

Biogeochemical Controls on the Bioavailability of Ni in Seawater

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The trace element Ni is an important micronutrient in the marine environment required by primary producers. Understanding the reactivity and cycling of Ni in seawater and marine sediments is therefore key to elucidating feedbacks between Ni concentration, speciation, oceanic productivity and ultimately air-sea gas exchange. The sequestration of Ni into marine sediments via Ni sorption to the manganese oxide birnessite provides the primary sink for Ni in the marine environment. In natural environments birnessite is precipitated via the microbial oxidation of Mn(II), and in marine sediments, birnessite subsequently undergoes diagenetic transformation to the manganese oxide todorokite. These sequestration and transformation processes, involving both geomicrobiological and biogeochemical phenomena, are therefore intimately interlinked and ultimately provide a first order control on Ni concentration, speciation and hence bioavailability in seawater.

Here we present the results of an ongoing study into the sorption of Ni by birnessite, the transformation of birnessite to todorokite, and the role these processes play in controlling Ni bioavailability in seawater. We use a combination of high resolution techniques, including transmission electron microscopy and X-ray absorption spectroscopy, together with time-series sorption and precipitation experiments, to characterise the behaviour of Ni with birnessite and during the transformation of birnessite to todorokite. Our results show that the sequestration of Ni by birnessite provides a first order control on Ni abundance in seawater, while the subsequent diagenetic transformation of birnessite to todorokite in marine sediments provides a secondary source of Ni to sediment porewaters and potentially a benthic flux of this important micronutrient back into the overlying water column.