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Patterns of trace element – metal oxide phase dynamics on an oxygenated continental margin

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The accumulation of manganese and iron oxyhydroxide minerals as seafloor nodules or microparticulates in pelagic clays exerts a major control on the oceanic distribution of many trace elements and their isotopes (TEIs) through adsorption and reactive isotopic fractionation. However, on continental margins, where most sediments are deposited, accumulating Fe- and Mn-oxyhydroxides undergo diagenetic recycling, involving dissolution and precipitation reactions as well as various redox-driven mineral transformations. In addition, changes in porewater composition drive variations in TE speciation and complexation, affecting the reactivity of TEs. These diagenetic processes influence both bulk and mineral-specific metal oxyhydroxide adsorption and isotope fractionation and thus affect the sediment-seawater fluxes of TEIs.

Here, we present TE data from sequential extractions that effectively distinguish between Mn- and Fe-oxyhydroxide-associated TE pools. We investigate continental margin sites in the fully oxygenated Skagerrak Sea, where benthic C-oxidation is dominated by either dissimilatory Fe or Mn reduction. This combination of sites and methods allows for a holistic analysis of the function, specificity, and interplay of Fe- and Mn-oxyhydroxide interactions with a suite of >16 TEs (V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Ba, REEs, W, Tl, Pb, and U).

We map out the specific affinities of TEs towards sediment metal oxyhydroxides find that while most TEs show comparable specific affinities for Fe- and Mn-oxyhydroxides, Fe-oxyhydroxides are the bulk TE host. We also estimate the magnitude of TE liberation associated with diagenetic Fe- and Mn-oxyhydroxide dissolution and transformation to quantify whether TE–metal oxyhydroxide associations result in TE loss or TE recycling within the marine realm. From this analysis, we provide an integrated overview of TE dynamics in relation to Fe- and Mn-oxyhydroxides in a continental margin environment. Our findings refine previous assumptions about TE–metal oxyhydroxide relationships and provide a first-order framework for incorporating the role of metal oxyhydroxides into predictive modeling of TE dynamics in continental margin settings.