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

Yang Li¹,²*, Xian-Hua Li³, David Selby⁴, and Jian-Wei Li⁵

¹Department of Earth Sciences, Durham University, DH1 3LE Durham, UK
²State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, 10029 Beijing, China
³State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, 430074 Wuhan, China

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 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 pulsated, 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 coolong 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 event (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 vein formation 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 $\delta^{18}O$ 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 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 $\delta^{18}O$ 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 $\Delta^{18}O_{\text{quartz-zircon}}$ 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 $\delta^{18}O_{\text{quartz}}$ 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 $\delta^{18}O_{\text{quartz}}$ regardless of the presence or absence of fractures and CL zonation (Figs. 2B and 2C). For the 12 veins, their $\delta^{18}O_{\text{quartz}}$ 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 (8.81‰–9.46‰).

DISCUSSION

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

Before using $\delta^{18}O_{\text{quartz}}$ values to trace fluid evolution, it is critical to evaluate the potential modification of $\delta^{18}O_{\text{quartz}}$ values through volume diffusion and precipitation of new material along microfractures (Valley and Graham, 1996; Allan and Yardley, 2007). The $\Delta^{18}O_{\text{quartz-zircon}}$ 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 $\delta^{18}O_{\text{zircon}}$ and $\delta^{18}O_{\text{quartz}}$ 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 $\delta^{18}O$ value.

For the 12 quartz veins, within-vein homogeneity of $\delta^{18}O_{\text{quartz}}$ and the absence of any relationships with microfractures rule out modification of the $\delta^{18}O_{\text{quartz}}$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ (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 $\delta^{18}O$ with previous estimates, we consider the magmatic fluid $\delta^{18}O$ estimated here (7.6‰ ± 1.0‰) is representative.

To calculate $\delta^{18}O_{\text{fluid}}$ from $\delta^{18}O_{\text{quartz}}$, 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...
Figure 3. $\delta^{18}O_{\text{quartz}}$ and $\delta^{18}O_{\text{fluid}}$ values for Qulong deposit (Tibet) presented against absolute time frame defined by Re-Os dating. $\delta^{18}O$ of magmatic-derived fluid is higher than $\delta^{18}O_{\text{fluid}}$ of Qulong vein samples, which indicates the magmatic fluid is balanced by meteoric water during ore formation. $\delta^{18}O_{\text{quartz}}$ and $\delta^{18}O_{\text{fluid}}$ in absolute time show periodic fluctuations, which indicates presence of three intermittent pulses of magmatic fluid flux. Gradual decreasing trend of $\delta^{18}O_{\text{fluid}}$ provide a proxy for flux of magmatic fluid and the mineralizing potential through time. See text for details.

The pulsed magmatic fluid flux inferred from $\delta^{18}O_{\text{fluid}}$ is in agreement with the cyclic mineralization process defined by Re-Os dating, 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 $\delta^{18}O_{\text{fluid}}$ would extend beyond the interval determined by Re-Os dating.

The $\delta^{18}O_{\text{fluid}}$ 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 $\delta^{18}O_{\text{fluid}}$ 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 $\delta^{18}O_{\text{fluid}}$ can be used as a proxy to trace the amount of metals available for precipitating through time. In this regard, the low $\delta^{18}O_{\text{fluid}}$ recorded by the sinusoidal 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 $\delta^{18}O_{\text{fluid}}$ values for Qulong deposit (Tibet) 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 $\delta^{18}O_{\text{fluid}}$ would extend beyond the interval determined by Re-Os dating.

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PULSED MAGMATIC-HYDROTHERMAL PROCESS

Hydrothermal processes at shallow crustal levels that are linked with the exsolution of magmatic fluids from deep magmatic reservoirs (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
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exploration as supported by the observations at Qulong that ~60% of the metals are deposited in its. 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 recharge 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., 2016; Tapster et al., 2016; Chelle-Michou et al., 2017; Li et al., 2017a).

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