Crystal-chemistry of Ni in marine ferromanganese crusts and nodules

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ABSTRACT

Marine ferromanganese crusts and nodules are highly enriched in transition metals such as Ni and Co, yet the crystal chemistry and mode of incorporation of these metals is poorly known. We characterized the crystal chemistry of Ni in two hydrothermal Pacific ocean ferromanganese crust samples and a hydrogenic nodule from the Madeira abyssal plain. Energy dispersive spectrometry shows that Ni is associated with the manganese oxide phases, in agreement with previous work. X-ray diffraction patterns show that the dominant Mn\(^{3+/4+}\) oxide is a phyllomanganate similar to hexagonal birnessite or \(\delta\)-MnO\(_2\). Extended X-ray absorption fine-structure spectroscopy shows that the coordination environment of Ni results from structural incorporation into the phyllomanganate phase by replacement of Mn\(^{3+/4+}\). In contrast, Ni initially sorbs to freshly prepared synthetic birnessite by surface complexation over vacancy sites in the MnO\(_2\) layer. We propose that the transformation of Ni sorption from surface complexation to structural incorporation provides a potentially irreversible sink for Ni in seawater.

Keywords: Nickel, ferromanganese, hexagonal birnessite, goethite, adsorption, solid solution, scanning electron microscopy, EXAFS spectroscopy

INTRODUCTION

The concentration of Ni in marine ferromanganese deposits, deep-sea sediments, and seawater can be strongly controlled by sorption onto Mn\(^{3+/4+}\) and Fe\(^{3+}\) (hydr)oxides (e.g., Goldberg 1954). Chemical analyses of Pacific Ocean ferromanganese nodules show a positive Ni-Mn correlation (e.g., Goldberg 1954; Willis and Ahrens 1962; Cronan 1969; Calvert and Price 1977). Several more recent sequential analysis studies have also shown a Ni-Mn association in Indian and Atlantic nodules (Moorby and Cronan 1981), in Pacific nodules and encrustations (Aplin and Cronan 1985), and in Pacific crusts (Koschinsky and Halbach 1995; Koschinsky and Hein 2003). Nickel-manganese spatial correlations have also been found with energy dispersive spectrometry (EDS) of Pacific nodules (e.g., Lei and Boström 1995) and Indian Ocean nodule and crust samples (e.g., Kumar et al. 1994; Dutta et al. 2001).

The association of Ni with Mn has been explained using the adsorption model of James and Healy (1972) (e.g., Li 1982; Koschinsky and Halbach 1995; Koschinsky and Hein 2003). This model assumes that metals sorb to mineral surfaces via purely electrostatic outer-sphere mechanisms. Nickel forms mainly hydrated divalent Ni\(^{2+}\) in seawater (e.g., Turner et al. 1981) and the model predicts that Ni\(^{2+}\) would be preferentially bound to the negative surface of MnO\(_2\) (pH\(_{ZPC}\) = 2.3 ± 0.2, Cats and Langmuir 1986). In the past 15 years, however, spectroscopic evidence has emerged that metals sorb to Fe and Mn oxides by forming inner-sphere surface complexes (Brown and Parks 2001 and references therein). Moreover, sorption might also occur via structural incorporation and replacement of Fe\(^{3+}\) or Mn\(^{3+/4+}\). Understanding the sorption mechanism is necessary before we can develop a thermodynamic model of trace-metal uptake. Even a qualitative understanding of the sorption mechanism can enable us to predict if trace metal-sorption is reversible (e.g., outer-sphere complexation) or irreversible (structural incorporation).

Extended X-ray absorption fine structure (EXAFS) spectroscopy can be used to investigate the coordination environment of Ni and, hence, if Ni is sorbed to Mn oxide phases via outer-sphere surface complexes, inner-sphere surface complexes, or structural incorporation. To our knowledge, there are no EXAFS studies of Ni associated with Mn in deep-sea ferromanganese deposits. However, EXAFS spectra have shown that divalent cations can adsorb above/below vacancy sites in the octahedral layers of synthetic hexagonal birnessite (e.g., Manceau et al. 2002a). However, EXAFS spectra of Ni in MnO\(_2\)-Al(OH)\(_3\), mixed-layer lithiophorite in soil ferromanganese nodules show isomorphic substitution of Ni\(^{2+}\) for Mn\(^{3+/4+}\) (Manceau et al. 2002b, 2005) and EXAFS spectra of Ni\(^{2+}\) in Co-Ni absolane show the formation of an intercalated Ni(OH)\(_2\) layer (Manceau et al. 1992). Recently, we have found that Ni\(^{2+}\) sorbs to synthetic hexagonal birnessite (Hx-birnessite) by surface complexation over vacancy sites in the MnO\(_2\) layer; however, Ni\(^{2+}\) sorbs to synthetic triclinic birnessite (Tc-birnessite) by forming surface complexes on edge sites of the MnO\(_2\) layers (Peacock and Sherman 2007).

Ferromanganese nodules and crusts consist of a variety of Mn\(^{3+/4+}\) oxides (such as \(\delta\)-MnO\(_2\), birnessite, and todorokite) and Fe\(^{3+}\) hydroxides (such as goethite). The structures of these minerals are based on sheets and chains of MnO\(_2\) and FeO\(_6\) octahedra, respectively (e.g., Burns and Burns 1977). Todorokite is a tunnel Mn oxide with diagnostic X-ray diffraction (XRD) peaks at ~10