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Unusually heavy Cu isotope signatures of the Changjiang (Yangtze) River: The impact of chemical weathering and delivery to the oceans

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The stable Cu isotope proxy in riverine samples bears the unique potential to trace continental weathering and anthropogenic activities and provides insights into biogeochemical metal cycling processes. δ^{65}Cu values in suspended particulate matter (SPM) and dissolved load (DCu) are presented for the Changjiang River basin (China) from its headwater on the Tibetan Plateau to its estuary. The Changjiang River samples show uncommonly heavy Cu isotopic compositions, 0.8–1 ‰ heavier than the global river average, initially attributed to anthropogenic influence. We demonstrate that Cu isotopic compositions show significant variations along the river that cannot be explained by human activities alone.

Cu_{SPM} isotopic compositions are relatively homogenous (δ^{65}Cu -0.04 to +0.34 ‰), despite their wide range in concentration (24 to 72 µg/g) and an average chemical index of alteration (CIA) value of 71.2. Correlations between Cu/Ca_{SPM}, Na/Ca_{SPM}, Mg/Ca_{SPM}, and Al/Ca_{SPM} argue for oxidative weathering of clay minerals with variable organic complexation. Furthermore, low trace metal (Cu, Cd, Ni, Zn) enrichment factors argue for limited anthropogenic sources of these metals.

DCu isotopic compositions are heavy and rather heterogenous (δ^{65}Cu +0.88 to +1.75 ‰, 0.52-18 nmol/L), indicating a variety of lithological weathering sources. Total dissolved solids together with high DCu concentration and low δ^{65}Cu values reveal extensive evaporite dissolution (SO_4, Cl) in the source of Changjiang River. High DCu concentrations and heavy δ^{65}DCu values in the Middle Lower Reaches (MLR) document the leaching of Cu deposits and sulfide weathering. Further, organic complexation and anthropogenic influences, including alterations in sediment flux caused by dams, significantly impacting trace metal cycling, play a role in the MLR.

In conclusion, we suggest that the Cu isotopic composition of the Changjiang River is primarily determined by isotopic fractionation during chemical weathering processes. Unusual heavy river-water Cu isotopic signatures require further investigation to understand the complexities of aqueous systems and river fluxes into the oceanic Cu mass balance. Our study shows the potential of the stable Cu isotope system to be used as a paleo-weathering proxy.