



Are Clay Minerals the Primary Control on the Oceanic Rare Earth Element Budget?

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The rare earth elements (REEs) are an important tool for understanding biogeochemical cycling and sedimentary processes in the global ocean. However, ambiguities in the marine REE budgets including the identification of the dominant source of REEs to the ocean hinder their utility. Recent work identifies a potentially dominant benthic sediment dissolution source of REEs to the ocean (Abbott et al., 2015), which would have widespread implications on the interpretation of marine REE records and of Nd isotope records. Here, we use new pore water REE, microbeam imaging and mineralogical data in combination with published pore water REE data to evaluate potential sedimentary REE host phases. Our goal is to identify the phase or phases that interact with the pore fluids and the mechanism behind this interaction to drive a sedimentary flux.

The sedimentary phase most commonly targeted for paleocirculation reconstructing has been Fe-Mn oxyhydroxides because they are assumed to 1) record seawater REE composition by precipitating directly from ambient seawater, and 2) be ubiquitously present as REE enriched, microscopic authigenic grain coatings. Crucially, the distribution, preservation, and formation of these coatings remains poorly understood with no direct, imaging-based identification of their systematic presence to date. Our new mineralogical and direct imaging observations show that authigenic Fe-Mn oxide phases are not sufficiently abundant to account for the large proportion of REEs recoverable in leaching procedures targeting oxide phases, supporting recent findings that REEs are not consistently associated with oxide phases. Alternatively, we propose pore water REEs are largely sourced from early diagenetic dissolution of ubiquitous, Fe-bearing clay minerals.

We demonstrate that pore water REE signatures are similar to those of river sourced clays (Bayon et al., 2015), consistent with a detrital clay dissolution source, and in agreement with recent suggestions that the dissolution of detrital siliciclastic materials in the ocean is a potentially important source of solutes to the ocean (e.g. Jeandel & Oelkers, 2015). We argue that the spread in middle REE enrichment and heavy to light REE enrichment in pore fluids relative to this clay source can be explained by fractionation during authigenic clay uptake of REEs. We conclude that clay mineral dissolution and authigenesis are likely the primary influences on REE cycling near the seafloor, with the balance between clay dissolution and authigenesis controlling the concentration, ratio of heavy and light REE abundances, and the isotopic composition of pore waters. We explore the implications of this hypothesis on the oceanic REE budget, and the use of authigenic neodymium isotopes as a paleoproxy for shifts in ocean circulation.

Abbott et al., 2015, The sedimentary flux of dissolved rare earth elements to the ocean: *Geochimica et Cosmochimica Acta*, v. 154, p. 186–200.

Bayon et al., 2015, Rare earth elements and neodymium isotopes in world river sediments revisited: *Geochimica et Cosmochimica Acta*, v. 170, p. 17–38.

Jeandel & Oelkers, 2015, The influence of terrigenous particulate material dissolution on ocean chemistry and global element cycles: *Chemical Geology*, 395, p. 50–66.