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Sorption of Ni by birnessite: Equilibrium controls on Ni in seawater

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Abstract

Synthetic hexagonal birnessite (Hx-birnessite) is a close analogue to natural poorly crystalline phyllomanganate phases found in soils and marine ferromanganese deposits. These phases are often highly enriched in trace metals such as Ni and Co. We measured the sorption of Ni(II) onto synthetic hexagonal birnessite (Hx-birnessite) from pH 1 to 7. EXAFS spectra show that, at pH 3.7, Ni is adsorbed to the Hx-birnessite surface above vacancy sites on {001} as a tridentate corner-sharing complex. We developed a surface complexation model for Ni adsorption based on the equilibria

$$3(\equiv Mn_2O^{-2/3}) + Ni^{+2} = (\equiv Mn_2O)_3Ni^0$$

$$3(\equiv Mn_2O^{-2/3}) + Ni^{+2} + H_2O = (\equiv Mn_2O)_3Ni(OH)^- + H^+$$

Using this surface complexation model, we predict the concentration of Ni in seawater in equilibrium with Ni-bearing birnessite found in hydrogenetic FeMn crusts and nodules. Our predicted results are in good agreement with observed Ni concentrations in seawater and suggest that the concentration of dissolved Ni in seawater is buffered by sorption to birnessite or a related MnO_2 phase. However, in addition to the surface complex, Ni also sorbs by structural incorporation into the vacancy site. In our synthetic samples at pH 7, EXAFS shows ~10% of Ni is structurally incorporated into Hx-birnessite. In natural birnessites found in marine ferromanganese crusts and nodules, EXAFS shows that all of the sorbed Ni is structurally incorporated. Structural incorporation suggests that Ni sorption may be irreversible.

Keywords: Nickel; Hexagonal birnessite; Adsorption; EXAFS spectroscopy; Surface complexation modelling

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1. Introduction

The aqueous geochemistry of Ni can be strongly controlled by sorption onto Mn(III, IV) oxides (such as birnessite and δ-MnO_2) and Fe (hydr)oxides (such as goethite, α-FeOOH). Sorption of Ni(II) to Mn oxides controls the release of Ni during pyrite oxidation (Larsen and Postma, 1997) while sorption to Fe (hydr) oxides retards its mobility during the chemical weathering of ore deposits and leads to secondary Ni enrichment (e.g., Som and Joshi, 2002). In the marine environment, Ni is enriched on the order 10^6 in deep-sea FeMn nodules (Arrhenius, 1963) relative to its average seawater concentration. Trace metal species appear to show a preference for sorption onto Fe- or Mn-rich phases in FeMn deposits; Ni–Mn spatial and compositional correlations have been found in both FeMn

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nodules and crusts (e.g., Kumar et al., 1994; Dutta et al., 2001).

Natural and synthetic birnessites can have a triclinic or hexagonal structure (Drits et al., 1997). However, “birnessite” was originally assigned to a natural mineral showing hexagonal sheet symmetry (cf. Jones and Milne, 1956) and hexagonal symmetry has been found in common among most natural birnessites (cf. Jones and Milne, 1956; McKenzie, 1989; Post, 1992) and synthetic δ-MnO_2 (Villalobos et al., 2003). In fact, δ-MnO_2 is not a separate mineral to hexagonal birnessite: δ-MnO_2 simply has fewer stacks of phyllomanganate sheets (Manceau, personal communication, 2005). In triclinic birnessite (Tc-birnessite), all octahedral layer positions are filled with Mn(IV) and Mn(III) cations (Drits et al., 1997) and negative charge generated within the octahedral layers is balanced exclusively by hydrated interlayer cations (Villalobos et al., 2003). In hexagonal birnessite (Hx-birnessite), however, negative layer charge arises from Mn(III)-octahedra vacancies (Fig. 1a) and Mn(III) for Mn(IV) substitutions and is compensated by a combination of protons and interlayer cations, depending on pH (Drits et al., 1997). The differences in structural composition between Tc-birnessites and Hx-birnessites will affect their reactivity and mechanism of metal uptake. Hx-birnessites, for example, are reported to sorb metals above/below vacancy sites (Fig. 1b) present in the octahedral sheets (e.g., Appelo and Postma, 1999; Manceau et al., 2002a). Tc-birnessites do not possess vacancy sites (Drits et al., 1997) and are therefore unable to sorb metals by this mechanism. If hexagonal symmetry is indeed in common among most natural birnessites (cf. Jones and Milne, 1956; McKenzie, 1989; Post, 1992), then synthetic sorption experiments must use Hx-birnessite (or δ-MnO_2) to accurately represent natural systems.

Before we can model the fate and transport of Ni(II) in low temperature ore deposits and in groundwater, we need to know the mechanisms and equilibria involved in sorption of Ni(II) onto Mn(III,IV) (hydr)oxide surfaces. Sorption edges and isotherms for Ni(II) on MnO_2 (Murray, 1975; Gray and Malati, 1979; McKenzie, 1980; Green-Pedersen et al., 1997) have been measured; however, fitting the sorption edges to a surface complexation model is difficult without molecular information about the identity of the surface complexes. Murray (1975) reported a protons released to metal adsorbed ratio of close to 1 for Ni^{+2} adsorbed on hydrous MnO_2 indicating the formation of monodentate surface complexes; only one type of surface sorption site was required to explain the available data. Green-Pedersen et al. (1997) described adsorption of Ni^{+2} on amorphous MnO with a Langmuir isotherm. Two-site surface complexation models (with $\equiv XOH$ and $\equiv YOH$ surface sites) have been invoked by Pretorius and Linder (2001) and Tonkin et al. (2004) to simulate divalent cation adsorption on δ-MnO_2 and model existing experimental data in the literature. Tonkin et al. (2004) successfully modelled the experimental data of Murray (1975) with the formation of $\equiv XONi^{+}$ and $\equiv XONiOH^{0}$ surface adsorption complexes. However, XAS data to date show most divalent cations adsorb to iron and manganese (hydr)oxides by forming bidentate and tridentate surface complexes, respectively (e.g., Peacock and Sherman, 2004a; Manceau et al., 2002a). It has been previously demonstrated that modelling alone cannot distinguish between otherwise plausible adsorption complexes (e.g., Westall and Hohl, 1980; Peacock and Sherman, 2004b), but to our knowledge there have been

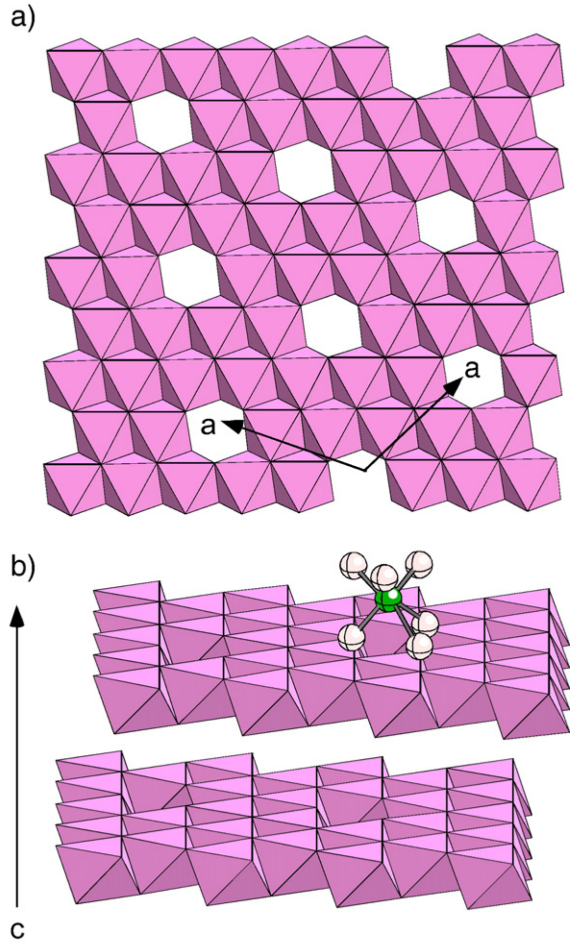

Fig. 1. (a) Structural model showing ordered vacancies in the phyllomanganate layer of Hx-birnessite. (b) Proposed surface complex for cations sorbed to Hx-birnessite. Surface complexes form above and below vacancy sites.