

## Initial Cu enrichment in sources of giant porphyry deposits revealed by Cu isotopes

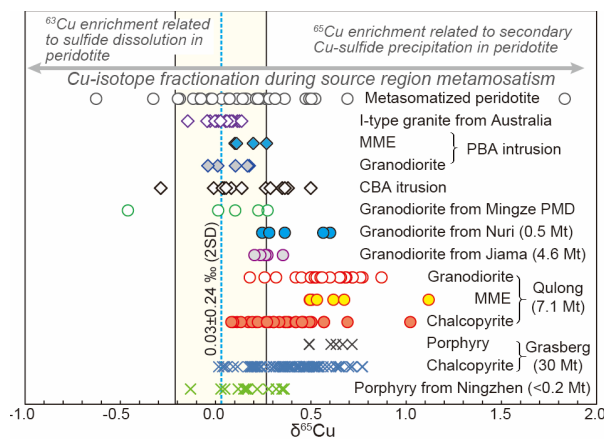
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Giant porphyry Cu deposits (PCDs) represent anomalously large accumulations of Cu in the upper continental crust, and provide nearly three-quarters of the world's Cu. One of key issues under debate is where the Cu in PCDs came from, and whether there is a unique, Cu-rich source region for giant PCDs. The PCDs in southern Tibet constitute the largest Cu metallogenic belt in China, comprising more than twenty ore districts, and have been regarded as typical collision-related PCDs. These 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 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.



**Figure 1.** The  $\delta^{65}\text{Cu}$  ranges of CBA intrusions, granodiorite and MME from PBA intrusions, and the PMD and PCDs, chalcopyrite from the Qulong deposit, normal I-type granites (Li et al., 2009), non-metasomatized (average  $\delta^{65}\text{Cu} = 0.03 \pm 0.24$ ) and metasomatized peridotites (Liu et al., 2015), porphyries and hydrothermal chalcopyrite from the Grasberg deposit in Irian Jaya (Graham et al., 2004), and porphyries from Ningzhen in south China (Zhang et al., 2015).

The collision-related PCDs in southern Tibet were formed *ca* 20–40 Ma after the initial collision of India and Asia plates (Hou et al., 2013). These deposits are dominated by Cu–Mo mineralization (e.g., Qulong, Jiama, and Nuri), while Mingze is a porphyry Mo deposit (PMD) without minable Cu mineralization. Intrusions associated with ore deposits commonly occur as isolated stocks of porphyritic monzogranite, granodiorite and granite. All porphyries were formed at 30–13 Ma and commonly contain mafic magmatic enclaves (MMEs). 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 lack. Several pre-ore collision-related barren adakite-like (PBA) intrusions (~38 Ma) containing abundant MMEs have been also 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 greater than 330°C in the giant Qulong deposit (Yang et al., 2009).

The CBA intrusions (Cu = 5.9–27.6 ppm) have  $\delta^{65}\text{Cu}$  values from  $-0.29\text{‰}$  to  $+0.50\text{‰}$  with a mean of  $+0.18 \pm 0.21\text{‰}$ , mostly falling within the range of the terrestrial mantle ( $0.06 \pm 0.20\text{‰}$ ). Rocks from Mingze PMD (Cu = 7.6–17 ppm) have  $\delta^{65}\text{Cu}$  from  $-0.46\text{‰}$  to  $+0.27\text{‰}$ . Notably, host rocks (Cu = 7–156 ppm) and their MMEs (Cu = 46.4–228 ppm) from PCDs have variable  $\delta^{65}\text{Cu}$  values ranging from  $0.18\text{‰}$  to  $0.87\text{‰}$  and  $0.49\text{‰}$  to  $1.12\text{‰}$ , respectively, while those from PBA intrusions vary from  $-0.04\text{‰}$  to  $0.18\text{‰}$  and  $0.10\text{‰}$

to 0.27‰, respectively. Chalcopyrites from the Qulong PCD have  $\delta^{65}\text{Cu}$  values from 0.08‰ to 1.01‰, which are significantly heavier than that of the terrestrial mantle.

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 global igneous rock average. These features are inconsistent with the known supergene processes after sulfide formation (e.g., leaching and weathering). Since sulfides formed from secondary Cu-rich fluids are enriched in heavy Cu isotopes, the elevated  $\delta^{65}\text{Cu}$  values and high Cu concentrations indicate that the Cu source for PCDs was a refertilized lithosphere enriched in sulfides. This reveals that initial Cu enrichment in magma sources could be a key step in the formation of giant PCDs in continental collision zones.

Investigations of the properties of host magmas (source region, redox state, and water content), compositions of magmatic and hydrothermal minerals, and hydrothermal alteration (Sillitoe, 2010) are all used in the exploration for PCDs. However, these approaches are circumstantial or qualitative, which limits their effectiveness for exploration. Taking southern Tibet as an example, the fertile rocks are all characterized by high water contents and oxidation states, relatively depleted Sr-Nd isotopes, and accompanied with widespread porphyry-type hydrothermal alteration, but their Cu reserves vary significantly, and no recoverable Cu occurs in PMDs. In this work, we have found that the  $\delta^{65}\text{Cu}$  values of fresh magmatic rocks are directly 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-isotope analysis can be used as an effective exploration tool, to identify prospective buried PCDs, and potentially to semi-quantitatively predict the metallogenic potential of porphyries.

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