THE GEOLOGICAL SOCIETY OF AMERICA®

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

Yang Li[1,2]*, Xian-Hua Li[2], David Selby[1], and Jian-Wei Li[3]
[1]Department of Earth Sciences, Durham University, DH1 3LE Durham, UK
[2]State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, 10029 Beijing, China
[3]State 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 $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ 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 pulsed, rather than being continuous. The overall highest $\delta^{18}O_{fluid}$ 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 (Glazner 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 veining 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 $\delta^{18}O_{fluid}$ 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.

*Current address: Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06511, USA; e-mail: yang.li@yale.edu; cugliyang@126.com.

 Data Repository item 2018001 | https://doi.org/10.1130/G39504.1

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 Repository[1]). 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 $\delta^{18}O$ 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) $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\Delta^{18}O_{quartz\text{-}zircon}$ 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 $\delta^{18}O_{quartz}$ 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 $\delta^{18}O_{quartz}$, regardless of the presence or absence of fractures and CL zonation (Figs. 2B and 2C). For the 12 veins, their $\delta^{18}O_{quartz}$ 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‰).

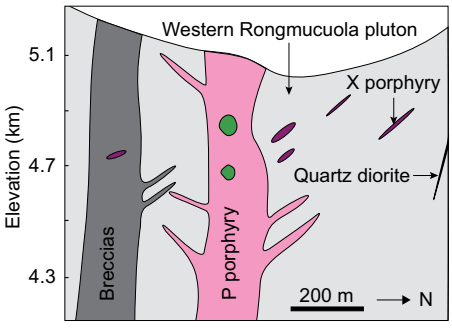

Figure 1. Cross section of Qulong (Tibet) porphyry Cu-Mo deposit.

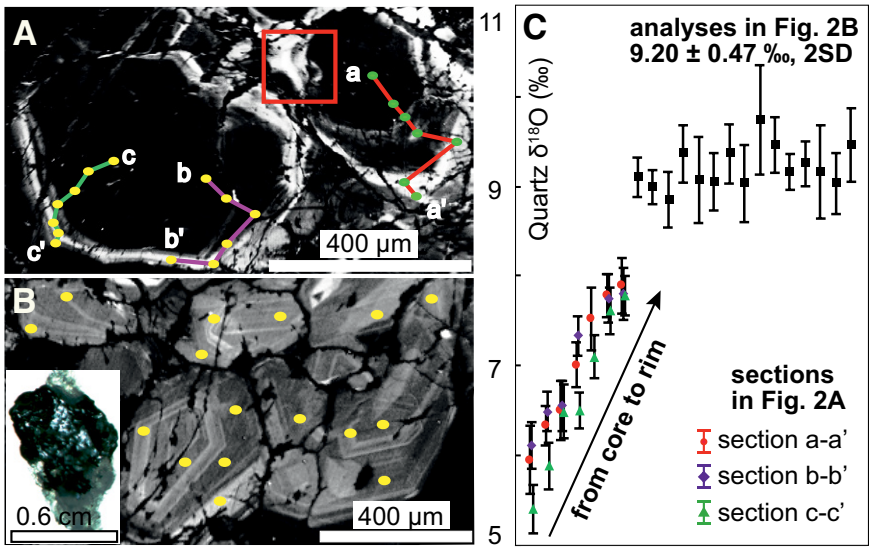

Figure 2. Representative cathodoluminescence (CL) images and *in situ* $\delta^{18}O_{quartz}$ from Qulong porphyry Cu-Mo deposit, Tibet. A: Quartz grains from sinusoidal quartz vein. Red box highlights resorption and dissolution of CL-dark core, which is overprinted by CL-bright overgrowth rim. B: Quartz grains from molybdenite-bearing vein possess euhedral growth zonation. C: $\delta^{18}O_{quartz}$ plot of three transects shown in A and analyzed quartz grains shown in B. Ellipses in A and B represent positions analyzed by secondary ion mass spectrometry. See text for discussion. SD—standard deviation.

DISCUSSION

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

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

[1]GSA Data Repository item 2018001, Tables DR1–DR3, deposit geology, methods, and quartz-water oxygen fractionation considerations, is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.

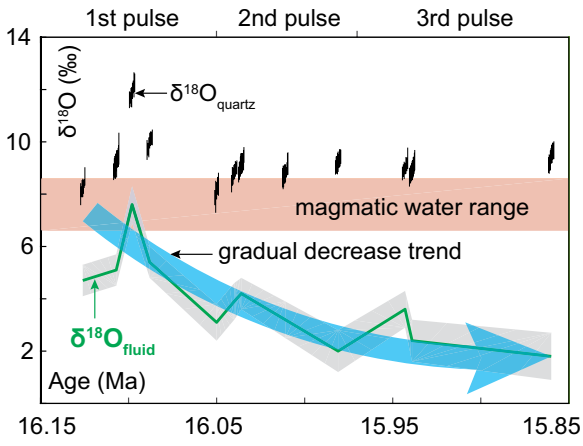

Figure 3. $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ values for Qulong deposit (Tibet) presented against absolute time frame defined by Re-Os dating. $\delta^{18}O$ of magmatic-derived fluid is higher than $\delta^{18}O_{fluid}$ of Qulong vein samples, which indicates the magmatic fluid is balanced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

water and quartz. The vein quartz at Qulong (~0.4 cm in size) potentially precipitated over ~409–66,906 yr (Pollington et al., 2016) at 425–280 °C (Li et al., 2017b), which is sufficiently longer than that needed for quartz and water to reach equilibrium (<20 yr; Fig. DR4B; Cole et al., 1992). Therefore, the $\delta^{18}O_{fluid}$ of each vein can be calculated from $\delta^{18}O_{quartz}$ using the equation of Matsuhisa et al. (1979) with the formation temperature of that vein.

A potential concern for the calculated $\delta^{18}O_{fluid}$ is the accuracy of the temperatures applied. Here we use trapping temperatures from fluid inclusion assemblages (FIAs; Li et al., 2017b), which represent the best estimates of the formation temperatures (Goldstein and Reynolds, 1994). The trends shown by the $\delta^{18}O_{quartz}$ and $\delta^{18}O_{fluid}$ values (Fig. 3), coupled with similar trends determined by using the highest, average, and lowest mineralization temperatures in PCDs (Fig. DR5), suggest that the evolution trend of ore-forming fluid is robust.

In terms of fluids with salinities of <10 wt.% (Li et al., 2017b), oxygen isotope fractionation between aqueous and vapor phases via boiling is typically <0.5‰ at 350–450 °C (Shmulovich et al., 1999), which is of the same order of magnitude as the uncertainties in SIMS analysis and the equilibrium fractionation equation. Moreover, fluid boiling only operated locally at Qulong (Li et al., 2017b), and therefore its effect on oxygen isotope fractionation is considered negligible.

Evolution of Ore-Forming Fluid in an Absolute Time Frame

The textures of quartz grains from the sinusoidal vein (barren of mineralization), including dissolution-resorption of cores and discordant overgrowth rims (Fig. 2A), suggest that the dissolution-resorption of the cores occurred during and/or before the overgrowths. Therefore, the progressive increase of $\delta^{18}O_{quartz}$ from core to rim (Fig. 2C) indicates that the cores were modified by a late ^{18}O-rich fluid. If the inner core recorded the most primary $\delta^{18}O_{quartz}$ (5.40‰ ± 0.27‰) during vein formation (~425 °C; Li et al., 2017b), the corresponding fluid has a $\delta^{18}O_{fluid}$ of 1.8‰ ± 0.5‰, which represents the $\delta^{18}O_{fluid}$ 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 $\delta^{18}O_{fluid}$ values show significant variation, as much as 5.8‰. In brief, during each of the three mineralization pulses defined by Re-Os dating, the $\delta^{18}O_{fluid}$ 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 $\delta^{18}O_{fluid}$ increased progressively from 4.7‰ to 7.6‰, and then decreased to 3.1‰. Overall, the first mineralization pulse had higher $\delta^{18}O_{fluid}$ values than the second and third pulses.

With the exception of the sample at 16.098 Ma, which possesses a $\delta^{18}O_{fluid}$ of 7.6‰ ± 0.5‰, all $\delta^{18}O_{fluid}$ 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 $\delta^{18}O_{fluid}$ 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 $\delta^{18}O_{fluid}$ (1.8‰ ± 0.5‰) of the sinusoidal vein. In the first mineralization pulse, the increase in the $\delta^{18}O_{fluid}$ 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 $\delta^{18}O_{fluid}$ 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 $\delta^{18}O_{fluid}$ would extend beyond the interval determined by Re-Os dating.

The $\delta^{18}O_{fluid}$ values decrease gradually from the first to the second and third mineralization pulses (Fig. 3), with the most pronounced magmatic flux occurring in the first pulse. As $\delta^{18}O_{fluid}$ 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 $\delta^{18}O_{fluid}$ can be used as a proxy to trace the amount of metals available for precipitating through time. In this regard, the low $\delta^{18}O_{fluid}$ 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 $\delta^{18}O_{fluid}$ 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 metals (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 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

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 recent 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., 2016; Tapster et al., 2016; Chelle-Michou et al., 2017; Li et al., 2017a).

ACKNOWLEDGMENTS

Y. Li thanks the CA-SIMS lab of Institute of Geology and Geophysics, Chinese Academy of Sciences, for the continuous support and providing a 2-month visiting fellowship. Selby acknowledges the Total Endowment Fund and a Natural Environment Research Council Isotope Geoscience Facilities grant (IP-1414-1113). J.-W. Li is funded by the Natural Science Foundation of China (grant 41325007). The constructive comments from Matt Leybourne, Massimo Chiaradia, and anonymous reviewers, and editorial handling by J. Brendan Murphy, are greatly appreciated.

REFERENCES CITED

Allan, M.M., and Yardley, B.W.D., 2007, Tracking meteoric infiltration into a magmatic-hydrothermal system: A cathodoluminescence, oxygen isotope and trace element study of quartz from Mt. Leyshon, Australia: Chemical Geology, v. 240, p. 343–360, https://doi.org/10.1016/j.chemgeo.2007.03.004.

Buret, Y., von Quadt, A., Heinrich, C., Selby, D., Walle, M., and Peytcheva, I., 2016, From a long-lived upper-crustal magma chamber to rapid porphyry copper emplacement: Reading the geochemistry of zircon crystals at Bajo de la Alumbrera (NW Argentina): Earth and Planetary Science Letters, v. 450, p. 120–131, https://doi.org/10.1016/j.epsl.2016.06.017.

Chelle-Michou, C., Rottier, B., Caricchi, L., and Simpson, G., 2017, Tempo of magma degassing and the genesis of porphyry copper deposits: Scientific Reports, v. 7, 40566, https://doi.org/10.1038/srep40566.

Cole, D.R., Ohmoto, H., and Jacobs, G.K., 1992, Isotopic exchange in mineral-fluid systems: III. Rates and mechanisms of oxygen isotope exchange in the system granite-H_2O ± NaCl ± KCl at hydrothermal conditions: Geochimica et Cosmochimica Acta, v. 56, p. 445–466, https://doi.org/10.1016/0016-7037(92)90144-8.

Cooke, D.R., Hollings, P., Wilkinson, J.J., and Tosdal, R.M., 2014, Geochemistry of porphyry deposits, *in* Turekian, H.D.H.K., ed., Treatise on Geochemistry (second edition): Oxford, UK, Elsevier, p. 357–381, https://doi.org/10.1016/B978-0-08-095975-7.01116-5.

Glazner, A.F., and Sadler, P.M., 2016, Estimating the duration of geologic intervals from a small number of age determinations: A challenge common to petrology and paleobiology: Geochemistry Geophysics Geosystems, v. 17, p. 4892–4898, https://doi.org/10.1002/2016GC006542.

Goldstein, R.H., and Reynolds, T.J., eds., 1994, Systematics of Fluid Inclusions in Diagenetic Minerals: SEPM Society for Sedimentary Geology Short Course Notes 31, 199 p., https://doi.org/10.2110/scn.94.31.

Johannes, W., 1984, Beginning of melting in the granite system Qz-Or-Ab-An-H_2O: Contributions to Mineralogy and Petrology, v. 86, p. 264–273, https://doi.org/10.1007/BF00373672.

Kamenov, G.D., Perfit, M.R., Jonasson, I.R., and Mueller, P.A., 2005, High-precision Pb isotope measurements reveal magma recharge as a mechanism for ore deposit formation: Examples from Lihir Island and Conical seamount, Papua New Guinea: Chemical Geology, v. 219, p. 131–148, https://doi.org/10.1016/j.chemgeo.2005.02.013.

Kouzmanov, K., and Pokrovski, G.S., 2012, Hydrothermal controls on metal distribution in porphyry Cu (-Mo-Au) systems, *in* Hedenquist, J.W., Harris, M., and Camus, F., eds., Geology and Genesis of Major Copper Deposits and Districts of the World: A Tribute to Richard H. Sillitoe: Society of Economic Geologists Special Publication 16, p. 573–618.

Li, Y., Selby, D., Condon, D., and Tapster, S., 2017a, Cyclic magmatic-hydrothermal evolution in porphyry systems: High-precision U-Pb and Re-Os geochronology constraints from the Tibetan Qulong porphyry Cu-Mo deposit: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 112, p. 1419–1440, https://doi.org/10.5382/econgeo.2017.4515.

Li, Y., Selby, D., Feely, M., Costanzo, A., and Li, X.-H., 2017b, Fluid inclusion characteristics and molybdenite Re-Os geochronology of the Qulong porphyry copper-molybdenum deposit, Tibet: Mineralium Deposita, v. 52, p. 137–158, https://doi.org/10.1007/s00126-016-0654-z.

Matsuhisa, Y., Goldsmith, J.R., and Clayton, R.N., 1979, Oxygen isotopic fractionation in the system quartz-albite-anorthite-water: Geochimica et Cosmochimica Acta, v. 43, p. 1131–1140, https://doi.org/10.1016/0016-7037(79)90099-1.

Mercer, C.N., Reed, M.H., and Mercer, C.M., 2015, Time scales of porphyry Cu deposit formation: Insights from titanium diffusion in quartz: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 110, p. 587–602, https://doi.org/10.2113/econgeo.110.3.587.

Pollington, A.D., Kozdon, R., Anovitz, L.M., Georg, R.B., Spicuzza, M.J., and Valley, J.W., 2016, Experimental calibration of silicon and oxygen isotope fractionations between quartz and water at 250 °C by in situ microanalysis of experimental products and application to zoned low δ^{30}Si quartz overgrowths: Chemical Geology, v. 421, p. 127–142, https://doi.org/10.1016/j.chemgeo.2015.11.011.

Richards, J.P., 2011, Magmatic to hydrothermal metal fluxes in convergent and collided margins: Ore Geology Reviews, v. 40, p. 1–26, https://doi.org/10.1016/j.oregeorev.2011.05.006.

Shmulovich, K.I., Landwehr, D., Simon, K., and Heinrich, W., 1999, Stable isotope fractionation between liquid and vapour in water-salt systems up to 600 °C: Chemical Geology, v. 157, p. 343–354, https://doi.org/10.1016/S0009-2541(98)00202-2.

Sillitoe, R.H., 2010, Porphyry copper systems: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 105, p. 3–41, https://doi.org/10.2113/gsecongeo.105.1.3.

Simmons, S.F., and Brown, K.L., 2006, Gold in magmatic hydrothermal solutions and the rapid formation of a giant ore deposit: Science, v. 314, p. 288–291, https://doi.org/10.1126/science.1132866.

Simmons, S.F., and Brown, K.L., 2007, The flux of gold and related metals through a volcanic arc, Taupo Volcanic Zone, New Zealand: Geology, v. 35, p. 1099–1102, https://doi.org/10.1130/G24022A.1.

Spencer, E.T., Wilkinson, J.J., Creaser, R.A., and Seguel, J., 2015, The distribution and timing of molybdenite mineralization at the El Teniente Cu-Mo porphyry deposit, Chile: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 110, p. 387–421, https://doi.org/10.2113/econgeo.110.2.387.

Stein, H.J., 2014, Dating and tracing the history of ore formation, *in* Turekian, H.D.H.K., ed., Treatise on Geochemistry (second edition): Oxford, UK, Elsevier, p. 87–118, https://doi.org/10.1016/B978-0-08-095975-7.01104-9.

Stock, M.J., Humphreys, M.C.S., Smith, V.C., Isaia, R., and Pyle, D.M., 2016, Late-stage volatile saturation as a potential trigger for explosive volcanic eruptions: Nature Geoscience, v. 9, p. 249–254, https://doi.org/10.1038/ngeo2639.

Tanner, D., Henley, R.W., Mavrogenes, J.A., and Holden, P., 2013, Combining in situ isotopic, trace element and textural analyses of quartz from four magmatic-hydrothermal ore deposits: Contributions to Mineralogy and Petrology, v. 166, p. 1119–1142, https://doi.org/10.1007/s00410-013-0912-3.

Tapster, S., Condon, D.J., Naden, J., Noble, S.R., Petterson, M.G., Roberts, N.M.W., Saunders, A.D., and Smith, D.J., 2016, Rapid thermal rejuvenation of high-crystallinity magma linked to porphyry copper deposit formation: Evidence from the Koloula Porphyry Prospect, Solomon Islands: Earth and Planetary Science Letters, v. 442, p. 206–217, https://doi.org/10.1016/j.epsl.2016.02.046.

Valley, J.W., and Graham, C.M., 1996, Ion microprobe analysis of oxygen isotope ratios in quartz from Skye granite: Healed micro-cracks, fluid flow, and hydrothermal exchange: Contributions to Mineralogy and Petrology, v. 124, p. 225–234, https://doi.org/10.1007/s004100050188.

Wilkinson, J.J., Stoffell, B., Wilkinson, C.C., Jeffries, T.E., and Appold, M.S., 2009, Anomalously metal-rich fluids form hydrothermal ore deposits: Science, v. 323, p. 764–767, https://doi.org/10.1126/science.1164436.

Williamson, B.J., Herrington, R.J., and Morris, A., 2016, Porphyry copper enrichment linked to excess aluminium in plagioclase: Nature Geoscience, v. 9, p. 237–241, https://doi.org/10.1038/ngeo2651.

Yang, Z.M., Hou, Z.Q., White, N.C., Chang, Z.S., Li, Z.Q., and Song, Y.C., 2009, Geology of the post-collisional porphyry copper-molybdenum deposit at Qulong, Tibet: Ore Geology Reviews, v. 36, p. 133–159, https://doi.org/10.1016/j.oregeorev.2009.03.003.

Zhao, J.X., Qin, K.Z., Xiao, B., McInnes, B., Li, G.M., Evans, N., Cao, M.J., and Li, J.X., 2016, Thermal history of the giant Qulong Cu-Mo deposit, Gangdese metallogenic belt, Tibet: Constraints on magmatic-hydrothermal evolution and exhumation: Gondwana Research, v. 36, p. 390–409, https://doi.org/10.1016/j.gr.2015.07.005.

Manuscript received 7 July 2017
Revised manuscript received 1 September 2017
Manuscript accepted 6 September 2017

Printed in USA