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Retention, release and isotopic fractionation of rare earth elements during manganese oxide transformation in marine sediments

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Rare earth elements (REEs) recorded in ocean sediments are powerful tracers for reconstructing past oceanic processes due to their predictable behaviour and unique fractionation patterns. The controls on the concentration and isotopic signatures of REEs in seawater and sediments however, are unclear. The REEs are delivered to the oceans mainly through weathering via rivers and ultimately deposited in marine sediments, where authigenic minerals act as their most important hosts. Among these authigenic minerals, manganese (Mn) oxides play a critical role in REE cycling by adsorbing and removing REEs from seawater and porewater and sequestering them over geological timescales. During early oxic sedimentary diagenesis, however, Mn oxides like birnessite can undergo transformation into secondary Mn oxide minerals like todorokite, which can release and recapture some of their sorbed-metal inventory, potentially alerting the REE concentrations and isotopic signatures sequestered by these minerals and re-entering the ocean from the seafloor [1,2,3]. Whether and to what extent these mineral transformation processes influence REE concentrations and isotopic signatures remains unclear, particularly in the presence of sedimentary organic matter.

Here we investigate the elemental and isotopic behaviour of REEs during the transformation of birnessite to todorokite under simulated diagenetic conditions. We age and transform synthetic inorganic and organic REE-sorbed birnessite at controlled transformation rates under a mild reflux procedure. We use solid-state techniques, including X-ray diffraction, and aqueous analyses, including multi-collector inductively-coupled plasma mass spectrometry, to analyse time-series samples from our experiments, and quantify REE concentrations and stable isotope fractionation in both solid and solution phases. Here we will discuss the mineralogical controls on REE release, retention, and isotopic fractionation in marine sediments and porewaters, and examine how sedimentary organic matter and mineral transformation rates affect REE mobility and burial.

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