Transformation of Ni-rich birnessite nanoparticles: Implications for the fate of bioessential Ni

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Nanoparticulate birnessite is ubiquitous in oxic marine sediments. Through coupled sorption and redox reactions this phase exerts a strong control on the speciation and bioavailability of trace-metals in the ocean [1]. In the modern oceans the uptake of Ni by birnessite is the primary control on oceanic Ni concentrations [4]. However, the phyllomanganate birnessite is highly transient, transforming under diagenesis and mild hydrothermal conditions to the tectomanganate todorokite [2-3]. Because Ni is a bioessential element, required by primary producers for nitrogen fixation [5], understanding the sequestration of Ni to birnessite, and its fate and mobility during transformation to todorokite, is key to elucidating feedbacks between Ni abundance, oceanic productivity and ultimately air-sea gas exchange. Here we present the results of a novel todorokite synthesis, where we age Ni-rich birnessite under mild hydrothermal conditions. We have performed a time resolved study, combining XRD, TEM-EDS and XAS, to fully characterize the transformation pathway and determine the fate of Ni during the transformation. We find that the transformation of birnessite to todorokite is a four-stage processes in which todorokite grows via the oriented attachment of primary todorokite particles. Crucially, Ni remains preferentially sorbed to the precursor birnessite during its progressive transformation to todorokite, but is released during a late stage dissolution recrystallization. At this point the precursor birnessite is near completely transformed, yet Ni does not sorb to the neo-formed todorokite. These results are consistent with our μ-XAS data for natural diagenetic and hydrothermal marine FeMn-rich sediments, which show Ni preferentially associated with birnessite in the presence of neo-formed todorokite. Our work indicates that in marine sediments this process is a source of Ni to the sediment porewaters.

[1]Burns & Burns (1977) In *Marine Manganese Deposits,* Elsevier. [2]Bodeï *et al* (2007) *GCA***71**, 5698 [3]Feng *et al* (2010) *GCA***74**, 3232 [4]Peacock & Sherman (2007) *Chem. Geol.***238**, 94 [5]Mulrooney & Hausinger (2006*) FEMS Microbiol. Rev*.**27**, 239