Pulsed magmatic fluid release for the formation of porphyry deposits: Tracing fluid evolution in absolute time from the Tibetan Qulong Cu-Mo deposit

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ABSTRACT

The magmatic-hydrothermal evolution of porphyry-style mineralization in the shallow crust that is linked to magmatic processes at depth has been extensively studied using bulk-sample isotopic analysis combined with relative timing constraints. However, a lack of evaluation of the fluid evolution process against an absolute time frame limits further understanding of the ore-forming process. Here, we quantify the fluid evolution process within an absolute time frame for the first time by integrating new in situ oxygen isotope data from the Qulong porphyry Cu-Mo deposit (Tibet) with existing fluid inclusion data and high-precision Re-Os dates of co-precipitated hydrothermal quartz and molybdenite, respectively. We demonstrate that vein quartz records primary oxygen isotopic compositions and reached oxygen isotope equilibrium with ore-forming fluids, and therefore is an archive of the isotopic composition and source of the ore-forming fluids. The δ18Oquartz and δ18Ofluid values, in absolute time, show periodic fluctuations that indicate the presence of three intermittent pulses of magmatic fluid flux, which have been balanced by meteoric water. As such, the flux of magmatic fluid during ore formation was pulsatile, rather than being continuous. The overall highest δ18Ofluid in the first pulse of mineralization, with a gradual decrease to the second and third pulses, is suggestive of a progressive reduction in the magmatic component of the hydrothermal fluids and, by inference, the mineralizing potential of the hydrothermal fluids. This view is supported by a decrease in sulfide-bearing fluid inclusions and metal grade through time. Our findings favor multiple fluid-release events from a single cooling magmatic reservoir, although multiple fluid-melt recharge events remain a competitive alternative. An additional implication is that the magmatic reservoir may have a lifespan of hundreds of thousands of years, with fluid release events occurring over tens of thousands of years.

INTRODUCTION

Porphyry copper deposits (PCDs) are the world’s primary source of Cu, Mo, and Au. Fundamental to the understanding of PCD formation is the evolution of the ore-forming fluid (Kouzmanov and Pokrovski, 2012). The current consensus is that the metals were transported via magmatic fluids (>600 °C) that were exsolved from a deep-seated magmatic system at 5–10 km, and ultimately precipitated as sulfides over a narrow temperature interval at shallow levels (425–320 °C, <3 km; Richards, 2011). Although PCDs are among the most extensively studied deposits, the fluid evolution path associated with metal deposition is constrained only in relative time frame (Cooke et al., 2014), resulting in an incomplete understanding of the hydrothermal processes associated with mineralization. For example, there is limited understanding regarding the precipitating rates of metals through absolute time.

Traditionally, the flux of magmatic fluid released from a deep magmatic reservoir is assumed to be continuous (Simmons and Brown, 2006, 2007). Such an assumption is used in numerical simulations to provide insights into the hydrothermal controls of ore formation. In contrast, a pulsed hydrothermal process is obvious for active magmatic systems, and also has been proposed for the formation of porphyry deposits, as shown by high-precision U-Pb zircon and Re-Os molybdenite dating (Stein, 2014; Spencer et al., 2015; Buret et al., 2016; Tapster et al., 2016; Li et al., 2017a). However, the duration of a geological event could be significantly underestimated from a relatively small number (e.g., <10) of chronologic determinations (Glasner and Sadler, 2016); hence, the intermittent pulses inferred from radiometric dating could be biased from dating a protracted event.

The magmatic process in the middle crust controlling the fluid release from the source pluton is debated. Proposed scenarios include multiple fluid release events from a single cooling magmatic reservoir or several fluid-melt recharging events (Stock et al., 2016; Williamson et al., 2016; Chelle-Michou et al., 2017). Tracing hydrothermal fluid evolution in an absolute time frame holds the promise to further understand these processes.

To provide robust constraints on the nature and evolution of ore-forming fluids, a temporal relationship between gangue (used to constrain fluid nature) and ore minerals must be established (Wilkinson et al., 2009). This relationship, however, has long been hampered by the ubiquitous overprinting and/or multi-stage growth of gangue minerals that are difficult to resolve by bulk analysis (Allan and Yardley, 2007). More importantly, it is critical to place the archive of ore-forming fluids into a robust temporal framework. Traditionally, this is done via the relative time frame defined by vein types, and in a single mineralization event/pulse, an A-type vein is earlier than a B-type vein, with a D-type vein being the latest (Sillitoe, 2010). However, the relative chronology of veinings cannot be correlated at a deposit scale confidently, especially with the presence of multiple mineralization pulses (Stein, 2014; Mercer et al., 2015; Spencer et al., 2015; Li et al., 2017a).

This study presents a novel approach to integrate in situ oxygen isotope data with fluid inclusion data and Re-Os chronology from co-precipitated vein quartz and molybdenite grains. The high-precision Re-Os dates from the Qulong porphyry Cu-Mo deposit in Tibet (Li et al., 2017a) permit, for the first time, evaluating the fluid evolution path under an absolute time frame. We propose that δ18Ofluid can be used as a proxy to trace the flux of magmatic fluid and mineralizing potential through time, and to probe the dynamic magmatic process of the deeply seated magmatic reservoir.
SAMPLES AND IN SITU δ¹⁸O ISOTOPE RESULTS

In brief, the Qulong deposit comprises the pre-ore Rongmucuola pluton (RP), pre-ore aplite, syn-ore P and X porphyries, a syn-ore breccia pipe, and post-ore quartz diorite (Fig. 1; Fig. DR1 in the GSA Data Repository1). As constrained by high-precision Re-Os molybdenite dating, copper-molybdenum mineralization occurred over 266 k.y., between 16.126 Ma and 15.860 Ma, with three short-lived intermittent mineralization pulses inferred at 16.126–16.050 Ma, 16.040–15.981 Ma, and ca. 15.981–15.860 Ma, respectively (Li et al., 2017a).

Magmatic quartz and zircon from the RP (n = 2), a sinusoidal quartz vein hosted by the aplite, and 12 molybdenite- quartz ± chalcopyrite veins were utilized to constrain the δ¹⁸O of magmatic and hydrothermal fluids of the Qulong porphyry system. For the 12 veins, quartz-hosted fluid inclusion analyses and Re-Os molybdenite dating were conducted in previous studies (Li et al., 2017a, 2017b), and quartz grains from the same sample set (Fig. DR3G) used in previous fluid inclusion studies were utilized in this study for secondary ion mass spectrometry (SIMS) δ¹⁸O analysis. Zircon and magmatic quartz from the RP instead of from P porphyry are utilized to assess the oxygen isotopic composition of magmatic fluid given the intensive alteration of the P porphyry (Yang et al., 2009; Li et al., 2017a).

Magmatic quartz and zircon possess mean δ¹⁸O values of 8.78‰ ± 0.65‰ (2 S.D. [standard deviation]) and 6.14‰ ± 0.39‰, respectively, show no cross-pluton variations, and yield a Δ¹⁸Oquartz-zircon of 2.64‰ ± 0.76‰ (Fig. DR2). The sinusoidal vein hosted by the aplite comprises euhedral quartz grains (0.2–0.5 mm), with cathodoluminescence (CL) images revealing core resorption-dissolution and rim overgrowth textures (Fig. 2A). Three core-to-rim transects show similar δ¹⁸Oquartz values and trends, increasing from ~5.40‰ (core) to ~7.89‰ (rim) (Fig. 2C).

Quartz grains from the 12 quartz-molybdenite veins generally exhibit clear euhedral oscillatory growth zones, indicating lack of overprinting (Fig. 2B). Individual veins have homogeneous δ¹⁸Oquartz values regardless of the presence or absence of fractures and CL zonation (Figs. 2B and 2C). For the 12 veins, their δ¹⁸Oquartz values vary significantly, between 8.12‰ ± 0.47‰ and 11.90‰ ± 0.51‰ (Fig. 3). The most pronounced fluctuation occurs from the first mineralization pulse, increasing from 8.27‰ to 11.90‰, and then decreasing to 8.12‰. The second and third pulses are marked by smaller variations (8.11‰–9.46‰).

DISCUSSION

Quartz as an Oxygen Isotopic Archive of Ore-Forming Magma and Fluids

Before using δ¹⁸Oquartz values to trace fluid evolution, it is critical to evaluate the potential modification of δ¹⁸Oquartz values through volume diffusion and precipitation of new material along microfractures (Valley and Graham, 1996; Allan and Yardley, 2007). The Δ¹⁸Oquartz-zircon value reported above yields an equilibrium oxygen isotope fractionation temperature of 674 ± 151 °C (Fig. DR2). The refractory and resistant nature of zircon, across-pluton homogeneous δ¹⁸Ozircon and δ¹⁸Oquartz values, and agreement between the quartz-zircon equilibrium temperature and the solidus temperature of granites (<720 °C; Johannes, 1984) imply that the magmatic quartz records the primary magmatic δ¹⁸O value.

For the 12 quartz veins, within-vein homogeneity of δ¹⁸Oquartz and the absence of any relationships with microfractures rule out modification of the δ¹⁸O via diffusion along fractures (Valley and Graham, 1996), and indicate that the vein quartz was either free from volume diffusion or experienced complete oxygen-isotope exchange. Complete oxygen-isotope exchange via volume diffusion for a 400 µm quartz grain is only achievable over ~1.3 and >10 m.y. at 400 and 300 °C, respectively (Fig. DR4A). Such conditions, however, are implausible at Qulong (Zhao et al., 2016). Therefore, we conclude that the studied vein quartz records primary δ¹⁸O values.

Equilibrium Oxygen Fractionation Between Quartz and Fluids

Using the equilibrium temperature (674 ± 151 °C) of zircon and quartz from RP, the magmatic fluid is estimated to have had a δ¹⁸O of 7.6‰ ± 1.0‰, which agrees well with previous estimates for Qulong (~7.7‰) and other PCDs (Yang et al., 2009; Cooke et al., 2014). Given that no cross-pluton variations in δ¹⁸O (in both quartz and zircon) are observed (Fig. DR2), and the pre-ore RP and syn-ore P and X porphyries have very similar Sr-Nd-Pb isotopic characteristics (Yang et al., 2009), plus the agreement of magmatic fluid δ¹⁸O with previous estimates, we consider the magmatic fluid δ¹⁸O estimated here (7.6‰ ± 1.0‰) is representative.

To calculate δ¹⁸Ofluid from δ¹⁸Oquartz, in addition to knowing the crystallization temperature, a further requirement is that the oxygen-isotope fractionation between quartz and water occurred under equilibrium conditions (Allan and Yardley, 2007; Tanner et al., 2013). Equilibrium is expected if the duration of quartz growth is longer than that of isotope exchange between

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1GSA Data Repository item 2018001, Tables DR1-DR3, deposition methods, and quartz-water oxygen fractionation considerations, is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.
The trends shown by the (Fig. DR5), suggest that the evolution trend of we use trapping temperatures from fluid inclu-

sional veins (barren of mineralization), includ-

ing dissolution-resorption of cores and discord-

ant overgrowth rims (Fig. 2A), suggest that the dissolution-resorption of the cores occurred during and/or before the overgrowths. Therefore, the progressive increase of δ\(^{18}\)O\text{aqueous} from core to rim (Fig. 2C) indicates that the cores were modified by a late O-rich fluid. If the inner core recorded the most primary δ\(^{18}\)O\text{quartz} (5.40‰ ± 0.27‰) during vein formation (~425 °C; Li et al., 2017b), the corresponding fluid has a δ\(^{18}\)O\text{fluid} of 1.80‰ ± 0.5‰, which represents the δ\(^{18}\)O\text{fluid} before the first mineralization pulse.

The isotopic evolution of the ore-forming fluids is presented in Figure 3 using the formation times and temperatures constrained by Re-Os dating and fluid inclusion studies (Li et al., 2017a, 2017b), respectively. The δ\(^{18}\)O\text{fluid} values show significant variation, as much as 5.8‰. In brief, during each of the three mineralization pulses defined by Re-Os dating, the δ\(^{18}\)O\text{fluid} increased from low to high values at the start of the mineralization pulse and then decreased to lower values toward the end of the pulse. For an instance, the first mineralization pulse, which had the most pronounced fluctuation, the δ\(^{18}\)O\text{fluid} increased progressively from 4.7‰ to 7.6‰, and then decreased to 3.1‰. Overall, the first mineralization pulse had higher δ\(^{18}\)O\text{fluid} values than the second and third pulses.

With the exception of the sample at 16.098 Ma, which possesses a δ\(^{18}\)O\text{fluid} of 7.6‰ ± 0.5‰, all δ\(^{18}\)O\text{fluid} values are lower than that of magmatic water (Fig. 3), and require the involvement of an isotopically lighter component, most likely meteoric water. Assuming a steady groundwater table during ore formation, which is reasonable given that no dramatic climatic changes are known for the mineralization period at Qulong, the trend in the δ\(^{18}\)O\text{fluid} values shown in Figure 3 is best interpreted as an interplay between magmatic fluid and meteoric water. Prior to the first mineralization pulse, the hydrothermal fluid system was dominated by an isotopically light water, likely meteoric water, as evidenced by the low δ\(^{18}\)O\text{fluid} (1.8‰ ± 0.5‰) of the sinuosoidal vein. In the first mineralization pulse, the increase in the δ\(^{18}\)O\text{fluid} at the beginning of the pulse indicates that the hydrothermal fluid was progressively dominated by magmatic fluid. The decreasing trend at the waning stage of the mineralization pulse indicates a decline in the magmatic fluid flux, which results in the hydrothermal system being dominated by meteoric water again. A similar process explains the trend observed in the second and third pulses.

The pulsed magmatic fluid flux inferred from δ\(^{18}\)O\text{fluid} is in agreement with the cyclic mineralization process defined by Re-Os dat-
ing, and therefore suggests that the three intermittent pulses defined by Re-Os dating (Li et al., 2017a) are robust, rather than an artifact caused by undersampling (Glazner and Sadler, 2016). For example, if the duration of the first mineralization pulse is underestimated, then the decreasing trend of δ\(^{18}\)O\text{fluid} would extend beyond the interval determined by Re-Os dating.

The δ\(^{18}\)O\text{fluid} values decrease gradually from the first to the second and third mineralization pulses (Fig. 3), with the most pronounced magmatic fluid occurring in the first pulse. As δ\(^{18}\)O\text{fluid} is positively linked with the flux of magmatic fluids, and considering a stable bulk chemistry of the magmatic fluid (Chelle-Michou et al., 2017), the δ\(^{18}\)O\text{fluid} can be used as a proxy to trace the amount of metals available for precipitating through time. In this regard, the low δ\(^{18}\)O\text{fluid} recorded by the sinuosoidal vein suggests that the initial fluid did not contribute significantly to the metal budget, which is supported by the barren nature of the earliest quartz veins (Yang et al., 2009; Li et al., 2017b). The highest δ\(^{18}\)O\text{fluid} value in the first mineralization pulse indicates that a considerable amount of metals (Cu, Mo) could be deposited from a hydrothermal fluid dominated by a magmatic component. Although we cannot correlate the metal grade absolutely with our high-precision dating, such a scenario is partially supported by observations at Qulong, which include the slightly later quartz-biotite-anhydrite alteration possessing ~60% of the met-

als (Yang et al., 2009), and that the majority of the fluid inclusions that contain sulfide minerals are documented in the first mineralization pulse (Li et al., 2017b). In addition, a relative decline in metal grade from early to late veins (Yang et al., 2009) further supports a decline of metals deposited throughout.

**PULSED MAGMATIC- HYDROTHERMAL PROCESS**

Hydrothermal processes at shallow crustal levels that are linked with the exsolution of magmatic fluids from deep magmatic reser-

voirs (Kouzmanov and Pokrovski, 2012) can be used to probe the dynamic processes occurring at depth. To explain the pulsed release of magmatic fluid, as observed at Qulong, two mechanisms are proposed, namely multiple fluid release events from the gradual cooling of a single magmatic reservoir (Chelle-Michou et al., 2017) and multiple fluid-melt recharging events feeding the source pluton (Kamenov et al., 2005; Williamson et al., 2016). For a gradually cooling magmatic reservoir, numerical modeling suggests that the fluids are released episodically, with most (50–75 wt.%) of the fluid being released during the first pulse (Chelle-Michou et al., 2017), which is our favored...
explanation as supported by the observations at Qulong that ~60% of the metals are deposited in the first pulse. The alternative mechanism is also possible if the amount of fluid and melt from the multiple recharging events also gradually drops. Based on the pulsed hydrothermal process suggested here, together with cyclic mineralization processes constrained by high-precision U-Pb and Re-Os dating, titanium diffusion modeling, and concentric excess aluminum in plagioclase (Mercer et al., 2015; Spencer et al., 2015; Tapster et al., 2016; Williamson et al., 2016; Li et al., 2017a), we propose that a pulsed magmatic-hydrothermal process is common in the formation of porphyry deposits. Such a process is most likely controlled by periodic fluid release during gradual cooling of the source pluton at depth (Chelle-Michou et al., 2017), although a decline in the amount of melt and fluid associated with multiple recharging events is a competitive alternative mechanism. By inference, the lifetime of the source pluton is estimated to be hundreds of thousands of years, with much shorter durations (tens of thousands of years) for the fluid release events (Mercer et al., 2015; Buret et al., 2015; Tapster et al., 2016; Chelle-Michou et al., 2017; Li et al., 2017a).

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