Geochemical Perspectives Letters

Dominant monosulfide solid solution fractionation causes Cu deficit in continental crust

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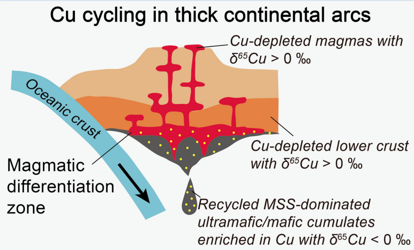
Abstract



It remains unclear how Earth's continental crust became deficient in Cu. Lower crustal cumulates from the Gangdese continental arc present key evidence. These cumulates are Cu-rich and exhibit significant $\delta^{65}Cu$ variability (−2.09 ‰ to +0.51 ‰), attributed primarily to the fractionation involving Monosulfide Solid Solution (MSS). Combined with the systematic Cu depletion and positive $\delta^{65}Cu$ signatures of the Gangdese differentiated arc magmas and the bulk continental crust, we propose that widespread MSS segregation occurs at the base of continental arcs. This process distinguishes continental arcs from island arcs: in the former, higher pressures promote earlier sulfide saturation, and MSS dominated segregation slows the rate of Cu depletion during differentiation. Ultimately, the continuous foundering of these sulfide-rich mafic cumulates drives the continental crust toward a silica-rich and Cu depleted bulk composition.

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Introduction

Present day continental crust on the Earth, thought to form mainly from mantle derived magmas at subduction zones, has a unique silicic bulk composition compared with other rocky planets in the inner Solar System (Rudnick, 1995). How such a silicic crust was generated from mantle derived magmas, which are primarily basaltic, remains enigmatic. Apart from Mg and Fe, the continental crust is also depleted in chalcophile elements (Cu, Ni, PGE, and S) relative to the primitive basaltic magmas (Rudnick and Gao, 2003; Park *et al.*, 2015). This coupled depletion suggests that chalcophile elements and their isotopes could hold crucial clues about the origin and evolution of the continental crust. In recent years, the foundering of sulfide-bearing mafic lower crust has been proposed to lead to the formation of a silicic continental crust depleted in chalcophile elements (Lee *et al.*, 2012; Chiaradia, 2014; Jenner, 2017). Notably, the decrease of Cu content in continental arc magmas, induced by sulfide segregation with differentiation, occurs earlier but proceeds more gradually than in island arc magmas (Chiaradia, 2014; Lee and Tang, 2020; Li *et al.*, 2021). This implies that the processes responsible for Cu depletion in continental arcs may differ from those in island arcs, a phenomenon that remains poorly understood.

Copper isotopes can be fractionated during a variety of high temperature geological processes, including source metasomatism, partial melting, magmatic differentiation, and fluid-rock interaction (Liu *et al.*, 2015, 2023; Luo *et al.*, 2023; Wang *et al.*, 2024). Because Cu is a strongly chalcophile element, its isotopic fractionation is highly sensitive to sulfide-related processes such as sulfide saturation, segregation, and decomposition. Meanwhile, substantial variations in Cu isotope compositions have been observed in continental arc magmas, continental crustal rocks, and cumulates (Moynier *et al.*, 2017; Liu *et al.*, 2023), in contrast to the relatively homogeneous values of the non-metasomatised mantle, island arc magmas, and mid-ocean ridge basalts (MORBs) (Liu *et al.*, 2015). This distinction suggests that Cu isotopes can offer valuable insight into the process of sulfide segregation during the differentiation of continental arc magmas. When combined with Cu contents, they may provide direct constraints on the mechanism responsible for chalcophile element deficiency in the continental crust, thereby yielding new perspectives on its origin and differentiation.

The Gangdese magmatic arc in southern Tibet (Fig. 1) was a typical Andean-type continental arc prior to the India-Asia collision (Zhu *et al.*, 2011). In its eastern segment, the lower crustal section is exposed as Mesozoic amphibolite to granulite facies, mafic-ultramafic metamorphic rocks, including meta-gabbros and hornblendites. The meta-gabbros are generally regarded as parental basaltic arc magmas, whereas hornblendites with cumulate textures represent the products of intracrustal differentiation (Xu *et al.*, 2019; Z. Zhang *et al.*, 2022). These cumulates have variable but in many cases elevated Cu contents (commonly >200 μg/g), potentially acting as a complementary Cu-rich reservoir to the Cu-depleted bulk continental crust. The co-existence of parental arc magmas and their lower crustal cumulates makes the Gangdese arc an ideal natural laboratory

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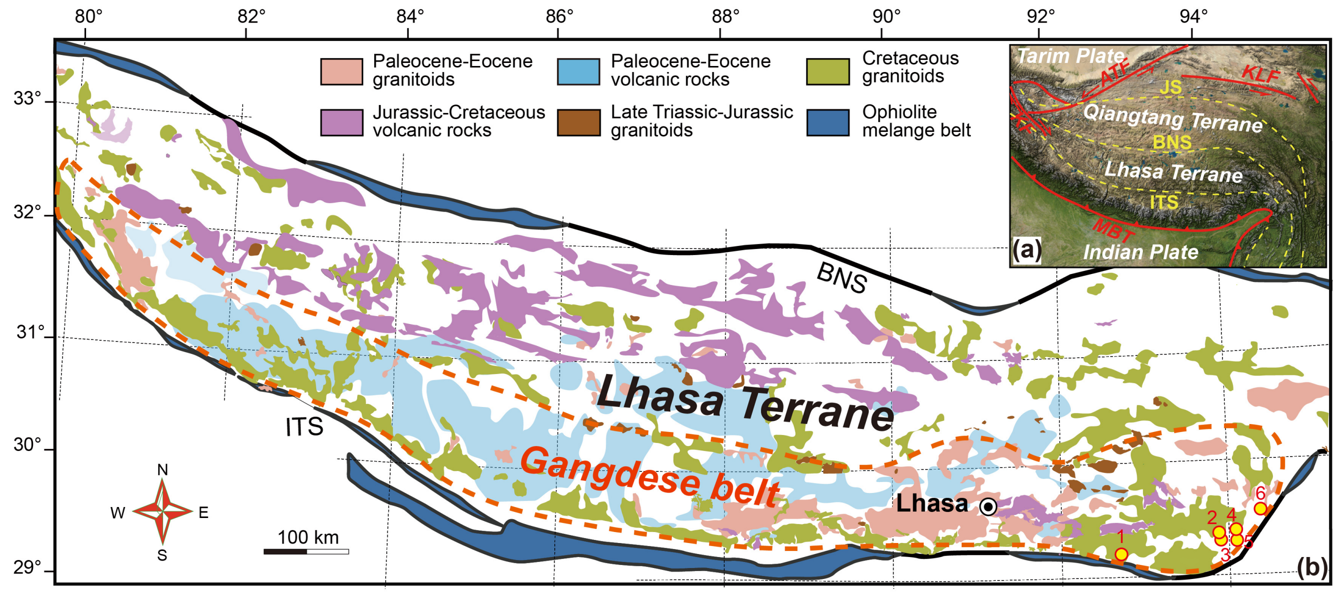

Figure 1 Geological map of the Gangdese continental arc and sampling locations. **(a)** Simplified geologic map of the Tibetan Plateau. **(b)** Tectonic framework of the Lhasa terrane, showing distribution of Gangdese arc magmas; JS = Jinsha suture, BNS = Bangong-Nujiang suture, ITS = Indus-Yarlung-Tsangpo suture, MBT = Main Boundary Thrust, ATF = Altyn Tagh fault, KF = Karakorum fault, KLF = Kunlun fault. Sampling locations: 1 = Cuijiu, 2 = Jinba, 3 = Sengbo, 4 = Zhangxiraodeng, 5 = Milin, 6 = Milin meta-gabbro.

for studying the origin and differentiation of continental crust from the perspective of its Cu systematics.

Discussion

Copper isotope fractionation in continental lower crustal cumulates. The most notable finding of this study is that the Cuijiu and Sengbo lower crustal cumulates in the Gangdese arc have very light Cu isotope compositions, whereas the Milin, Zhaxiraodeng, and Jinba counterparts have compositions similar to the bulk silicate Earth (Fig. S-3). The samples were collected from newly excavated railway tunnels and are pristine, showing no signs of secondary sulfides or oxides replacing primary sulfides (Fig. S-1), thereby preventing potential effects from the surface weathering and alteration.

Copper isotope compositions of the lower crust can also be modified by metasomatism or partial melting. In sulfate-rich fluids/melts, Cu^{2+} dominates and exhibits positive δ^{65}Cu; metasomatism by such agents, accompanied by the formation of secondary sulfides, would cause the lower crust to inherit heavy isotope signatures (Luo *et al.*, 2023), inconsistent with the light Cu isotope enrichment observed in the Cuijiu and Sengbo cumulates. Alternatively, if oxidised fluids/melts dissolved primary sulfides in the lower crust during metasomatism, ^{65}Cu would be preferentially released as Cu^{2+}, resulting in a residue enriched in light Cu isotopes (G. Zhang *et al.*, 2022; Luo *et al.*, 2023). However, no evidence of dissolution or oxidation is present along sulfide grain boundaries or fractures (Fig. S-1), and the Cuijiu and Sengbo samples with negative δ^{65}Cu values are also Cu-rich (Fig. 3a), both of which argue against this process as the primary control. Partial melting of sulfide-rich lower crust likewise fails to explain the data: preferential partitioning of ^{63}Cu into the extracted sulfide melt which would leave the residue with elevated δ^{65}Cu (Luo *et al.*, 2023), opposite to that observed in the Cuijiu and Sengbo cumulates.

Globally, non-metasomatised mantle and various types of basalts (continental basalts, arc basalts, MORBs, and OIBs) exhibit broadly similar and homogeneous δ^{65}Cu values (Fig. S-3), indicating that Cu isotopes are little fractionated during mantle partial melting (Liu *et al.*, 2015; Huang *et al.*, 2017; Wang *et al.*, 2019). Therefore, arc magmas may directly inherit their Cu isotope signatures from the mantle source. However, while metasomatised mantle peridotites show significant δ^{65}Cu heterogeneity (−0.64 ‰ to +1.82 ‰) (Liu *et al.*, 2015; Huang *et al.*, 2017), this range does not reach the strongly negative δ^{65}Cu observed in our samples (Fig. S-3). Furthermore, all cumulate samples analysed here have similar whole rock Sr-Nd isotopic compositions (Fig. S-5), indicating a shared mantle source. Meanwhile, the Milin meta-gabbros, which represent parental magmas, show relatively homogeneous δ^{65}Cu values similar to those of the Milin, Zhaxiraodeng, and Jinba cumulates, and comparable to values for non-metasomatised mantle (Liu *et al.*, 2015) (Fig. S-3). Consequently, the pronounced negative δ^{65}Cu of the Cuijiu and Sengbo cumulates is unlikely to reflect mantle inheritance.

With alternative mechanisms excluded, sulfide segregation during magmatic differentiation emerges as the most likely process governing the observed Cu isotope signatures. In the Gangdese cumulates, the positive correlation between Cu and S contents indicates that Cu occurs predominantly in sulfides (Fig. S-2b), consistent with Cu enrichment through sulfide accumulation. Although sulfides are known to preferentially incorporate ^{63}Cu during segregation, thereby enriching the cumulates in light isotopes (Liu *et al.*, 2023), the key controlling factors remain unclear. Experimental data show that Cu isotopes are only slightly fractionated during high Ni sulfide (~25 wt. % Ni in sulfide) segregation, but experience significant fractionation during the segregation of low Ni sulfides (0.1 to 1.2 wt. % Ni in sulfide), prompting the interpretation that Ni content exerts primary control (Xia *et al.*, 2019). In the case of Gangdese cumulates, sulfides typically contain <2.0 wt. % Ni (Table S-2), falling within the low Ni category defined by Xia *et al.* (2019). Yet, not all of these samples display negative δ^{65}Cu (Fig. 3), challenging this interpretation. A similar inconsistency is evident in island arc systems.

Sulfide inclusions in Kohistan cumulates, representative of island arc lower crust, primarily consist of sulfide melts with Ni contents usually <2.0 wt. % (J. Zhang et al., 2022) (Table S-2). If segregation of low Ni sulfide genuinely drove

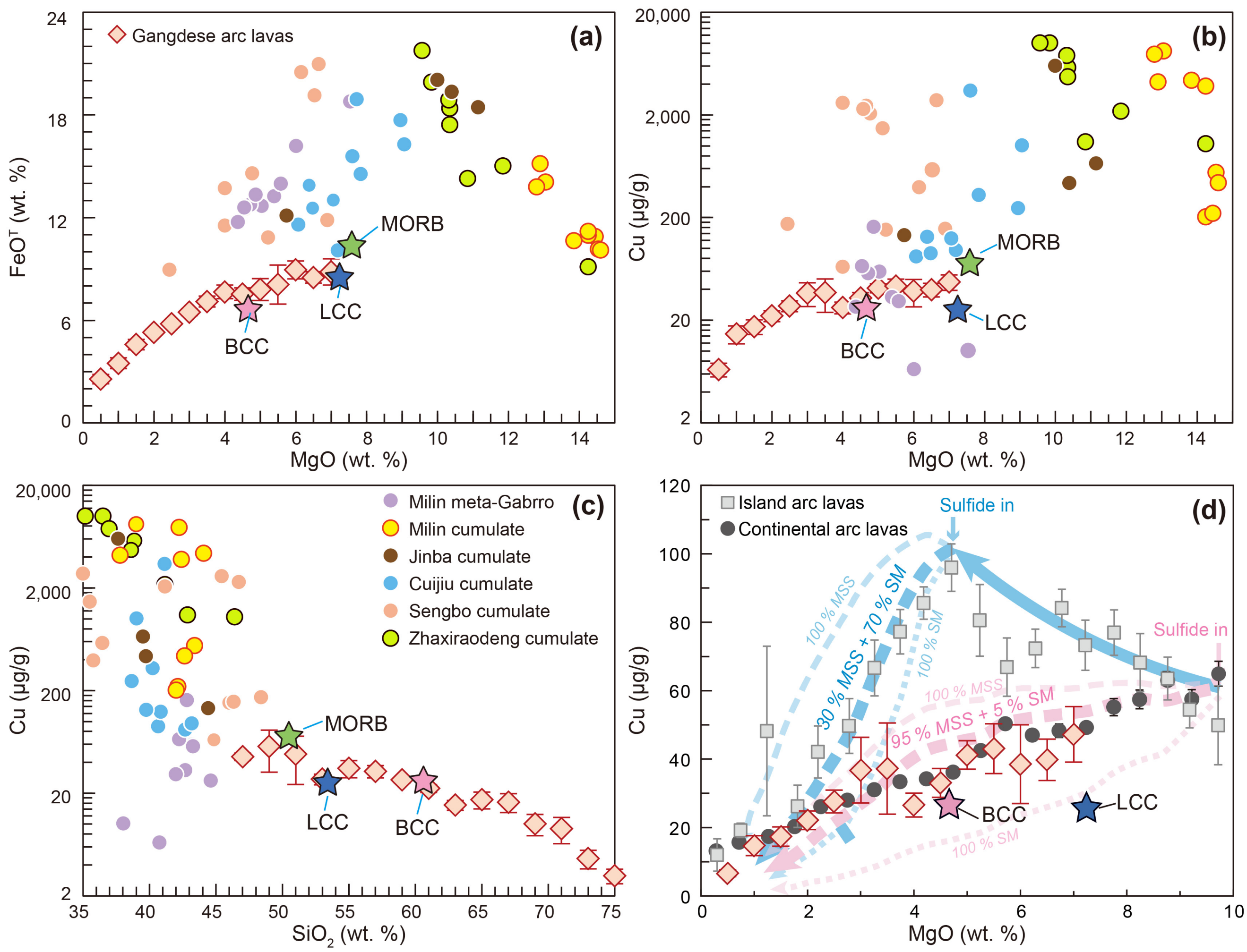

Figure 2 Elemental variations of the lower crustal cumulates and arc magmas from the Gangdese arc. **(a)** FeO^T *versus* MgO, **(b)** Cu *versus* MgO, **(c)** Cu *versus* SiO_2, and **(d)** Observed *vs.* modelled Cu evolution trends in island, continental and Gangdese arc lavas. Individual symbols of Gangdese arc lava in **(a)**, **(b)**, and **(d)** represent FeO^T and Cu contents of 0.5 wt. % of MgO intervals; the Gangdese arc lava individual symbols in **(c)** represent Cu contents at 2 wt. % at SiO_2 intervals. In **(d)**, the curves show quantitative modelling results based on crystallisation experiments on hydrous arc magmas (Nandedkar *et al.*, 2014) and experimentally constrained partitioning of Cu between sulfide phases and silicate melt (Li and Audétat, 2015), reflecting ideal equilibrium behaviour. The blue solid line with an arrow represents Cu evolution before sulfide saturation, whereas the blue dashed lines represent that sulfide saturation occurs at ~4.8 wt. % MgO, followed by sulfide precipitation. The thick blue dashed line shows sulfide composition of 30 % MSS + 70 % SM, whereas the thin blue dashed line represents 100 % MSS, and the thin blue dotted line represents 100 % SM. The thick pink dashed line displays the precipitating sulfide at beginning with 95 % MSS and 5 % SM, with the thin pink dashed line representing 100 % MSS, and the thin pink dotted line representing 100 % SM. (See Supplementary Information for numerical modelling details). Error bars on the data points represent 2 standard deviations (s.d.). Data for global island and continental arc volcanic rocks (Cascades, Andes, and Mexico) are from the PetDB (https://search.earthchem.org/) and GEOROC databases (https://georoc.eu/georoc/). The average MORB, bulk continental crust (BCC), and lower continental crust (LCC) value are from Gale *et al.* (2013) and Rudnick and Gao (2003), respectively. MSS = monosulfide solid solution, SM = sulfide melt.

^{63}Cu enrichment, then differentiated island arc magmas should display positive δ^{65}Cu. Instead, observations show that their δ^{65}Cu values cluster around zero, comparable to those of MORBs and non-metasomatised mantle (Liu *et al.*, 2015; Wang *et al.*, 2019) (Fig. S-3). This means that intense Cu isotope fractionation is not controlled by the Ni content of the segregated sulfide, but is likely caused by other factors.

Sulfur in basaltic melt is saturated as immiscible sulfide melt and/or MSS. In the experiments of Xia *et al.* (2019), high Ni sulfides were mainly sulfide melt, whereas low Ni sulfides were dominated by MSS (Fig. S-4). A more plausible explanation, therefore, is that the significant Cu isotope fractionation observed in those experimental products could be attributed to the segregation of MSS at relatively lower temperatures, whereas MSS segregation at higher temperatures or sulfide melt segregation alone induces only limited fractionation. This framework explains the lack of pronounced Cu isotope variation in island arc systems (Fig. S-3), where sulfide melt segregation dominates despite low Ni contents (J. Zhang et al., 2022); it is also consistent with the Cu isotope characteristics of the Gangdese continental arc. As shown in Figure S-4, the primary segregated sulfide in the Gangdese cumulates is MSS. The Cuijiu and Sengbo samples have markedly lower MgO contents (Fig. 2) and predominantly fall on the third segment of the Z-shaped cumulate line (Fig. S-2a), along with lower amphibole crystallisation temperatures (Fig. S-6), indicating crystallisation from more evolved, lower temperature parental magmas. At relatively lower temperatures, the segregation of MSS led to substantial Cu isotope fractionation, enriching the cumulates in light Cu isotopes (Fig. 3), as well as driving the differentiated Gangdese arc magmas toward positive δ^{65}Cu (Liu *et al.*, 2023; Wang *et al.*,

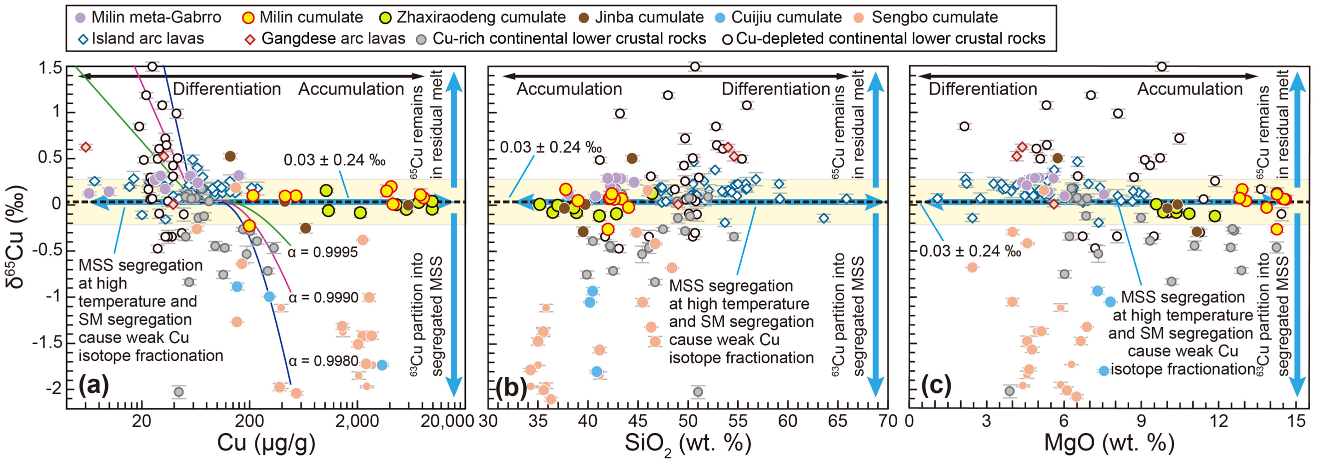

Figure 3 The δ^{65}Cu variation of Gangdese lower crustal cumulates. **(a)** δ^{65}Cu *versus* Cu, **(b)** δ^{65}Cu *versus* SiO_2, **(c)** δ^{65}Cu *versus* MgO. Data for global island and Gangdese arc lavas, and continental lower crustal rocks are shown for comparison (Liu *et al.*, 2015, 2023; Wang *et al.*, 2019). The horizontal dashed line and yellow shaded area in each panel represent the δ^{65}Cu range of non-metasomatised mantle (δ^{65}Cu = +0.03 ‰ ± 0.24 ‰). Error bars on the data points represent 2 standard deviations (s.d.). The isotope fractionation factors ($\alpha_{\text{sulfide -silicate magma}}$) were assigned at 0.9995, 0.9990 and 0.9980, respectively; MSS = monosulfide solid solution, SM = sulfide melt.

2024). In contrast, the Milin, Zhaxiraodeng, and Jinba cumulates, which mainly occupy the second segment of the Z-shaped trend, crystallised from more primitive magmas at higher temperatures, producing only weak Cu isotope fractionation during MSS segregation.

The capacity of MSS to fractionate Cu isotopes arises from its preferential incorporation of Cu^{+}, which drives a redistribution of Cu^{+} and Cu^{2+} between the segregated MSS and the residual silicate melt. Such a process is analogous to redox reaction, a mechanism well known to strongly induce Cu isotope fractionation (Mathur *et al.*, 2009). When magmatic differentiation occurs at relatively lower temperatures, ^{63}Cu would tend to concentrate in Cu^{+}-rich MSS, yielding a negative δ^{65}Cu signature in the cumulates. This mechanism has been confirmed in magmatic Ni-Cu deposits, where Cu isotope variations of up to 2 ‰ were recorded during MSS sulfide melt fractionation in the Tulaergen deposit, Xinjiang, China (Zhao *et al.*, 2017).

Implications for origin of Cu-depleted silicic continents. About 80–95 % of the continental crust is thought to have formed in subduction zones through the accretion of arc magmas (Rudnick, 1995). Relative to primitive basaltic arc magmas, the andesitic continental crust is depleted in Mg, Fe, and Cu, suggesting extensive differentiation. Owing to the high sulfide/silicate melt partition coefficients ($D_{\text{sulfide melt/silicate melt}}$ = 1100–8400, $D_{\text{MSS/silicate melt}}$ = 530–1700) (Li *et al.*, 2021), Cu would be stripped away from the magma and sequestered into segregated sulfides as differentiation proceeds. Thus, in the Gangdese arc, the systematic Cu depletion in intermediate-felsic magmas relative to basaltic magmas (Fig. 2b-d) indicates the extensive development of Cu-rich mafic-ultramafic cumulates in the lower crust (Xu *et al.*, 2019; Z. Zhang et al., 2022). Similarly, a depletion in Cu is also characteristic of differentiated arc magmas globally (Chiaradia, 2014; Jenner, 2017), implying that the formation of Cu-rich cumulates is a pervasive process in the lower crust of both continental and island arcs (Lee *et al.*, 2012; Lee and Tang, 2020).

Although variables such as oxygen fugacity and H_2O content may influence sulfide saturation (Wang *et al.*, 2024), the decrease of Cu with magmatic differentiation occurs systematically earlier in continental arcs with thick crust than in island arcs with thin crust (Fig. 2d), implicating pressure as a first order control. Increased pressure not only directly reduces sulfur solubility in silica melts (Maréchal *et al.*, 1999), but also indirectly favours sulfide saturation by promoting the fractionation of mafic minerals (*e.g.*, garnet) and Fe oxides, which leads to simultaneous Fe depletion and magma reduction (Jenner *et al.*, 2010; Lee and Tang, 2020; Tang *et al.*, 2020). Specifically, under otherwise equivalent conditions, increased pressure facilitates the crystallisation of MSS but suppresses sulfide melt exsolution (Bockrath

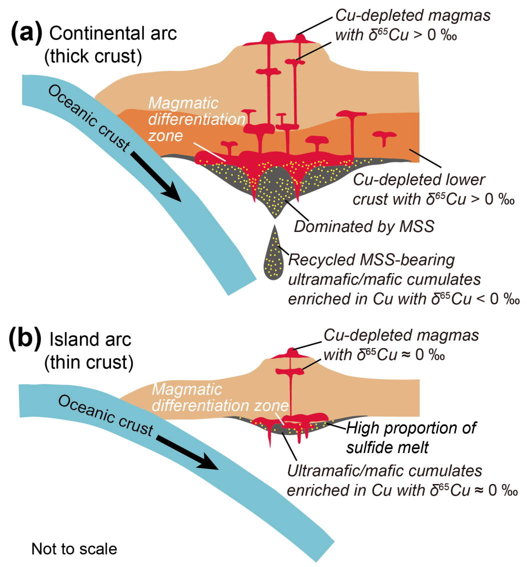

Figure 4 Cartoon showing intracrustal sulfide fractionation in continental arcs *vs.* island arcs. Continental arcs with thicker crust induce abundant MSS crystallisation but suppress sulfide melt fractionation, leading to earlier yet more gradual Cu depletion during differentiation compared with island arc magmas. Fractionation of MSS also results in enrichment of the lighter Cu isotopes in continental arc cumulates, leaving behind differentiated magmas characterised by low Cu content and high δ^{65}Cu. In contrast, sulfide melt fractionation is unable to induce significant Cu isotope fractionation in island arcs. Co-segregation of sulfides, mafic minerals and Fe oxides at the roots of continental arcs removes Cu, Mg and Fe from the magmas. Foundering of dense, Cu-rich mafic/ultramafic cumulates drives the continental crust toward a silicic bulk composition deficit in Cu.

et al., 2004). This could be the major reason why MSS and sulfide melt are dominant in the lower crust of continental and island arcs, respectively, as inferred from the compositions of Cu isotopes and of hosted magmatic sulfide inclusions (Figs. 3, S-4). Since the partition coefficient of Cu in MSS is lower than that in sulfide melt (Li *et al.*, 2021), the MSS dominated fractionation would cause Cu contents in continental arc magmas to decrease more gradually, despite earlier saturation, than in island arc magmas (Fig. 2d). This inference is supported by the Cu content of sulfide inclusions found within the continental lower crustal cumulates from the Gangdese arc and the North China Craton, which exhibit an average Cu content of 4.0 wt. %, markedly lower than the 23.5 wt. % average observed in those from the Kohistan island arc (Fig. S-4, Table S-2).

In the deep roots of thick continental arcs, the simultaneous separation of MSS dominated sulfides, mafic minerals, and Fe oxides results in the enrichment of Mg, Fe, and Cu, as well as light Cu isotope compositions, in the lower crustal cumulates. The complementary overlying crustal sections, by contrast, are depleted in Cu and display positive δ^{65}Cu values (Liu *et al.*, 2023). With continued crustal thickening, the mafic-ultramafic cumulates at the base of continental arcs are progressively metamorphosed into eclogite or garnet-bearing amphibolite. Such eclogitised lower crust, together with the subcontinental mantle, is denser than the underlying peridotitic mantle and is thought to eventually founder *en masse* into the convecting mantle. This process would drive the continental crust toward a silica-rich and Cu-depleted bulk composition (Fig. 4).

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The data supporting the findings of this study are also available at the figshare data repository.

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2601.

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