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Release of Ni from birnessite during transformation of birnessite to todorokite: Implications for Ni cycling in marine sediments

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Abstract

The phyllomanganate birnessite is the main Mn-bearing phase in oxic marine sediments where it exerts a primary control on the concentration of micronutrient trace metals in seawater. However, during sediment diagenesis and under mild hydrothermal conditions birnessite transforms into the tectomanganate todorokite. We have recently shown that the transformation of birnessite to todorokite proceeds via a four-stage nucleation and growth mechanism, beginning with todorokite nucleation, then crystal growth from solution to form todorokite primary particles, followed by their self-assembly and oriented growth via oriented attachment to form crystalline todorokite laths, culminating in traditional crystal ripening (Atkins et al., 2014). Here we determine the fate and mobility of Ni sorbed by birnessite during this transformation process. Specifically, in our recent work we predict that the presence of Ni within the phyllomanganate matrix will disrupt the formation of todorokite primary particles. As such, contrary to current understanding, we suggest that Ni sorbed by birnessite will slow the transformation of birnessite to todorokite and/or be released to marine porewaters during sediment diagenesis. Here we transform a synthetic, poorly crystalline, Ni-sorbed (~1 wt% Ni) hexagonal birnessite, analogous to marine birnessite, into todorokite under a mild reflux procedure, developed to mimic marine diagenesis and mild hydrothermal conditions. We characterise our birnessite and reflux products as a time series, including X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM) and extended X-ray absorption fine structure (EXAFS) spectroscopy. In addition we determine Ni speciation and mineral phase associations in a suite of natural marine ferromanganese precipitates, containing intermixed phyllomanganate and todorokite. Our work shows for the first time that Ni significantly slows the transformation of birnessite to todorokite and reduces the crystallinity of the neo-formed todorokite phase, but does not alter the mechanism and pathway of todorokite formation, compared to a Ni-free system. Furthermore, in systems tending towards todorokite as the final diagenetic product, we see that up to 50% of the Ni originally sequestered by birnessite is released to solution during the transformation. Our work indicates that the transformation of birnessite to todorokite in oxic marine sediments likely provides a significant source of Ni to marine sedimentary porewaters and potentially a hitherto unrecognized benthic flux of Ni to seawater.

Keywords: Vernadite; Birnessite; Buserite; Todorokite; Nickel; Manganese oxide; Ferromanganese; Transformation; Oriented aggregation; Seawater

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1. INTRODUCTION

The phyllomanganates birnessite and buserite, together with the tectomanganate todorokite, are the dominant Mn-bearing minerals in oxic marine sediments and ferromanganese deposits, where they are typically found as poorly crystalline and intermixed nanoparticulate phases (e.g., Goldberg, 1954; Burns and Burns, 1977; Usui and Terashima, 1997; Banerjee and Nesbitt, 1999; Post, 1999). Birnessite and buserite in particular are highly reactive and through coupled sorption and redox reactions exert a strong control on the concentration, speciation and bioavailability of trace metals and micronutrients in seawater (e.g., Post, 1999). Indeed, the poorly crystalline phyllomanganates present in ferromanganese crusts and nodules are typically enriched in trace metals such as Ni, Cu and Zn by $\sim 10^6$ over their respective concentrations in seawater (e.g., Arrhenius, 1963; Koschinsky and Hein, 2003). Specifically with regard to Ni, ferromanganese oxides dispersed in pelagic sediments and precipitated as discrete crusts and nodules provide the only known sinks for Ni in the modern marine Ni cycle (Gall et al., 2013). These minerals typically contain between ~0.2 and 1 bulk wt% Ni, exclusively sorbed to the Mn-rich fraction (e.g., Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003; Peacock and Sherman, 2007a), as a result of a sorption equilibrium between Ni and poorly crystalline phyllomanganate that is predicted to provide a primary control on the concentration of Ni in the modern oceans (Peacock and Sherman, 2007b).

In oxic marine sediments however, the poorly crystalline phyllomanganates transform into todorokite during oxic diagenesis and under mild hydrothermal conditions. In the case of Ni, previous work shows that dissolved Ni is readily sequestered to birnessite via surface complexation above and below Mn octahedral vacancy sites present on the birnessite [001] surface (space group p63/mmc) (e.g., Manceau et al., 2007a,b; Peacock and Sherman, 2007a,b; Peacock, 2009; Peña et al., 2010). Subsequent to this initial sequestration, with ageing and under pH conditions relevant to the marine environment, surface complexed Ni progressively migrates into the birnessite crystal lattice to become structurally incorporated (Peacock, 2009), and in natural marine ferromanganese precipitates Ni is found entirely incorporated into birnessite and buserite (Peacock and Sherman, 2007a). Despite our understanding of Ni sequestration by phyllomanganates, the mobility and fate of Ni and other micronutrients during the transformation of these phases into todorokite remains unclear. Our recent work on the mechanism of todorokite nucleation and growth suggests that, contrary to current understanding, trace metals like Ni might slow the transformation of birnessite to todorokite and be released to marine sedimentary porewaters during this diagenetic process, thus potentially providing a benthic flux of these micronutrients to seawater (Atkins et al., 2014). A complete knowledge of the controls on Ni concentrations and isotopic compositions in seawater is important for our understanding of the modern marine Ni cycle (e.g., Cameron and Vance, 2014), and also for the interpretation of palaeo Ni signals recorded in marine sedimentary archives (e.g., Cameron et al., 2009; Konhauser et al., 2009).

In the natural environment Mn(III/IV) oxides are thought to form via the microbial oxidation of Mn(II) (e.g., Brouwers et al., 2000; Francis et al., 2001; Bargar et al., 2000, 2005; Villalobos et al., 2003; Tebo et al., 2005; Webb et al., 2005a,b; Saratovsky et al., 2006; Spiro et al., 2010). However, although todorokite is often found intimately associated with turbostratic phyllomanganate (termed vernadite) and both 7 Å (birnessite) and 10 Å (buserite) semi-coherently stacked phyllomanganates (here all collectively termed poorly crystalline phyllomanganates) in marine ferromanganese precipitates (e.g., Burns and Burns, 1978a,b; Siegel and Turner, 1983; Usui and Terashima, 1997; Banerjee and Nesbitt, 1999; Bodeï et al., 2007; Peacock and Moon, 2012), it is thought to only form during the transformation of a phyllomanganate during oxic sediment diagenesis and under low temperature hydrothermal conditions (e.g., Burns and Burns, 1978b). Indeed, observations from both natural ferromanganese samples and experiments largely support this assertion. For example, todorokite is rarely found in hydrogenetic ferromanganese crusts precipitated directly from ambient seawater, but is found to varying extents in diagenetic ferromanganese nodules formed at the sediment–seawater interface with influence from sediment porewaters, and is prevalent in hydrothermal ferromanganese deposits formed in close proximity to hydrothermal fluids (e.g., Burns and Burns, 1977). Moreover, all todorokite synthesis procedures to date involve the transformation of a phyllomanganate via either a high temperature and pressure hydrothermal treatment (e.g., Giovanoli et al., 1975; Golden et al., 1987; Shen et al., 1993; Feng et al., 1995, 1998; Tian et al., 1997; Vileno et al., 1998; Ching et al., 1999; Luo et al., 1999; Malinger et al., 2004; Liu et al., 2005) or a more mild refluxing process at atmospheric pressure, designed to better simulate todorokite formation in natural environments (e.g., Feng et al., 2004, 2010; Cui et al., 2006, 2008, 2009; Atkins et al., 2014). To best replicate the morphological and structural features of natural marine todorokite, these syntheses are typically performed in a Mg-rich electrolyte (~1 M $MgCl_2$) where Mg is prevalent in marine sediment porewaters and acts as a templating ion, expanding the precursor birnessite interlayers from ~7 Å to ~10 Å (e.g., Bodeï et al., 2007), which closely matches the eventual tunnel dimensions of the neo-forming todorokite (where ideal todorokite consists of triple chains of edge-sharing MnO_6 octahedra that share corners to form 3D tunnels equating to $\sim 10 \times 10$ Å (Burns et al., 1985; Post and Bish, 1988; Post et al., 2003)). Attempts to synthesise todorokite using Ca as a templating ion (likely more relevant to terrestrial todorokite) typically result in an incomplete transformation (e.g., Golden et al., 1987) and may in part explain the relative rarity of todorokite in terrestrial *vs.* marine settings (e.g., Chukhrov and Gorshkov, 1981; Dixon and Skinner, 1992; Manceau et al., 2007a,b). The necessity for a high ionic strength is also demonstrated in the work to date, where relatively low concentrations of $MgCl_2$ (~0.01 M) result in an intermediate birnessite with an interlayer spacing that is somewhat larger (e.g., Cui et al., 2006) than that