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Cu isotopes reveal initial Cu enrichment in sources of giant porphyry deposits in a collisional setting

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ABSTRACT

Porphyry copper deposits (PCDs) represent the most important type of Cu reservoir on Earth, but the mechanism of Cu enrichment in PCDs is debated due to the lack of direct constraints. This issue may be resolved by the study of copper isotopes (δ^{65}Cu), which are strongly fractionated during formation and/or precipitation of sulfides. Here we report high-precision Cu-isotope data on a large set of porphyries, mafic magmatic enclaves (MMEs), and sulfide ores from PCDs in southern Tibet. For comparison, barren intrusions from southern Tibet were also analyzed. The fertile porphyries and MMEs from PCDs have high Cu contents and elevated δ^{65}Cu values compared with the barren intrusions and global average felsic rocks. These features are inconsistent with the known supergene processes after sulfide formation (e.g., leaching and weathering). Because sulfides formed from secondary Cu-rich fluids are enriched in heavy Cu isotopes, the elevated Cu contents and Cu-isotope ratios indicate that the Cu source for PCDs was a refertilized lithosphere enriched in sulfides. This suggests that initial Cu enrichment in magma sources could be a key step in the formation of giant PCDs in continental collision zones.

INTRODUCTION

Giant porphyry copper deposits (PCDs) represent anomalously large accumulations of Cu in the upper continental crust, and provide nearly three-quarters of the world's Cu production (Sillitoe, 2010). One of the key issues under debate is where the Cu in PCDs came from, and whether there is a unique, Cu-rich source region for giant PCDs. The Cu of giant PCDs has been attributed to a Cu-rich mantle wedge (McInnes et al., 1999), a subcontinental lithospheric mantle (SCLM) or crustal source that was fertilized by arc magmatism and slab-derived fluids (Richards, 2009; Sillitoe, 2012; Griffin et al., 2013; Chiaradia, 2014; Hou et al., 2015), or a Cu-rich subducting oceanic slab (Mungall, 2002). Alternatively, the formation of giant PCDs has been believed to be controlled by the nature of magmas, e.g., high water contents (>4 wt% H_2O) and high oxygen fugacity (f_{O_2}) of the magmas are the *sine qua non* for the formation of PCDs (Richards, 2011), rather than the Cu content of the source regions. Other studies have indicated that the timing of sulfide saturation relative to volatile saturation during magma differentiation may play a more critical role in the genesis of giant PCDs than the nature of the source region (Park et al., 2015).

The best approach to constraining the source of ore-forming metals is indubitably the use of their own isotopes, although other isotopic systematics (e.g., sulfur, lead, and osmium) may provide indirect constraints (e.g., McInnes et al., 1999). Copper isotopes (expressed as δ^{65}Cu relative to U.S. National Institute of Standards and Technology [NIST] standard 976) are only slightly fractionated during partial melting (Liu et al., 2015), magmatic differentiation (Liu et al., 2015), volcanic degassing (Huang et al., 2016), and sulfide-fluid segregation at high temperatures (Mathur et al., 2009). For instance, most granitoids have δ^{65}Cu values identical to those of basaltic rocks (Li et al., 2009). In contrast, mantle metasomatism involving sulfide formation in the sources of igneous rocks can strongly fractionate Cu isotopes (Liu et al., 2015). For example, mantle peridotites that have undergone metasomatism with reprecipitation of sulfides have δ^{65}Cu shifted toward much higher values relative to that of the primitive mantle (Liu et al., 2015). This means that Cu isotopes may provide direct constraints on the enrichment mechanism of Cu in the source of PCDs.

The PCDs in southern Tibet constitute the largest Cu metallogenic belt in China, comprising more than 20 ore districts (Fig. 1), and have been regarded as typical collision-related PCDs (e.g., Hou et al., 2013). These

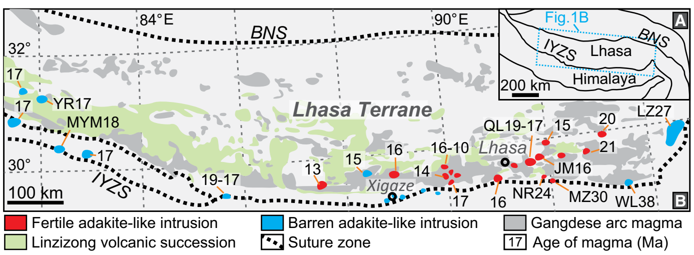

Figure 1. A: Simplified geologic map of Tibetan Plateau. B: Tectonic framework of Lhasa terrane, showing distribution of collision-related adakite-like rocks (after Zheng et al., 2012). BNS—Bangong-Nujiang suture; IYZS—Indus-Yarlung-Tsangpo suture. JM—Jiama; LZ—Linzhi; MYM—Mayum; MZ—Mingze; NR—Nuri; QL—Qulong; WL—Wolong; YR—Yare.

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deposits show broad similarities in their formation ages, mineralization styles, and alteration zones, but their Cu reserves vary significantly. Many barren intrusions occur in spatial and temporal association with these PCDs. Therefore, differences in Cu-isotope ratios between the barren and fertile intrusions, and how these differences arise, may help understand the mechanism of Cu enrichment in PCDs.

GEOLOGICAL SETTING AND SAMPLES

The collision-related PCDs in southern Tibet were formed at ca. 40–20 Ma, after the initial collision of the India and Asia plates (Fig. 1) (Hou et al., 2013). These deposits are dominated by Cu-Mo mineralization (e.g., Qulong, Jiama, and Nuri deposits), while Mingze is a porphyry Mo deposit (PMD) without economic Cu mineralization. Intrusions associated with ore deposits commonly occur as isolated stocks of porphyritic monzogranite, granodiorite, or granite (Fig. DR1 in the GSA Data Repository[1]). All porphyries were formed at 30–13 Ma and commonly contain mafic magmatic enclaves (MMEs) (Zheng et al., 2012). Many coeval barren adakite-like (CBA) intrusions (29–15 Ma) have been identified, including granodiorite, granite, and two-mica granite, in which MMEs are commonly lacking (Fig. DR1). Several pre-ore collision-related barren adakite-like (PBA) intrusions (ca. 38 Ma) containing abundant MMEs have also been recognized, and they show similarities in mineral assemblages to their counterparts from the fertile intrusions. Whole-rock samples free of hydrothermal alteration and surface weathering were collected from porphyries outside the zones of mineralization, while chalcopyrite separates were collected from vein-type ores with formation temperatures >330 °C in the giant Qulong deposit (Yang et al., 2009).

METHODS AND RESULTS

Detailed sample descriptions and methods for Cu-isotope analysis are given in the Data Repository. The CBA intrusions (Cu = 6–28 ppm) have δ^{65}Cu values from −0.29‰ to +0.50‰ with a mean of +0.18‰ ± 0.21‰ (two standard deviations, 2SD), mostly falling within the range of the terrestrial mantle (0.03‰ ± 0.24‰). Rocks from the Mingze PMD (Cu = 8–17 ppm) have δ^{65}Cu from −0.46‰ to +0.27‰. Notably, host rocks (Cu = 7–156 ppm) and their MMEs (Cu = 46–228 ppm) from PCDs have variable δ^{65}Cu values ranging from 0.18‰ to 0.87‰ and 0.49‰ to 1.12‰, respectively, while host rocks (Cu = 10–22 ppm) and their MMEs (Cu = 22–169 ppm) from PBA intrusions vary from −0.04‰ to 0.18‰ and 0.10‰ to 0.27‰, respectively. Chalcopyrites from the Qulong PCD have δ^{65}Cu values from 0.08‰ to 1.01‰, which are significantly higher than that of the terrestrial mantle (Figs. 2 and 3; Table DR1 in the Data Repository).

DISCUSSION

The most noticeable finding of this study is that porphyries and MMEs from the PCDs have heavier Cu-isotope compositions compared with the PMD and barren intrusions as well as with the global average igneous rock (Fig. 2). Because Cu isotopes are almost unfractionated during partial melting, there are four mechanisms that may fractionate Cu isotopes in igneous rocks: (1) surface alteration and weathering; (2) isotopic fractionation during aqueous fluid–melt segregation; (3) isotopic fractionation during sulfide fractionation; and/or (4) isotopic variation in the magma source.

Surface alteration and weathering involving redox reactions are known to strongly fractionate Cu isotopes (e.g., Mathur et al., 2009; Liu et al., 2014). However, the preferential release of ^{65}Cu during alteration would not produce the elevated δ^{65}Cu observed in porphyries and MMEs from the PCDs (Fig. 2). The fact that samples with elevated δ^{65}Cu have high Cu contents (Fig. 3) also argues against any significant loss of light Cu isotopes after formation of the porphyries and MMEs.

[1]GSA Data Repository item 2019053, petrography of samples, methods, literature data sources, Figures DR1–DR4, and Table DR1, is available online at www.geosociety.org/pubs/ft2019.htm, or on request from editing@geosociety.org.

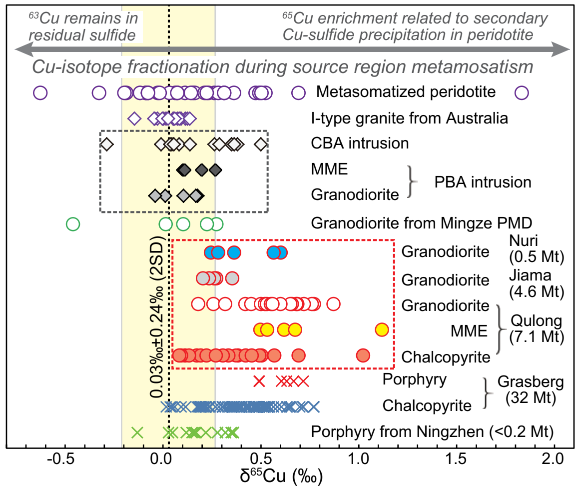

Figure 2. δ^{65}Cu ranges of coeval barren adakite-like (CBA) intrusions; granodiorite and mafic magmatic enclaves (MMEs) from pre-ore collision-related barren adakite-like (PBA) intrusions; Mingze porphyry Mo deposit (PMD); porphyry Cu deposits; chalcopyrite from Qulong deposit; normal I-type granites (Li et al., 2009); non-metasomatized (average δ^{65}Cu = 0.03‰ ± 0.24‰ [2 SD], *n* = 16; vertical dotted line and yellow bar) and metasomatized peridotites (Liu et al., 2015); porphyries and hydrothermal chalcopyrite from the Grasberg deposit in Irian Jaya (West Papua) (Graham et al., 2004); porphyries from Ningzhen in southern China (Zhang et al., 2015). Black and red dashed boxes represent δ^{65}Cu ranges of barren intrusions and porphyry copper deposits (PCDs), respectively. Mt—Million tons of Cu.

Theoretical and experimental studies indicate that Cu isotope fractionation occurs during volcanic degassing (liquid-vapor equilibrium) and precipitation of sulfides from hydrothermal fluids (liquid-sulfide equilibrium) (Seo et al., 2007; Fujii et al., 2013). However, studies on arc magmas and highly differentiated tephra show that the evolved magmas have Cu-isotope compositions comparable to those of their parent basaltic magmas (Liu et al., 2015; Huang et al., 2016). Additionally, if the elevated δ^{65}Cu values of rocks from the PCDs resulted from preferential loss of ^{63}Cu into fluids during the segregation of aqueous fluid–melt at high temperature (>330 °C), the vein-type chalcopyrite should have negative δ^{65}Cu values, which is inconsistent with our observations. Again, the elevated δ^{65}Cu coupled with high Cu concentration of the PCDs (Fig. 3) conflicts with any significant loss of light Cu isotopes during formation of the porphyries and MMEs.

Sulfide fractionation from a S-saturated magma will lead to high δ^{65}Cu in the residual magma due to the enrichment of ^{63}Cu in sulfide relative to coexisting silicates (Savage et al., 2015; Zhao et al., 2017). If sulfide fractionation is important, it should have developed more easily in the CBA intrusions (Richards, 2009), because they have lower f_{O_2} than the fertile and PBA intrusions, as constrained by trace-element patterns in zircon (Fig. DR2). Consequently, higher δ^{65}Cu values would be expected in the CBA intrusions relative to the fertile and PBA intrusions, which again is contrary to the observations (Fig. 2). Thus, sulfide fractionation does not appear to be important during formation of the collision-related rocks, which in turn indicates that the timing of sulfide saturation relative to volatile saturation during magma differentiation is not critical to the formation of giant PCDs in southern Tibet, although it is a prerequisite for PCDs in general (cf. Park et al., 2015).

It is therefore most likely that the elevated δ^{65}Cu values of the host rocks and chalcopyrite in PCDs have been inherited from their magma sources. Cu-isotope compositions of primary peridotites could be strongly modified by metasomatism via sulfide dissolution and/or breakdown or precipitation during melt and/or fluid-rock interaction (Liu et al., 2015).

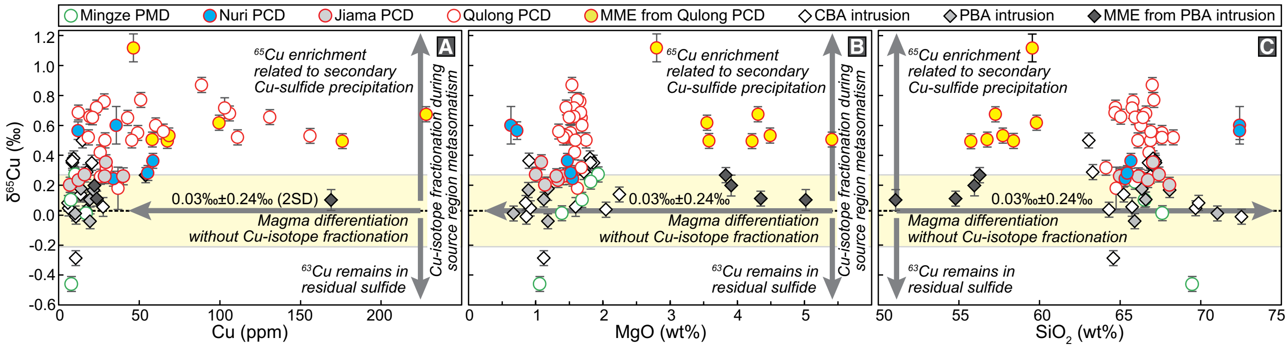

Figure 3. Correlation of Cu-isotope compositions with Cu (A), MgO (B), and SiO_2 (C) concentrations in coeval barren adakite-like (CBA) intrusions; granodiorite and mafic magmatic enclaves (MMEs) from pre-ore collision-related barren adakite-like (PBA) intrusions; Mingze porphyry Mo deposit (PMD); porphyry Cu deposits (PCDs), southern Tibet. Horizontal dotted line and yellow bar represent the δ^{65}Cu range of non-metasomatized peridotites. Error bars on the data points represent 2 standard deviations (SD).

The released Cu is isotopically heavy when redox reactions are involved (Fernandez and Borrok, 2009), and then Cu-sulfides reprecipitated from the ^{65}Cu-rich fluids are relatively enriched in heavy isotopes (Liu et al., 2015). The similarity of δ^{65}Cu values in PBAs, CBAs, PMDs, and global non-metasomatized peridotites indicates very limited precipitation of secondary sulfides. Without intensive hydrous metasomatism and formation of a significant amount of secondary sulfides in the sources, the metallogenic fertility of Cu in PBAs, CBAs, and PMDs is low (Fig. 4). In contrast, the elevated δ^{65}Cu values in PCDs, especially the giant Qulong deposit (Fig. 2), suggest the presence of substantial amounts of secondary sulfides in their source due to metasomatism. This is strongly supported by trace-element data, e.g., the high Pb/Ce and Ba/La ratios suggest that magma source of the giant PCDs experienced strong hydrous metasomatism (Fig. DR3).

A heavy Cu-isotope signature has also been found in other PCDs from Irian Jaya (West Papua) and southern China (Graham et al., 2004; Zhang et al., 2015). For example, chalcopyrites in fresh ore-forming diorites and quartz veins of porphyry-type ores from the giant Grasberg porphyry Cu-Au deposit (Irian Jaya; up to 32 Mt Cu) have δ^{65}Cu up to 0.72‰ and 0.77‰, respectively (Graham et al., 2004). These values are comparable to those from the giant Qulong PCD, and significantly higher than those from ore-forming intrusions in small-scale porphyry-skarn deposits (<0.2 Mt Cu) in southern China (Fig. 2) (Zhang et al., 2015).

IMPLICATIONS FOR GENESIS AND Cu SOURCE OF GIANT PCDs

Only two of the Tibetan porphyry intrusions contain giant PCDs, and most contain non-giant PCDs or no porphyry-type Cu mineralization (e.g., Mingze PMD and PBA), although they commonly have high water contents (>4 wt% H_2O) and high f_{O_2} (Figs. DR2–DR4). This agrees with many other observations that only a limited number of giant PCDs may occur within a huge magmatic arc, or giant PCDs commonly formed in a relatively short time interval within the life of a long-lived magmatic arc, although arc magmas are also commonly characterized by high water and relatively high oxidation states (Sillitoe, 2010). The key controls on the generation of giant PCDs thus are still unclear.

In contrast to PCDs in arc settings, it is likely that Cu and ore-forming magmas in collision-related PCDs in Tibet were not directly derived from a subducted oceanic slab or a sulfide-rich asthenosphere, but from a continental lithosphere (SCLM and lower crust). The reason is that the subducted oceanic slab had detached from Greater India at ca. 45 Ma (Van der Voo et al., 1999), long before the intrusion of the host rocks. The possibility of Cu in PCDs being directly derived from the subducted oceanic slab is further precluded by the distinct Cu-isotope composition of the host rocks and mid-oceanic ridge basalts (Fig. 2). On the other hand, partial melting of ancient SCLM or lower crust is unfavorable for fertile magma formation (Griffin et al., 2013), because these sources are commonly depleted in Cu, as revealed by Cu-isotope compositions of the CBAs derived from a source region dominated by ancient materials.

Prior to continental collision, subduction of oceanic slabs would produce a flux of oxidizing fluids, which would intensively metasomatize and oxidize the mantle wedge (Hedenquist and Lowenstern, 1994). These oxidizing fluids would dissolve primary sulfides under subsolidus conditions and redistribute them into the hydrous assemblages (McInnes et al., 1999). Such processes could result in enrichment of the hydrous assemblages in heavy Cu isotopes; the more secondary sulfides precipitate, the higher the δ^{65}Cu values developed within the hydrous assemblages (Fernandez and Borrok, 2009). Preferential melting of these hydrous assemblages would produce basaltic magmas, which would stall at the base of the upper-plate crust. Cu sulfides and hydrous minerals would then accumulate in the juvenile refertilized lithosphere (both SCLM and lower crust) (Richards, 2009; Griffin et al., 2013). Partial melting of the refertilized lithosphere can produce hydrous magmas with high f_{O_2}, required for the formation of PCDs. High f_{O_2} would enhance the breakdown of sulfides in the source and increase the solubility of Cu and S in a SO_4^{2-}-rich environment (Richards, 2009). High water contents promote aqueous saturation of magmas at shallow crustal levels and transport of Cu to form PCD mineralization (Sillitoe, 2010). These fertile magmas should inherit the positive δ^{65}Cu values of their primary metasomatized mantle-wedge source. The highest δ^{65}Cu found in the giant Qulong PCD implies that only a refertilized

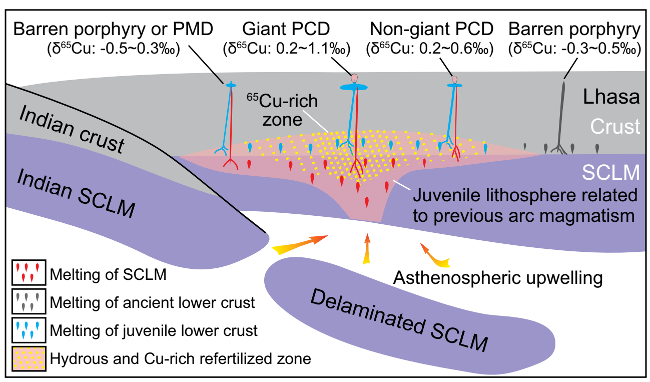

Figure 4. Generation of collision-related porphyry Cu deposits (PCDs) by remelting of refertilized lithosphere. Porphyries derived from ancient or juvenile lithosphere with low degrees of hydrous metasomatism and low contents of secondary sulfides will tend to be free of mineralization. Hydrous metasomatism in source regions is *sine qua non* for formation of PCDs, and only those magmas derived from Cu-rich source have potential to develop giant PCDs. Thinning and partial melting of Lhasa lithosphere in post-collisional settings was induced by asthenospheric upwelling. PMD—porphyry Mo deposit; SCLM—subcontinental lithospheric mantle.

lithosphere, enriched in accumulated sulfides and hydrous minerals, can produce fertile magmas that have the potential to form giant PCDs.

Like ancient SCLM and lower crust, the initial subarc mantle wedge is also typically strongly depleted in Cu (Griffin et al., 2013). The positive δ^{65}Cu values of the ore-forming diorites from the giant Grasberg PCD in the Irian Jaya arc indicate that significant Cu-sulfide refertilization should have also occurred in the magma source regions of the subduction-related PCDs (Graham et al., 2004), which is supported by osmium isotopic observations (McInnes et al., 1999). However, further work is necessary to constrain the occurrence of initial Cu enrichment either in the subarc mantle wedge (McInnes et al., 1999) or in the overlying SCLM of magmatic arcs by previous, even ancient, subduction events (Pettke et al., 2010; Sillitoe, 2012).

CONCLUSIONS

The large difference in δ^{65}Cu of porphyries and MMEs in giant PCDs with that of the barren intrusions in southern Tibet provides new constraints on the mechanism of Cu enrichment in PCDs. It suggests that Cu in the giant PCDs is derived from a refertilized lithosphere enriched in accumulated sulfides and hydrous minerals, rather than from a subducted oceanic slab or directly from a metasomatized subarc mantle wedge in a collision setting (Fig. 4).

Copper-isotope signatures of these fertile rocks are inherited from the magma source. δ^{65}Cu values of fresh magmatic rocks are closely related to the Cu tonnage of PCDs, and rocks from the giant PCDs have Cu-isotope compositions distinct from those of non-giant PCDs, PMDs, and barren intrusions. Thus, Cu isotopes are an effective exploration tool to identify prospective buried PCDs, and potentially to semiquantitatively predict their metallogenic potential.

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