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Formation of Todorokite in Marine Sediments: Mechanism, Pathway and Fate of Bio-essential Elements

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Abstract

Birnessite is the dominant Mn oxide in marine sediments. However, under diagenesis and mild hydrothermal conditions the phylломanganate birnessite transforms to the tectomanganate todorokite [1-3]. Across significant areas of the seafloor birnessite is therefore a transient mineral phase. This is important because scavenging of dissolved trace metals to birnessite exerts a strong control on the concentration of these species in seawater. In particular, in the modern oceans the sorption of Ni to birnessite is the primary control on Ni oceanic concentration [4]. Ni is a bioessential element, required by primary producers and methanogenic bacteria [5]. As such understanding the sequestration of Ni to birnessite, and its fate and mobility during the transformation of birnessite to todorokite, is key to elucidating the feedbacks between Ni abundance, oceanic productivity and ultimately air-sea gas exchange.

The presence of Ni in birnessite is traditionally believed to aid recrystallization to todorokite, where Ni is eventually retained in the todorokite structure, providing a potential sink for dissolved Ni [2]. Here we present the results of a novel todorokite synthesis, where we transform pure and Ni-rich birnessite under conditions representative of marine diagenetic and mild hydrothermal settings. We have performed a time resolved study, combining XRD, BET, HR-TEM and XAS to fully characterise the transformation mechanism and pathway and determine the fate and mobility of Ni during the transformation. Results facilitate our interpretation of recently collected μ -XRF and μ -XAS data, mapping Ni speciation and distribution in natural diagenetic and hydrothermal marine ferromanganese-rich sediments. Ultimately we find that Ni retards the transformation of birnessite to todorokite under diagenetic and mild hydrothermal conditions, and is ultimately rejected from the neoformed todorokite during a late stage dissolution recrystallization process.

[1] Burns & Burns (1977) Mineralogy of ferromanganese deposits. In Marine Manganese Deposits (Elsevier, Amsterdam). [2] Bodeř 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.