

The Cu Conundrum: Cu Budget During Partial Melting of Earth's Upper Mantle

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Abstract

Primitive basaltic glasses from mid-ocean ridges (MORB), ocean islands (OIB) and arcs contain three to five times the Cu as the currently accepted primitive upper mantle (PUM) value, suggesting a bulk partition coefficient $D_{\text{Cu}}^{\text{mantle/melt}}$ of ~ 0.20 . Sulfide, with a $D_{\text{Cu}}^{\text{sulfide/melt}}$ of > 250 is presumed to be ubiquitous in the mantle, but its presence during melting is not commensurate with the Cu abundances in most basalts. To address this conundrum we determined D_{Cu} in olivine and orthopyroxene at 1250–1525 °C and 1.0 GPa in a hydrous basalt and KLB1 peridotite, at $f\text{O}_2$ near to melting conditions of the upper mantle. The measured $D_{\text{Cu}}^{\text{ol/liq}}$ of 0.06–0.21 and $D_{\text{Cu}}^{\text{opx/liq}}$ 0.15–0.82 do not vary with melt fraction, nor significantly with $f\text{O}_2$, and can be combined with estimates for D_{Cu} for clinopyroxene into melting models to examine the Cu contents of mantle-derived melts. The Cu abundances for MORB, OIB, and arc glasses are all explicable by the melting (up to 15%) of the silicate-only portion of the mantle in which Cu behaves as a mildly incompatible element $D_{\text{Cu}}^{\text{mantle/melt}}$ of ~ 0.26 . For Cu to be enriched in basaltic melts in the presence of sulfide, the melt/sulfide ratio, or the oxidation state of the mantle during melting, must be significantly high to diminish the potential of sulfide to sequester any Cu.

Conclusion

Our results suggest the role of sulfide during mantle melting may be insignificant in regards to controlling the concentration of moderately chalcophile elements like Cu, and confirm that the previously estimated Cu content for PUM of 20 ppm is correct.

The dynamic nature of iron oxyhydroxides on modes of ion retention

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Introduction

Iron oxyhydroxides exert a dominant control on the fate and transport of numerous elements ranging from arsenic to phosphate to uranium. Owing, in part, to the redox active metal center, iron oxyhydroxides are dynamic solids within soils and sediments. As a consequence, iron retention is not strictly an adsorption phenomena but rather commonly also entails uptake into the mineral structure.

Conclusions

The iron oxide ferrihydrite is particularly prone to Fe(II) induced transformation to thermodynamically more stable phases such as goethite. Upon formation of the secondary phases, elements such as arsenic and uranium can be incorporated into the surface structure or adsorbed on the mineral surface; in the case of uranium, we also see reduction and secondary precipitation of UO_2 as a common retention mechanisms. However, competing ions such as phosphate as well and structural dopants (e.g., Al) modify the transformation pathway of ferrihydrite and may therefore limit formation of secondary phases that can host arsenic and uranium. The mode of retention is, however, often not singular, with multiple mechanisms in operation. Further, geochemical gradients, and in particular redox gradients resulting from variations in oxygen egress, lead to progressive changes in retention mechanisms. As an example, uranium retention often occurs via adsorption at high oxygen concentrations and progresses through a coprecipitated phase to a heterogeneously nucleated uraninite phase with successfully lower oxygen partial pressures. Here, variation in retention mechanisms and their spatial distribution within soil/sediment assemblages are illustrated.