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Copper isotope fractionation during lower crustal sulfide accumulation

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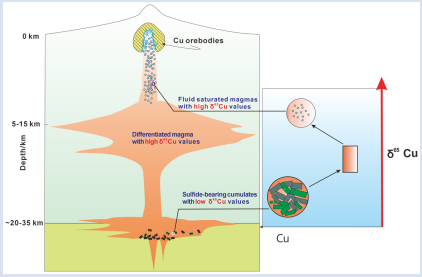
Abstract



Copper isotopes are key tracers for understanding metal behaviour in porphyry Cu deposits, the dominant global source of the copper. However, although shallow magmatic-hydrothermal processes are well studied, the isotopic fingerprint of sulfide saturation at depth, *i.e.* a pivotal control on porphyry Cu formation, remains enigmatic. We analyse Cu isotopes in sulfide-rich cumulate xenoliths and genetically linked porphyries from Tongling ore district, China. The cumulates are relatively enriched in Cu (263 ± 163 ppm, $n = 4$) and light Cu isotopes (–0.19 ± 0.04 ‰) compared to the porphyries (Cu = 55.4 ± 41.5 ppm, $n = 17$; $\delta^{65}Cu = +0.20 \pm 0.21$ ‰) in porphyries. This dichotomy reflects isotopic fractionation during early sulfide saturation, where sulfides sequester light Cu, enriching residual melts in ^{65}Cu. Synthesising global datasets, we identify a systematic $\delta^{65}Cu$ enrichment trajectory from mantle sources through lower crustal cumulates (–0.19 ‰) to upper crustal porphyries (+0.20 ‰). This depth dependent isotopic stratification implies that near surface ^{65}Cu enrichment signatures may serve as a first order exploration vector, particularly where erosional windows expose upper level porphyries.

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Introduction

Isotopic systems, including light stable isotopes (*e.g.*, H, O, and S) and radiogenic isotopes (*e.g.*, Pb, Os), have long been used to trace metal sources and understand metal transport processes in ore deposits (*e.g.*, Mathur *et al.*, 2000). However, these systems often offer indirect constraints when compared to the direct application of the metal's own isotopes. Copper, a strongly chalcophile element with two stable isotopes, ^{63}Cu (69.2 %) and ^{65}Cu (30.8 %) (Shields *et al.*, 1965), exists in nature in three oxidation states — Cu^0, Cu^+, and Cu^{2+} (Shields *et al.*, 1965). Following the advent of high precision Cu isotope measurements using MC-ICP-MS (Maréchal *et al.*, 1999), Cu isotopic analysis has become a valuable tool for studying various mineral deposits (*e.g.*, magmatic Ni-Cu sulfide deposits, Ripley *et al.*, 2015; skarn deposits, Maher and Larson, 2007; porphyry Cu deposits, Li *et al.*, 2010). Because porphyry Cu deposits contribute ~75 % of copper resources worldwide they have received the greatest attention from researchers using copper isotopes (Mathur *et al.*, 2009; Li *et al.*, 2010). Significant Cu isotope fractionation has been documented within individual chalcopyrite samples (*e.g.*, Zhu *et al.*, 2000) and between samples from different porphyry Cu deposits (*e.g.*, Li *et al.*, 2010). Factors influencing Cu isotope fractionation include fluid exsolution (Guo *et al.*, 2020), late stage fluid boiling (Rempel *et al.*, 2012), sulfide precipitation (Li *et al.*, 2010), and redox processes (Zhu *et al.*, 2002). However, the majority of these studies have focused on the shallow magmatic-hydrothermal processes that occur within the upper crust or the water-rock interactions that occur during weathering of Cu sulfide-rich rocks in the supergene environment, leaving the deeper processes of magma differentiation largely unexplored.

In the sulfide saturated magmatic systems, the sulfide segregation during magmatic differentiation at mantle conditions has been observed as a key step in producing significant copper isotope fractionation (*e.g.*, Savage *et al.*, 2015; Zhao *et al.*, 2017; Kempton *et al.*, 2022; Liu *et al.*, 2023). The parent magmas of a porphyry Cu deposit system generally contain several hundred to a few thousand ppm S (Richards, 2011). The high sulfur content promotes persistent sulfide saturation during magmatic evolution, distinguishing these systems from barren ones (*e.g.*, Lee and Tang, 2020); consequently early sulfide saturation may serve as an indicator for potential mineralised porphyry. To date, despite its critical role, deep sulfide saturation during lower crustal magma differentiation remains poorly understood because of the rare preservation of representative samples linked to a porphyry Cu ore deposit.

In this study, we investigate Cu isotope variation during deep sulfide accumulation through a valuable collection of amphibole-rich cumulate xenoliths and intermediate-felsic porphyries from the Tongling mining district, China. These samples are unequivocally linked in both time and space to the magmas that formed porphyry Cu deposits, and the mineralised porphyries represent the derivatives of basaltic magmas that underwent sulfide fractionation at mid- to lower-crustal levels (Du and Audétat, 2020). By examining these samples, we aim to shed light on the role of deep sulfide saturation in Cu isotope fractionation and its implications for porphyry Cu deposit formation.

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Samples

The Tongling mining district hosts 28 porphyry-skarn Cu (Au, Mo) deposits with a combined resource of ~3.3 Mt Cu and 160 t Au (Fig. S-1; Du and Audétat, 2020). All the ore deposits are hosted by the Early Cretaceous porphyry intrusions composed of pyroxene diorite, granodiorite, and quartz diorite (Fig. S-1; Du and Audétat, 2020). These ore-forming porphyries host abundant amphibole-rich cumulate or megacryst xenoliths. Zircon U-Pb age data indicate that both amphibole-rich xenoliths and the ore-forming porphyries formed at ~140 Ma (Fig. S-2). The investigated samples consist of five amphibole-rich, cumulate xenoliths-porphyry pairs and thirteen mineralised porphyries sampled from three different Early Cretaceous intrusive centres within the Tongling mining district. The amphibole-rich cumulate xenoliths are composed of 70–85 % amphibole, 5–20 % clinopyroxene, and lesser amounts of phlogopite, magnetite, and apatite (Fig. 1); they lack exsolution in the primary mineral phases and typically show little evidence for zoning or secondary melting along the grain boundaries. The cumulate samples show typical accumulate textures and no signs of modal metasomatism, such as veins or presence of interstitial amphibole or mica (Fig. 1). The amphibole-rich cumulate xenoliths contain about 0.1 to ~0.6 vol. % sulfide inclusions but in sample JY-6 no sulfide inclusions are detected. Sulfides are all solitary inclusions with spherical habitats that are enclosed within the primary silicate phases. Early studies show that these sulfide inclusions are dominantly trapped in the form of monosulfide solid solutions (MSS) with Cu contents of 1 to 5.8 wt. % (Du and Audétat, 2020). The studied porphyry assemblage includes two gabbro porphyry, seven pyroxene diorite porphyry, two granodiorite/granodiorite porphyry, six diorite porphyry/quartz diorite, and one granite porphyry samples. Petrographic observations reveal that these samples are generally devoid of late stage sulfide veins and contain neither fluid nor sulfide inclusions within their phenocrysts. However, minor sulfide inclusions are present in sample K6-68, and fluid inclusions are found in JY-6h (Du and Audétat, 2020).

Results

The whole rock and Cu isotope data of amphibole-rich cumulate xenoliths and ore-forming porphyries in this study and other published whole rock data of Tongling ore-forming porphyries are provided in Table S-1. The ore-forming porphyries and cumulates exhibit a calc-alkaline differentiation trend (Fig. S-3). Both the cumulate xenoliths and ore-forming porphyries display geochemical features similar to the arc basalt (Du and Audétat, 2020). The data of silicate melt inclusions revealed that these cumulates crystallised from a basic magma (48–52 wt. % SiO_2; Du and Audétat, 2020). In the Sr/Y *versus* Y and Dy/Yb *versus* SiO_2 diagrams (Fig. S-4a), the magmatic evolution starts in the field of ordinary arc magmas and proceeds into the adakite field, a trend that is indicative of hornblende-dominated fractionation at high pressure (*e.g.*, Loucks, 2014). Hornblende dominated fractionation is also indicated by a negative correlation between Dy/Yb and SiO_2 (Davidson *et al.*, 2007; see Fig. S-4b). Pressure-temperature conditions reconstructed by compositions of amphibole and clinopyroxene within cumulates (Table S-2) show that these cumulates crystallised at 969–1083 °C and 3.8–7.0 kbar (converted to 13–27 km using an

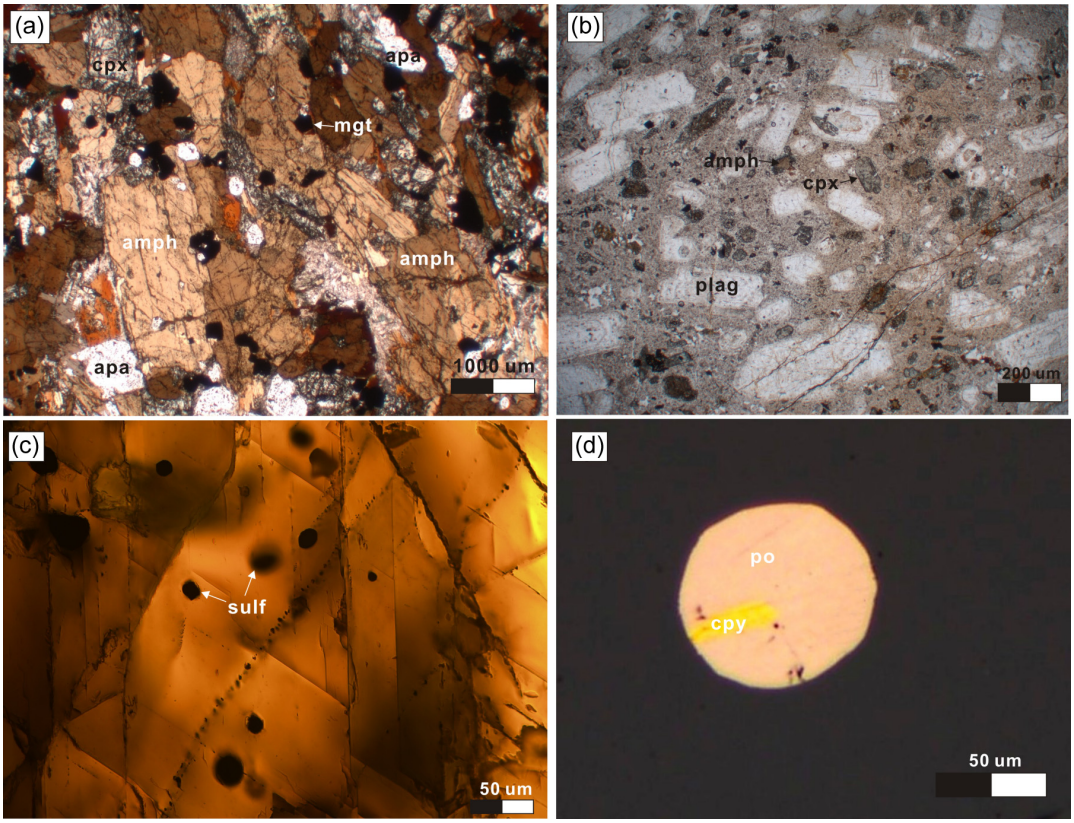

Figure 1 Typical images of cumulates and porphyries from Tongling mining district, southeastern China. **(a)** Amphibole-clinopyroxene cumulate xenolith. **(b)** Thin section of pyroxene diorite porphyry. **(c)** Sulfide inclusions (black) within amphiboles of cumulates. **(d)** Exposed sulfide inclusions comprising of 95 vol. % po and 5 vol. % cpy (po-pyrrhotite, cpy-chalcopyrite, amph-amphibole, cpx-clinopyroxene, apa-apatite, sulf-sulfide). **a**, **b**, and **c** were taken in transmitted light; **d** in reflected light.

average crustal density of 2.7 g cm^{-3}). The mass balance calculation of amphibole dominated fractionation yielded a good fit between estimated and actual residual melt (Table S-3). These lines of evidence, combined with the consistent crystallisation age of cumulates to ore-forming porphyries (Fig. S-2), strongly suggests that the ore-forming magmas in the Tongling mining district experienced significant clinopyroxene and amphibole fractionation at mid- to lower-crustal levels.

Copper isotopic analyses were performed by a sample standard bracketing method with purification using ion chromatography (BioRad AG-MP-1M strong anion resin) on a Thermo Scientific Neptune Plus MC-ICP-MS at University of Science and Technology of China (USTC). The long term external precision of δ^{65}Cu data is better than 0.05 ‰ (2 s.d.) (details in Supplementary Information). The Cu isotopic ratios of these rocks display correlations with their Cu contents and indicators of magmatic differentiation such as SiO_2, MgO, FeO^t, and Al_2O_3 abundances (respectively $r^2 = 0.37$, 0.55, 0.51 and 0.67; Fig. 2). The sulfide-bearing amphibole-rich cumulate xenoliths generally have high Cu contents of 87 to 528 ppm (average value = 26 ppm, $n = 4$) and light Cu isotopic compositions with δ^{65} Cu values ranging from –0.25 ‰ to –0.17 ‰ except one sulfide-free sample JY-6 (Cu content of 77 ppm, δ^{65}Cu = 0.58 ‰). The ore-forming porphyries have lower Cu contents of 17 to 201 ppm (average value = 55 ppm, $n = 17$) and higher δ^{65}Cu values of –0.04 ‰ to 0.37 ‰ (average value = 0.27 ‰, $n = 16$) except the outlier of sulfide-bearing sample K6-68, with an apparently lower δ^{65} Cu value of –0.24 ‰. The porphyry sample JY-6h hosts higher Cu contents than other porphyries, possibly caused by the fluid inclusions within its phenocryst.

Discussion

The copper isotope compositions of our data are systematically divided into two groups: the sulfide saturated cumulates with negative δ^{65}Cu values; the porphyries with positive δ^{65}Cu values. Below we explore the possible causes for the copper isotope variations including (1) fluid saturation and exsolution, (2) redox effects, (3) mantle metasomatism, and (4) fractional crystallisation and sulfide segregation.

Partitioning of Cu isotopes between hydrothermal fluids and precipitating Cu sulfides could generate significant Cu isotope fractionation (up to 1.2 ‰) (*e.g.*, Li *et al.*, 2010). The fresh nature of the analysed samples and the absence of fluid inclusions within the phenocrysts exclude this interference. Redox related Cu isotope fractionation processes have played an important role in generating the high δ^{65}Cu signatures (*e.g.*, Zhu *et al.*, 2002) because Cu^{2+} species preferentially incorporate heavier isotopes which have shorter, stronger bonds compared to Cu^{+} species (*e.g.*, Markl *et al.*, 2006). Liu *et al.* (2015) have observed significant Cu isotope variation (from −0.64 to 1.82 ‰) during oxidative dissolution of sulfides. The encapsulation of sulfide inclusions within silicate minerals and the absence of magnetite in these inclusions indicate minimal oxidation occurs (Fig. 1). Mantle metasomatism is treated as another predominant control on the isotopic variation. This process involves fluids derived from the recycled ocean-crustal material interaction with the mantle xenoliths that formed by fractional crystallisation of basalts (Liu *et al.*, 2015; Kempton *et al.*, 2022). The hornblendites in our study have a typical mechanical cumulate origin, that is greatly different from those metasomatic mantle xenoliths which often display a poikilitic texture and host interstitial sulfide grains or veins (*e.g.*, Kempton *et al.*, 2022).

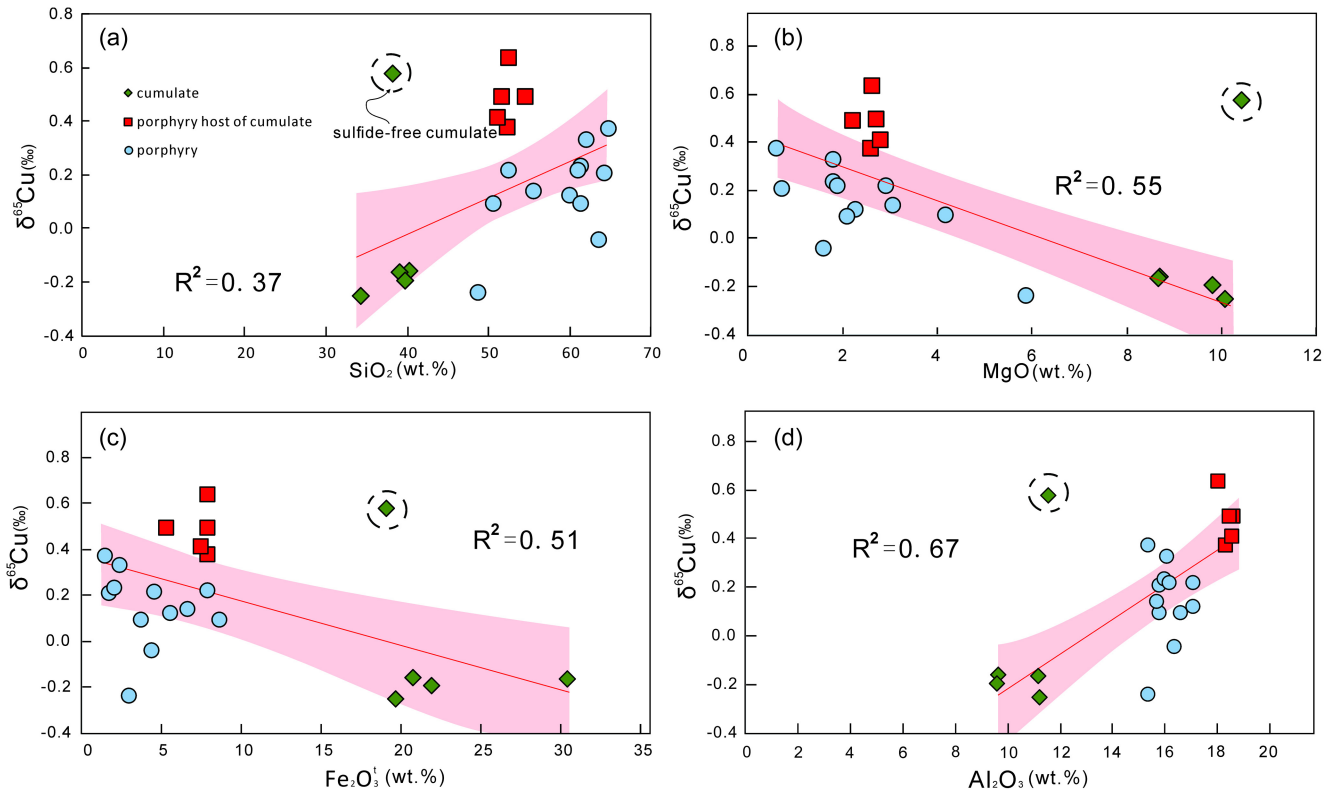

Figure 2 The correlation between δ^{65}Cu and whole rock **(a)** SiO_2, **(b)** MgO, **(c)** $Fe_2O_3^t$, and **(d)** Al_2O_3 contents. Overall, the δ^{65}Cu of the cumulates and ore-forming porphyries shows an increasing tendency with magmatic differentiation, though the porphyry hosts of cumulates do not match well with the quantitative relationship. The δ^{65}Cu of cumulates samples shows a stable range with magmatic fractionation.

The correlation between $\delta^{65}Cu$ and magmatic differentiation indicators such as SiO_2, MgO, FeO^t, and Al_2O_3 abundances (respectively $r^2 = 0.37$, 0.55, 0.51 and 0.67; Fig. 2) highlights the major role of magmatic processes. Our data show that mineral phases like clinopyroxene and amphibole in the studied cumulates have low Cu budgets (*e.g.*, 1.4–3.3 ppm; Table S-4). Consequently, their crystallisation is unlikely to cause substantial Cu isotope fractionation and cannot account for the high Cu budgets (87–528 ppm) of the bulk cumulates. Fe-Ti oxides, also analysed from these cumulates, contain negligible Cu (~0.54 ppm; Table S-4). In contrast, sulfide inclusions contain 1.1–5.8 wt. % Cu, contributing ~100–500 ppm to whole rock budgets and dominating the Cu inventory. Experimental studies indicate sulfide melts preferentially incorporate light Cu compared to coexisting silicate melts ($\Delta^{65}Cu_{sulfide-silicate} \leq 0$; Fig. 3; Savage *et al.*, 2015). It is also noted that the variation of Ni content in sulfides from ~25–27 wt. % to 1 wt. % could generate Cu isotopic fractionation (Xia *et al.*, 2019; Ni *et al.*, 2024). The narrow range of Cu isotopic compositions, along with low Ni content (<0.1 wt. %) in sulfide inclusions of cumulates (Du and Audétat, 2020), indicates rapid sulfide formation, justifying the modelling of the entire cumulate as a single unit. Therefore, the measured bulk rock $\delta^{65}Cu$ variations of these cumulates should reflect the integrated composition of the sulfide inclusions and the shift in Cu isotope composition likely results from sulfide segregation from the melt. In the sulfide saturated (Ripley *et al.*, 2015; Zhao *et al.*, 2017; Liu *et al.*, 2023) magmatic system, sulfide segregation from basaltic magmas could result in the residual melt being more enriched in $\delta^{65}Cu$ (Fig. 3). Therefore, the isotopically light Cu cumulate segregation will generate an isotopically heavy upper continental crust (Liu *et al.*, 2023).

To better understand the effect of sulfide segregation during fractional crystallisation on the variation of Cu isotopic compositions, we conducted simulations using the Rayleigh fractionation equations as follows in Equations (1) to (3):

$$C_{silicate\ melt} = C_0 * F^{(D-1)} \quad \text{Eq. 1}$$

$$\delta^{65}Cu_{silicate\ melt} = (\delta^{65}Cu_0 + 1000) * f^{(\alpha-1)} - 1000 \quad \text{Eq. 2}$$

$$\delta^{65}Cu_{cumulate} = (\delta^{65}Cu_0 + 1000) * (1 - f^{\alpha})/(1 - f) - 1000 \quad \text{Eq. 3}$$

where α represents the equilibrium Cu isotope fractionation factor between sulfide and the residual silicate melt; C_0 and $C_{silicate\ melt}$ are element concentrations of the initial and the evolving silicate melts; D is the partitioning coefficient of Cu between cumulate and silicate melt; F denotes the mass fraction of the evolving silicate melt. The fraction of Cu remaining in the residual melt (f) is calculated by $f = (1 - F) * (C_{silicate\ melt}/C_0)$, assuming an initial Cu content of ~60 ppm, typical of primary continental arc basalts, and a $\delta^{65}Cu$ of 0.06 ‰, consistent with the Bulk Silicate Earth (see Fig. 3; Liu *et al.*, 2015). Choosing different initial Cu or $\delta^{65}Cu$ values in the model may lead to different $\delta^{65}Cu$ values for the predicted melts but would not change the relative $\delta^{65}Cu$ variation between the parental melts and evolving melts. The $\alpha_{sulfide\ melt\text{-}silicate\ melt}$ is assumed to remain constant during magmatic differentiation. Because of the insignificant Cu content in silicates and oxides, $\alpha_{sulfide\ melt\text{-}silicate\ melt}$ is approximately equal to $\alpha_{cumulates\text{-}silicate\ melt}$. These cumulates have crystallisation temperatures (969–1083 °C), pressures (3.8–7.0 kbar) and oxygen fugacities of ΔFMQ +0.7 to +1.3 (Table S-2). Under these conditions and Ni-poor sulfides, the Cu^+ dominates in the silicate melt and sulfide melt and the

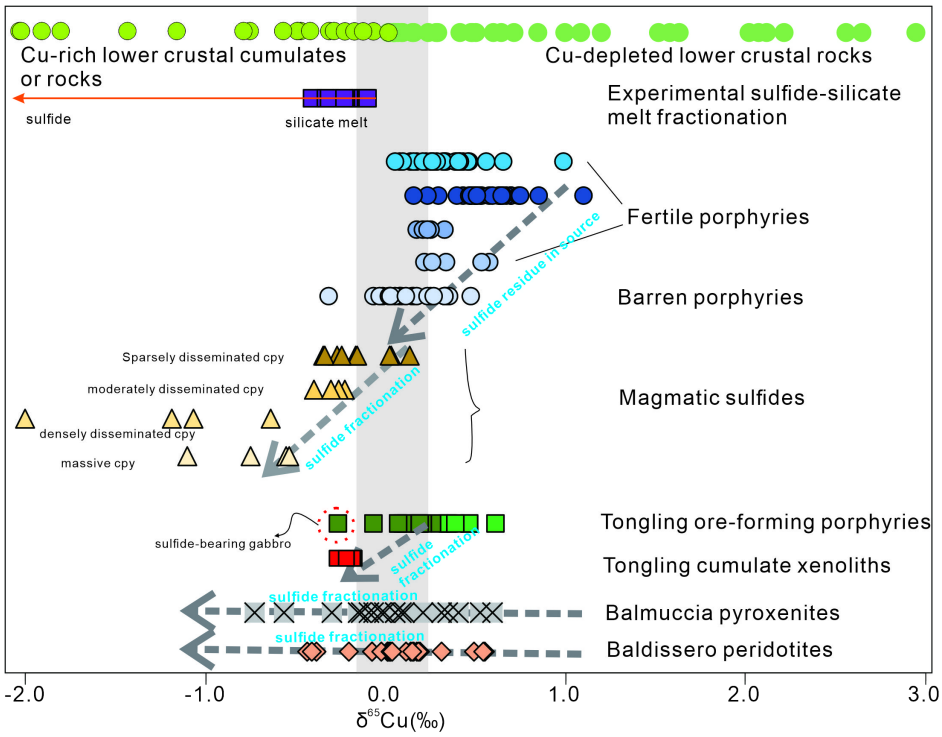

Figure 3 Copper isotopes of ore-forming porphyries and sulfide-bearing cumulate xenoliths in Tongling ore district compared with other sulfide saturated magmatic systems worldwide. Data sources as follows: fertile and barren porphyries in the porphyry Cu system (Zheng *et al.*, 2019); sparsely/moderately/densely/massive chalcopyrite (cpy) in a magmatic sulfide ore system (Zhao *et al.*, 2017); sulfide saturated mantle peridotites or pyroxenites (Huang *et al.*, 2017; Zou *et al.*, 2019). The equilibrium Cu isotope fractionation between sulfide and silicate melts is from the experimental work of Xia *et al.* (2019); Cu-rich lower crustal cumulate or rocks and Cu-depleted lower crustal rocks (Liu *et al.*, 2023 and references therein). Noting that sulfide segregation (or the residue in the source) will consistently enrich the differentiated melt in $\delta^{65}Cu$. Gray band represents the range for Bulk Silicate Earth from Liu *et al.* (2015).

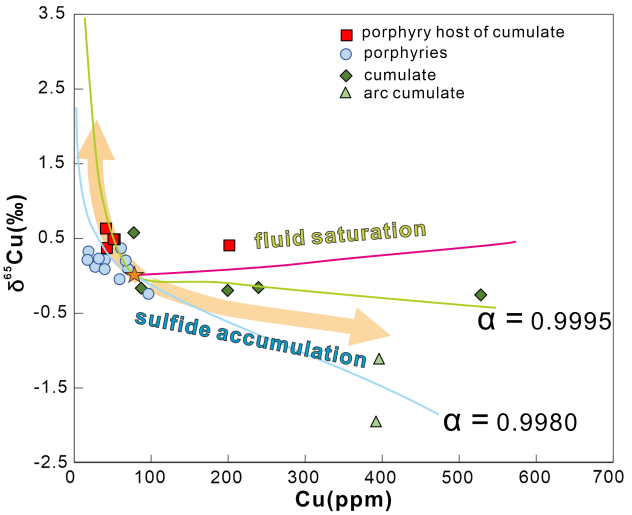

Figure 4 The correlation between δ^{65}Cu and Cu content for cumulates and ore-forming porphyries at Tongling mining district. After sulfide segregation in the cumulates, the ore-forming porphyries obviously move towards more Cu depletion and a heavy copper isotopic trend. In the modelling, the initial melt (star) has ~60 ppm Cu and Cu isotopic composition (δ^{65}Cu) of 0.06 ‰ equal to that of the BSE (Liu *et al.*, 2015); the *D* value is 8, assuming sulfide fraction is 0.01 and $D_{sulfide/melt}$ = 800 (Lee *et al.*, 2012). The δ^{65}Cu and Cu content of arc cumulates are collected from Liu *et al.* (2023). The pink line represents the modelling of fluid saturation process as described in Guo *et al.* (2020).

corresponded equilibrium Cu isotope fractionation factors ($\alpha_{sulfide-silicate\ melt}$) are ~0.9995 to 0.9980 (Xia *et al.*, 2019). It is obvious that the sulfide-bearing cumulates tend to show lower δ^{65}Cu relative to the initial basaltic melt and the differentiated magmas show higher δ^{65}Cu (Fig. 4). Though the model makes little difference to the overall δ^{65}Cu enrichment trend caused by sulfide segregation during magmatic differentiation, with one fluid inclusion-bearing sample deviating (sample JY-6h).

Geological Implications

Porphyry Cu (Au, Mo) deposits are typically hosted in rocks ranging from intermediate to felsic compositions, which have undergone a range of geological processes from the mantle source to the surface (Sillitoe, 2010). During partial melting of the mantle, copper isotopes are essentially unfractionated, with the copper isotopic compositions of basaltic magma or mantle rocks closely aligning with values representative of the Bulk Silicate Earth (−0.14 to ~+ 0.20 ‰; Savage *et al.*, 2015; Liu *et al.*, 2015). As the basaltic magmas stagnate at or near the crust-mantle boundary, deep crustal differentiation processes facilitate a substantial loss of metals from the magma to crystallising cumulate sulfides (Du and Audétat, 2020). This process is pivotal in imprinting heavy copper isotopic signatures onto evolved, intermediate composition porphyries (Fig. S-5). As derivative intermediate magmas ascend to shallow depths (5–15 km), fluid saturation and exsolution occur (Fig. S-5). The exsolved fluid phases are enriched in heavy Cu isotopes (^{65}Cu) relative to the coexisting silicates (Fig. 4; Guo *et al.*, 2020), continuous migration of low density hydrothermal fluids from the mineralisation centre leads to a systematic increase in Cu isotope ratios from centre outward (Li *et al.*, 2010; Mathur *et al.*, 2009). This overall Cu isotopic evolution of porphyry Cu ore deposit leads to a continuous increase in Cu isotopic signatures from the source to the final deposition site. The porphyry rocks with elevated concentrations of heavier copper isotopes should identify potential porphyry Cu orebodies. This assertion is supported by the findings of Zheng *et al.* (2019), who have shown that many fertile porphyries show heavier copper isotopes than barren ones. On the premise that Cu isotope behaviour is well estimated in the weathering processes, the heavy Cu signature may be an exploration vector in detrital materials or downstream of a porphyry.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2545.

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