

Metal isotope signatures in Mn-rich pelagic sediments: Implications for oceanic budgets

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The isotope systems of trace metal micronutrients like Zn, Cu and Ni offer considerable potential as tracers of the past ocean carbon cycle and/or past ocean oxygenation [e.g., 1]. To ground-truth the use of these novel proxies, recent studies have begun to document the isotope composition of the major oceanic input and output fluxes [2 – 5]. In the case of Zn, the characterised fluxes are approximately in isotopic balance [3]. However, this is not the case for Cu [4]. The budgetary imbalance is particularly marked for Ni [5], for which the known inputs are isotopically light (at about +0.8‰) relative to seawater (at about +1.3‰), while the output to sediments is similar to or isotopically heavier than seawater [5, 6].

A key oceanic output flux of Zn, Cu and Ni is sorption to dispersed Fe-Mn oxide phases found throughout oxic sediments, for which the isotope composition of Fe-Mn crusts has been used as a proxy [2, 6]. In Fe-Mn crusts, trace metals are sorbed to the phyllo-manganate birnessite (δ -MnO₂). However, during diagenesis birnessite transforms to the tectomanganate todorokite. Recent experiments suggest that up to 50% of sorbed Ni is released during this transformation process [7], providing a significant source of Ni to porewaters and, potentially, a benthic return flux to seawater. The isotope effect of this process has not yet been evaluated.

We present Zn, Cu and Ni isotope data for samples from a Mn-rich hemipelagic setting. We find notably isotopically light Ni, Cu and Zn values compared to those observed in Fe-Mn crusts [2, 6, 8]. We attribute these signatures to the diagenetic transformation of birnessite to todorokite, redox-related partitioning, or to a hydrothermal source of metals, and discuss these possibilities in view of the whole oceanic mass balance of these important micronutrients.

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