled variations of oxygen isotope compositions of hydrothermal vein quartz using secondary ion mass spectrometry (SIMS), to interpret these characteristic quartz textures and quantify the variations of meteoric and magmatic fluid contribution during the evolution of magmatic-hydrothermal ore veins.

2. Methods

We obtained a total of 298 in-situ $\delta^{18}\text{O}$ measurements of vein quartz from individual zones identified on the basis of variations in CL intensity. The $\delta^{18}\text{O}$ values of the associated fluid was calculated using fluid inclusion temperatures. We used doubly polished sections of vein quartz from previous studies (Audétat et al., 1998; Landtwing et al., 2005; Stefanova et al., 2014) in which detailed and texturally controlled fluid inclusion data had been obtained that allow reconstructing the precipitation temperature of individual quartz growth stages. Textural control was ensured by SEM-CL imaging. High-resolution, in-situ $\delta^{18}\text{O}$ analyses of individual growth stages were then obtained by secondary ion microprobe.

Sample preparation of the polished chips required a special mounting technique by pressing the chips into indium in the sample holder. In this way we could ensure a perfectly horizontal mounting and avoid re-polishing, which might have compromised the precise correlation between previously established microthermometric data of thin, individual growth zones and healed fractures and the oxygen isotope spot analysis targeting these zones.

$^{18}\text{O}/^{16}\text{O}$ ratios were measured using the SwissSIMS Cameca IMS 1280HR at the Institute of Earth Sciences of the University of Lausanne (Switzerland). We used a 10kV Cs^+ primary ion beam, a ~ 2 nA current, resulting in a ~ 10 μm beam size. The electron flood gun was used to compensate charges. ^{16}O and ^{18}O secondary ions were accelerated by 10kV and analyzed at 3000 in FC multi-collection mode. Faraday cups are calibrated at the beginning of the session. Mass calibration was performed at the beginning of each session and every 12h. Each analysis took less than 4 minutes, including pre-sputtering (30 sec) and automated centering of secondary electrons. The internal uncertainty of each analysis was better than 0.3‰ (2SD). A grain of UNIL-Q1 standard was inserted in each mount to correct for mount-specific mass fractionation variations. A set of 4 UNIL-Q1 analyses were used to bracket every 15-20 analyses to monitor instrument stability. The measurements were conducted in 3 different sessions, with one session lasting up to 48h, over a period of 7 months. The variation of the UNIL-Q1 standard for all sessions is less than 0.4‰ (2SD). The uncertainties reported for samples reflected the 2SD of the bracketing UNIL-Q1 analysis for each analysis block.

Panchromatic Cathodo-luminescence (CL) images were acquired using a scanning electron microscope (SEM, EOscan VEGA XL by Tescan, Czech Republic) equipped with a motor-

driven elliptical mirror focusing the CL signal onto a standard photomultiplier detector. The SEM was operated at accelerating voltage of 20kV and beam current of 5nA.

For the calculation of $\delta^{18}\text{O}$ values of the fluid, we re-fit experimental data for quartz – water fractionation for supercritical fluids and aqueous liquids between 800°C and ~100°C (for details of the re-fitting procedure see details in the Supplementary material, Fig. S1) to obtain a consistent expression for the wide temperature range of interest:

$$1000\ln\alpha_{\text{Quartz-Water}} = 3.3308(10^6/T^2) - 2.7734.$$

In magmatic-hydrothermal systems, fluid phase separation has the potential to influence isotope fractionation between vapor and liquid phases. Shmulovich et al. (1999) reported experiments indicating that H_2O vapor is as much as 2 permil lower in $\delta^{18}\text{O}$ compared with the coexisting saline liquid under halite-saturated conditions between 350°C and 600°C. Data by Driesner and Seward (2000) indicate that this fractionation is less than 1 permil for liquid salinities around 20 wt. % NaCl. Based on these experimental results, we can assume that our equation adequately represents the fractionation between quartz and the bulk hydrothermal fluid, irrespective of the proportion of saline liquid and vapor in the two-phase region, but note that the vapor-dominated fluids could be slightly lower in $\delta^{18}\text{O}$ than calculated with this equation.

3. Samples

The Yankee Lode Sn deposit is located at the southwestern margin of the Early Triassic Mole Granite, a large intrusion that generated a polymetallic ore province in Eastern Australia. We

investigated the sample Yank 21 from Audétat et al. (1998), in which quartz crystallized into open space together with cassiterite and tourmaline. CL-petrography (Fig. 1A and 1B) shows four main growth zones (Q1-Q4) with finer zonation throughout the entire section. Cassiterite precipitation took place in the Q2 and Q3 stages accompanied by ilmenite and tourmaline precipitation forming inclusions in the respective growth zones. Chlorite and muscovite occur in the outermost zone (Q4). Homogenization temperatures represent true crystallization temperatures (Audétat et al., 1998) and range from ca. 500 °C in Q1 just prior to cassiterite precipitation to less than 290 °C for post-ore Q4 (Fig. 2A, Table 1). A late generation of quartz (Q5) with high luminescence appears in late fractures crosscutting the zoned crystal (Fig. 1A). Crystallization temperatures are not available from this late quartz precipitation event due to the lack of measurable fluid inclusions.

The Late Cretaceous *Elastite porphyry Cu-Au deposit* is part of the Apuseni-Banat-Timok-Srednogorie magmatic and metallogenic belt in Southeastern Europe. We used the original sample 1150NE12 analyzed by Stefanova et al. (2014), which shows three main growth stages with several substages (Q1 – Q3, Fig. 1C). Sulfide mineralization postdates most quartz precipitation, indicated by Q2c quartz-chalcopyrite veins which cut the Q1, Q2a, and Q2b stages. Q3 is the latest quartz generation which precipitated as a thin rim on Q2b quartz after partial re-dissolution of the latter. Precipitation temperatures range between ≥ 640 °C for Q1 and 460 °C for Q2c, followed by a gap in quartz precipitation until cooling to a temperature of about 150 °C (Fig. 2B, Table 1).

At the Late Eocene *Bingham Canyon Cu-Au-Mo porphyry deposit* in Utah (USA), the strongest mineralization is related to the earliest of five porphyry intrusions. A high density of

quartz stockwork veins and intense potassic alteration characterize the mineralized zone (Redmond et al., 2004). We used a section of the sample D211-19 analyzed by Landtwing et al. (2005), which shows early (Q1) and late (Q2) quartz generations, based on textural relationships (Fig. 1D). Fracturing and re-dissolution of Q1 allowed Q2 precipitation along grain boundaries and in open cracks. Based on different textural features (overgrowth vs. crack fillings) and luminescence light intensities, both generations can be subdivided into two subgroups (a and b). Textural observations and fluid inclusion analyses suggest that copper precipitation took place after Q1 and before or during Q2 crystallization (Landtwing et al., 2010). Crystallization temperatures range from about 505 °C for Q1 to 318 °C for Q2 (Fig. 2C, Table 1).

4. Results

Results from the Yankee Lode sample range from $\delta^{18}\text{O} = -4.6\text{‰}$ to 12.9‰ (Fig. 1A, 1B and 2A, Table 1), showing near constant values for Q1 and Q2, followed by a continuous, gradual decrease from the cassiterite-bearing zone (Q2 and Q3a) to the outermost rim of the crystal (Q4). The light luminescent quartz (Q5), which is overgrown on Q3 and Q4, shows heavy values similar to the core of the crystal (Fig. 1A, Table 1). Calculated $\delta^{18}\text{O}$ values of the fluids show an overall decrease from initial magmatic values of about 10‰ in Q1 and Q2 to values of $\sim -15\text{‰}$ in Q4 (Fig. 2A), consistent with the values from Sun and Eadington (1987) obtained by conventional oxygen isotope analysis. The decrease commences in stages Q3a and is most pronounced in Q3b (tourmaline appearance) and Q4. Light luminescence Q5 quartz postdates cassiterite deposition but the isotopic composition of the fluid precipitating this quartz generation cannot be calculated because it does not contain any measurable fluid inclusions.

Results from the euhedral quartz sample from Elatsite (Fig. 1C and 2B, Table 1) are relatively homogenous (8.2 ‰ – 9.7 ‰) in the Q1a to Q2c stages. Q2c quartz generally shows higher values (9.2 ‰ – 9.7 ‰) than the earlier quartz, but the increase is insignificant given the scatter of the measurements and the ± 0.3 ‰ analytical uncertainty. The outermost zone (Q3) has heavier values (15.4 ‰ – 20.0 ‰). The $\delta^{18}\text{O}$ values of fluids from the Elatsite deposit (6.6 to 8.1‰) indicate minimal systematic variation in the pre-ore stages Q1 to Q2b (Fig. 2B). A small decrease (5.7 ‰ – 6.3 ‰) occurs during the formation of Q2c quartz that immediately predates or is coeval with the first sulfide precipitation (Stefanova et al., 2014). The latest, post-ore generation Q3 was precipitated together with zeolite minerals from an isotopically light fluid with a $\delta^{18}\text{O}$ value of -1.2 to 3.8 ‰. Independent estimates of contemporaneous meteoric water give $\delta^{18}\text{O}$ values of -3 ± 2 ‰ (Lerouge et al., 2006).

Results of the Bingham Canyon sample (Fig. 1D and 2C, Table 1) show $\delta^{18}\text{O}$ values of about 9.8 ± 1 ‰, which are essentially uniform within analytical uncertainty for both quartz generations. Despite this uniform $\delta^{18}\text{O}$ value of quartz, the isotopic composition of the quartz-precipitating fluids in the Bingham Canyon deposit vary between 4.6 ‰ – 8.8 ‰ and -0.1 ‰ – -5.7 ‰ for Q1 and Q2, respectively (Fig. 2C), based on the variation in temperature from fluid inclusion homogenization values. Precise determination of the $\delta^{18}\text{O}$ value of the fluid is difficult, due to the large scatter and partial overlap of possible precipitation temperatures (Landtwing et al., 2005; Landtwing et al., 2010). On average, however, the results also point towards a significant shift from initially magmatic-like values to lighter $\delta^{18}\text{O}$ values during the later quartz stage associated with Cu-Fe sulfides.

5. Discussion

5.1 Meteoric water incursion into magmatic-hydrothermal ore systems

The temporal variation in $\delta^{18}\text{O}$ of the quartz and fluid recorded by the Yankee Lode tin deposit (Fig. 2A) links the compositional fluid history of mineral precipitation described by Audétat et al. (1998) with regional evidence for isotopic and mineralogical zoning around the giant Mole Granite intrusion (Sun and Eadington, 1987). Our data indicate that meteoric water was progressively mixed with a magmatic saline liquid during ore deposition, thus validating our approach to high-resolution fingerprinting of meteoric water incursion into a magmatic-hydrothermal system. Combining our results with published microchemical evidence from fluid inclusions (Audétat et al., 1998) provides additional details for the dilution process, and suggests that such dilution was most likely the chemical driving force for tin precipitation. Cassiterite started to precipitate at the onset of Q2 deposition from an isotopically heavy fluid with $\delta^{18}\text{O}$ values around 8‰ – 10‰ (Fig. 2A) which is typical for magmatic fluids (5.5‰ – 10‰; Taylor, 1977). By the end of stage Q3, fluid salinity had decreased from ~ 35 wt% to 1-3 wt%, indicating a 10-30-fold dilution of the magmatic saline liquid. However, the isotopic signature of this fluid is only shifted by 20-60‰ towards the meteoric end-member value. A strong salinity decrease with only a modest shift in fluid isotope composition towards meteoric water may be explained in two possible ways. A first possibility is that the diluting fluid is of entirely meteoric origin, but had previously been modified by isotope exchange with silicate rocks at high temperature, which may be possible at the high temperature of 390°C indicated by fluid inclusions in this evolution stage. An alternative is that the diluting fluid is a mixture of meteoric water with low-salinity magmatic vapor that had previously condensed into this low salinity liquid. This process has been proposed by Audétat et al. (2008) to explain the chemical observation that the admixing low-salinity fluid is enriched in B, Cu and possibly other elements that are preferentially transported by magmatic vapor.

Most tin deposition took place during deposition of Q3 quartz, followed by tourmaline, and variable mixing of the two fluids is displayed by the fluctuation in the $\delta^{18}\text{O}$ values (Fig. 2A). Low and dominantly meteoric $\delta^{18}\text{O}$ values calculated for fluids that precipitated the outermost zone (Q4) are consistent with the low salinity and trace element content of fluid inclusions associated with Q4 quartz (Audétat et al., 1998). The high $\delta^{18}\text{O}$ values of the crosscutting high luminescent Q5 quartz bands (Fig. 1A) reflect late pulses of a fluid with an isotopically heavy value, possibly consistent with a magmatic fluid, but no fluid inclusions can be related to this late quartz generation to test this possibility quantitatively.

The samples from the two porphyry deposits show a similar shift with time from constant magmatic-like $\delta^{18}\text{O}$ values of the pre-ore stage fluids to isotopically lighter fluid compositions that commences around the time of ore mineral precipitation. At Elatsite, the $\delta^{18}\text{O}$ value of the fluid precipitating the youngest quartz (Q3; Fig. 2B) approaches the Late Cretaceous local meteoric water (Lerouge et al., 2006) composition. At Bingham, there is a trend towards lighter $\delta^{18}\text{O}$ values, consistent with admixture of a minor component of meteoric water to the system (Fig. 2C).

Pressure estimates of fluid inclusions from all three samples suggest a transition from lithostatic to hydrostatic fluid pressures during the temporal evolution of the respective system (Audétat et al., 1998; Landtwing et al., 2010; Stefanova et al., 2014), which allows the incursion of meteoric water into the hydrothermal system. Overpressured fluids can sustain a purely magmatic fluid plume and displace meteoric water convection, whereas hydrostatic pressures are required for density-driven thermal convection through permeable rocks (Fournier, 1999; Weis et al., 2012). Numerical simulations of high-enthalpy geothermal systems show that up-flow zones above magma chambers are characterized by gradual mixing of cooler fluids from the side. This leads to sharp reductions in the enthalpy of the magmatic

fluid upon advective ascent from the heat source (Scott et al., 2015), indicating that fluid mixing is an integral process of hydrostatically pressured convection systems.

5.2 Contrasting fluid evolution paths

Both porphyry Cu samples record stages of quartz dissolution and gaps in quartz precipitation and in the concomitant fluid inclusions record during the interval of ore mineral precipitation, in contrast to the Sn-vein example. Combining our isotope data with microthermometry and calculated quartz solubility values explains the different fluid evolution paths. We calculated the quartz solubility (Akinfiev and Diamond, 2009) on curved sections through the H₂O-NaCl phase diagram (Driesner and Heinrich, 2007) that follow the temperature-pressure path reconstructed from fluid inclusions at Yankee Lode and Elatsite, respectively (Fig. 3A and 3B).

Continuous quartz precipitation without dissolution events at Yankee Lode is only possible if meteoric water gradually mixes with a magmatic saline liquid (which may at the beginning have coexisted with minor amounts of vapor phase; Fig. 3A). Minor dissolution may have occurred between 440 and 425°C, an interval where fluid inclusions were not recorded. The meteoric water was heated during flow through the hornfelsed contact aureole, as indicated by distal quartz – sphalerite – galena veins that formed from a solution consisting of >90% meteoric water at ~280°C (Eadington, 1983; Sun and Eadington, 1987). The shallow emplacement depth of a horizontal igneous intrusion in the upper crust (Kleeman et al., 1997) favors direct interaction of magmatic heat and fluid with convecting meteoric water, resulting in fluid mixing and cassiterite precipitation in the upper part of the crystallizing granite (Fig. 4A).

In contrast, a low- to intermediate-salinity magmatic fluid plume interacting with meteoric water is predicted to undergo a stage of quartz dissolution after initial quartz deposition in veins, as observed in many porphyry copper deposits. At Elatsite (Fig. 3B), a magmatic-hydrothermal fluid maintaining an initial bulk salinity of 6-9wt% (Stefanova et al., 2014) precipitates quartz during cooling from magmatic temperatures to a temperature of 430°C. On further cooling, dissolution begins, as observed in the sample 1150NE12 (Stefanova et al., 2014), even if bulk salinity increases due to phase separation. If the system exclusively contained a magmatic two-phase fluid and continued to cool, it would start to precipitate quartz again below about 400 to 350°C, depending on bulk salinity (Landtwing et al., 2010). Yet, at Elatsite, the fluid inclusion data indicate an interval of non-precipitation from 460 °C to 150°C, which is best explained by a change in the hydrothermal flow regime as suggested by numerical simulations (Weis et al., 2012). A given location in the ore zone first experiences upward flow of hot, purely magmatic fluids. During the following gradual downward propagation of meteoric water convection (Fig. 3B), a packet of meteoric water will experience a temperature increase while flowing downward and towards the magmatic fluid-meteoric water interface, making it dissolve quartz at the given sample site. The Elatsite sample was taken in the outer parts of the ore zone, where this process is indeed predicted to occur: in Figure 4B, the green circle (estimated sample location) is located at the side of the near-lithostatically pressured magmatic fluid plume at a pre-ore stage (dashed line) and is later located within the upflow zone of near-hydrostatically pressured meteoric water convection along the flanks of the magmatic fluid plume in the post-ore stage (dotted line). While the boundary between the meteoric and the magmatic flow regime gradually moves downward (from dashed to the dotted line in Fig. 4B), the magmatic intrusion remains insulated from the convecting meteoric water by magmatic fluid expulsion over most of the lifetime of the hydrothermal system.

Fluid inclusion, microtextural and stable isotope data at Bingham Canyon were obtained on granular vein quartz, where no open space remained, which may explain the lack of late-stage quartz with pure meteoric values. Reconstructing the quartz solubility evolution at Bingham Canyon is complicated by likely salt precipitation on the three-phase vapor-liquid-halite surface in the center of the magmatic fluid plume where our sample was taken (Landtwing et al., 2010; Lecumberri-Sanchez et al., 2015). The calculated stable isotope evolution of the fluids appears to follow the same trend as in Elatsite, although the near constant $\delta^{18}\text{O}$ of the quartz itself could alternatively be interpreted as local re-equilibration of residual magmatic fluids with previously precipitated high-temperature quartz (Fig. 2C).

5.3 Contrasting cooling mechanisms of hydrous magma chambers

The results presented here may be relevant for the on-going debate on magma chamber formation (e.g. Dilles, 1987; Halter et al., 2005; Michel et al., 2008; Annen et al., 2015). Plutons can experience contrasting cooling histories depending on differences in the physical hydrology of magmatic-meteoric fluid interactions, which in turn may relate to different shapes and emplacement depths of the intruded magmatic bodies. A flat-topped, horizontal intrusion at shallow crustal levels enables direct interaction of meteoric water convection and magmatic processes (Fig. 4A). In contrast, hot magmatic fluid plumes displace meteoric water and thereby insulate the upper side of deeper crystallizing plutons from cooling by meteoric convection (Fig. 4B). This shielding allows replenishment of magma chambers by subsequent injections before complete solidification of earlier magma batches, and may favor the build-up of voluminous bodies required for the formation of large porphyry copper deposits (Dilles, 1987; Sillitoe, 2010; Steinberger et al., 2013).

6. Conclusions

We investigated the variation of oxygen isotope ratios in hydrothermal quartz in three magmatic-hydrothermal ore deposits from different geological settings. In combination with detailed petrographical observations and microchemical fluid inclusion analyses, the results demonstrate the extent of interaction of meteoric water with magmatic fluids during ore deposit formation. Moreover, such data may provide valuable constraints on the structure and temporal evolution of cooling magma chambers in the upper crust and their associated magmatic-hydrothermal systems.

The different behavior of the Elatsite and Bingham Canyon porphyry copper deposits and the tin mineralized Yankee Lode veins can be best explained by differences in the physical hydrology at their magmatic – meteoric interface. At Yankee Lode, gradual mixing of meteoric water into a saline liquid-dominated magmatic fluid reservoir straddling the flat top of a large shallow intrusion is consistently indicated by the new $\delta^{18}\text{O}$ data, computed quartz solubility and published fluid-chemical data for tin precipitation. In porphyry copper deposits, sulfide precipitation is controlled by the interface between a near-lithostatically pressured upflow zone of a magmatic two-phase fluid mixture and convection of meteoric water under near-hydrostatic fluid pressures (Hedenquist et al., 1998; Fournier, 1999; Weis et al., 2012). Progressive incursion of meteoric water that caused the large-scale cooling of the hydrothermal system into individual veins is indicated by spatially-resolved $\delta^{18}\text{O}$ variations in the fluid, as recorded by successive generations of quartz analyzed by high-resolution ion probe microanalysis. Thermodynamic modelling of quartz solubility for fluid evolution paths reconstructed from fluid inclusion data and microtextural studies provide an explanation for the absence of quartz precipitation during copper sulfide precipitation, reported from many porphyry copper deposits.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at

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Fig. 1. Temporal evolution of quartz precipitation showing in-situ $\delta^{18}\text{O}$ microanalyses from three magmatic-hydrothermal ore deposits. (A) and (B) are sections from a euhedral quartz crystal from the Yankee Lode Sn vein deposit, insert shows the full euhedral crystal, indicating the location of the sections (Audétat et al., 1998). (C) Euhedral quartz crystal from the Elatsite Cu-Mo-Au porphyry deposit (Stefanova et al., 2014, insert shows the association of Q2c with copper precipitation). (D) Vein quartz from the Bingham Canyon Cu-Mo-Au porphyry deposit (Landtwing et al., 2005). Q1-5: quartz generations, Cst: cassiterite, Tur: tourmaline, Cpy: chalcopyrite; solid white and yellow lines: boundary of different quartz generations; blue tint highlighted by image processing: Q2 quartz.

Fig. 2. Evolution of oxygen isotope compositions of quartz and hydrothermal fluids sorted by successive quartz generations. Fluid compositions (blue) are calculated for temperatures from published fluid inclusion data (Audétat et al., 1998; Landtwing et al., 2010; Stefanova et al., 2014). Results from Yankee Lode (A), Elatsite (B) and Bingham Canyon (C) suggest incursion of meteoric water during ore precipitation. The $\delta^{18}\text{O}$ scales of each deposit are normalized to the respective local magmatic signatures (red line) and meteoric water compositions (purple line) from independent sources (Sun and Eadington, 1987; Abruzzese et al., 2005; Lerouge et al., 2006). Q1-4: quartz generations, Cst: cassiterite, Ilm: Ilmenite, Tur: tourmaline, Chl: chlorite, Ms: muscovite, Cpy: chalcopyrite.

Fig. 3. Reconstructed fluid evolution paths in a temperature – salinity phase diagram contoured for silica solubility. Red dots show temperature, pressure and salinity conditions from fluid inclusion data used to construct the specific pressure - temperature sections through the NaCl-H₂O phase diagram (black lines; Driesner and Heinrich, 2007). Dashed contours (red) show bulk quartz solubility (Akinfiev and Diamond, 2009) in vapor (V), liquid (L) and heterogeneous phase mixtures (VL). The pink area shows conditions of retrograde quartz solubility (i.e., solubility increasing with decreasing temperature). (A) Fluid mixing at Yankee Lode leads to continuous quartz precipitation. (B) Fluid mixing at Elatsite leads to quartz dissolution in the cooling interval where Cu-Fe-sulfides are precipitated.

Fig. 4. Contrasting cooling mechanisms of magmatic-hydrothermal systems. (A) Convection of meteoric fluid directly cools a shallow, crystallizing intrusion (grey area) from above. Sn mineralization (brown area) is located in the roof of the flat magmatic body at the interface between overpressured magmatic fluid expulsion (red arrows) and meteoric water convecting in the hydrostatic regime (blue arrows). The black lines illustrate the retreat of this interface from pre-ore (dashed) to post-ore (dotted) stages. (B) Magmatic fluids released from a deep-seated magma chamber develop a magmatic fluid plume reaching to shallower depths. Cu mineralization is located at the interface of this plume and meteoric convection. Magma chamber geometries, sample locations (green circles) and fluid flow vectors are simplified from geological and geophysical observations (Kleeman et al., 1997; Sillitoe, 2010) and results of numerical simulations (Weis et al., 2012).

Table 1

Temperature and oxygen isotope composition ranges of quartz generations

Deposit	Quartz	Temperatures (°C)	$\delta^{18}\text{O}$ quartz (‰)	$\delta^{18}\text{O}$ fluid (‰)
Yankee Lode ¹	Q1	500	12.9 - 10.9	8.1 - 10.1
	Q2	500 - 455	12.6 - 11.4	9.8 - 7.9
	Q3a	455 - 413	8.8 - 6.1	8.8 - 6.1
	Q3b	413 - 365	5.8 - -5.8	5.8 - -5.8
	Q4	365 - 220	-5.5 - -15.4	-5.5 - -15.4
	Q5	-	12.8 - 10.6	-
Elatsite ²	Q1a	640	9.3 - 8.7	8.1 - 7.4
	Q1b	640	8.8 - 8.1	7.5 - 6.9
	Q2a	600	9.5 - 8.7	7.9 - 7.1
	Q2b	600	9.2 - 8.2	7.6 - 6.6
	Q2c	460 $\pm$ 5	9.7 - 9.2	5.7 - 6.3
	Q3	145 $\pm$ 2	20.0 - 15.4	3.7 - -1.2
Bingham Canyon ³	Q1a	585 - 425	10.5 - 9.1	8.7 - 5.0
	Q1b	585 - 425	10.6 - 8.7	8.8 - 4.6
	Q2a	380 - 255	10.5 - 9.1	5.4 - -0.1
	Q2b	380 - 255	10.6 - 8.7	5.7 - 0.7

Temperature values taken from:

¹Audétat et al. (1998), ²Stefanova et al. (2014), ³Landtwing et al. (2005)