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Ligand-induced isotopically heavy Zn release during marine birnessite transformation to todorokite

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The phyllomanganate birnessite minerals are highly reactive and exert an important control on the concentration and isotopic composition of a number of trace elements in the ocean through often coupled sorption and redox reactions. In oxic marine sediments however, birnessite transforms to todorokite during oxic diagenesis and under mild hydrothermal conditions. How this mineralogical transformation effects metal concentrations and isotopes in sediments, porewaters and overlying seawater are largely unknow. In this regard we investigate the concentration and isotope behaviour of the bioessential metal Zn during the transformation of birnessite to todorokite, to shed light on the controls of Zn distribution and abundance in the marine environment and the oceanic mass balance of Zn in the modern oceans.

We transform Zn-doped birnessite to todorokite under a mild reflux procedure and investigate the influence of organic ligands on Zn concentration and isotope behaviour by mimicking the speciation of inorganic and organic Zn in seawater. In the absence of organic ligand, Zn is released to solution during the transformation and is isotopically lighter than the mineral phase with an isotopic fractionation factor of $\Delta^{66}Zn_{solution\text{-}mineral}$ = -0.08 ± 0.03‰ after 4 weeks. In the presence of organic ligand, Zn is released to solution, but is heavier than the mineral phase with an isotopic fractionation factor of $\Delta^{66}Zn_{solution\text{-}mineral}$ = 0.12 ± 0.04‰ after 4 weeks. Our results show that the presence of the organic ligand induces an isotopically different Zn release relative to the inorganic system, and we demonstrate that a heavy Zn source from porewaters to the overlying water column can balance the marine Zn budget. We expect organic ligands to similarly effect the isotopic signal of metals released to porewaters during similar transformations of Mn oxides in marine sediments.