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The copper isotope geochemistry of rivers and the oceans

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The trace metal geochemistry of the oceans has undergone a flowering of interest over the past decade. This new impetus has often focused on the role of trace metals in biological functions. Though most attention has focused on Fe, it is also clear that many other trace metals have important biological functions that partially control trace metals in the oceans. Among the transition metals - and in addition to Fe - Zn, Cd, Mn, Co, Ni and Cu all have clear biological roles. For some of these metals, however, scavenging by particulates plays a role that is at least as important as direct biological cycling. The complexities of the marine geochemistry of many trace metals might be addressed through the extra information available from their isotopic systems. Here, we present the first extensive dataset for copper (Cu) isotopes in aqueous samples from the surface Earth.

An array of rivers, from a variety of tectonic and climatic settings, exhibit a range in dissolved δ^{65}Cu (relative to NIST SRM 976) of 0 to +1.6 per mil. The discharge-weighted average δ^{65}Cu and Cu concentration for the studied rivers, representing around 25% of the global riverine water discharge, are 0.68 ‰ and 18.8 nmol kg^{-1}, respectively. Isotopic data for the dissolved phase in small estuaries exhibit only minor variation and pseuso-conservative behaviour. The dissolved Cu in the studied rivers and the estuaries is isotopically heavy, while analyses of the particulate phase in the estuaries reveal a complementary light pool. The isotopic composition of the total Cu inventory is, however, close to the ultimate source of the riverine Cu, rocks. Data for seawater samples exhibit even heavier Cu isotopic compositions than the riverine input, at δ^{65}Cu = 0.8-1.5 ‰.

These data, along with published constraints, suggest an origin for the heavy dissolved phase in rivers in a competitive partitioning of a weathered pool of Cu between an isotopically light fraction adsorbed to particulates and a heavy dissolved fraction dominated by Cu bound to strong organic complexes. The even heavier isotopic composition of seawater is unlikely to arise from additional non-riverine sources, but rather originates from intra-oceanic processes. The small dataset presented here is most consistent with further intra-oceanic isotopic partitioning between an isotopically light scavenged pool adsorbed to particulates and a heavy dissolved pool strongly bound to organic ligands. Scavenging appears to have greatest impact in the surface ocean and least in both the oxygen minimum zone and the ocean bottom, perhaps reflecting the relative importance of scavenging and the sequestration of light Cu to particulate material at different depths.