

## Mechanisms of nickel sorption by a bacteriogenic birnessite

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## Abstract

Bacteriogenic birnessite nanoparticles have a large capacity to adsorb metal cations due to their high proportion of cation vacancy defects. In the current study, a synergistic experimental-computational approach was used to study the molecular-scale mechanisms of Ni sorption at varying loadings and at pH 6-8 using the hexagonal birnessite produced by *Pseudomonas putida* GB-1. We found that Ni is scavenged effectively by the biomass-birnessite assemblages. At surface excess values below  $0.18 \text{ mol Ni kg}^{-1} \text{ sorbent}$  ( $0.13 \text{ mol Ni mol}^{-1} \text{ Mn}$ ), the biomass component of the sorbent did not interfere with Ni sorption on mineral sorption sites. Extended X-ray absorption fine structure (EXAFS) spectra showed two dominant coordination environments: Ni bound as a triple-corner-sharing (Ni-TCS) complex at vacancy sites and Ni incorporated (Ni-inc) into the  $\text{MnO}_2$  sheet, with the latter form of Ni favored at high sorptive concentrations and decreased proton activity. In parallel to spectral analysis, first-principles geometry optimizations based on density functional theory (DFT) were performed to investigate the structure of Ni surface complexes at vacancy sites. Excellent agreement was achieved between EXAFS- and DFT-derived structural parameters for Ni-TCS and Ni-inc. Reaction path calculations revealed a pH-dependent energy barrier associated with the transition from Ni-TCS to Ni-inc. Our results are consistent with the rate-limited incorporation of Ni at vacancy sites in our sorption samples, but near-equilibrium state of Ni in birnessite phases found in nodule samples. This study provides direct and quantitative evidence of the factors governing the occurrence of Ni adsorption and Ni incorporation in hexagonal birnessite, a key mineral in the manganese cycle.

## 1. INTRODUCTION

The mobility and bioavailability of Ni in metal-impacted ecosystems is significantly influenced by sorption on Mn(IV) oxide minerals. For example, chemical analysis of sediment samples from Pinal Creek, Arizona, an aquatic ecosystem adversely impacted by copper mining (Fuller and Harvey, 2000; Kay et al., 2001), and field measurements made on biofilms formed in acid rock drainage from a Ni mine in Ontario, Canada, (Haack and Warren, 2003) revealed that Ni was depleted from the water column by sorption to MnO<sub>2</sub>. Microbial catalysis of Mn(II) oxidation to form MnO<sub>2</sub> also was found to be significant at both field sites. Microorganisms have in fact been shown to play a central role in the oxidation of Mn(II) to Mn(IV) in terrestrial and aquatic environments, thereby precipitating nanocrystalline Mn(IV) oxides (Tebo et al., 2004; Hochella et al., 2005; Bargar et al., 2009). There is now consensus that these biogenic MnO<sub>2</sub> minerals are widespread, serving as effective sinks for toxicant metal cations such as Ni<sup>2+</sup> due to their abundant cation vacancy defects and nanoscale particle size.

The biogenic MnO<sub>2</sub> found in field settings, as well as that produced by model bacteria in laboratory culture, is typically a poorly-crystalline layer-type mineral with hexagonal symmetry (hexagonal birnessite) and significant sheet-stacking disorder along the *c*-axis (Friedl et al., 1997; Villalobos et al., 2003; Tebo et al., 2004; Webb et al., 2005; Bargar et al., 2009). Villalobos et al. (2006) have proposed



as the empirical formula for the nanoparticulate hexagonal birnessite produced by the model bacterium, *Pseudomonas putida* (Tebo et al., 2004). In **Eq. 1**, the metal cations to the left of the square brackets are hydrated interlayer species balancing the negative structural charge

created by cation vacancy sites ( $\square$ ) and the stoichiometric coefficient of the proton in the formula (a) varies according to the charge of the interlayer metal cations. An external crystallographic surface area of  $607 \text{ m}^2 \text{ g}^{-1}$  can be estimated for particles with an average 50 nm radius in the *ab* plane and 2 nm thickness along the *c*-axis; whereas  $\text{N}_2$  specific surface areas of  $100 - 220 \text{ m}^2 \text{ g}^{-1}$  have been measured by Villalobos et al. (2003) and Duckworth and Sposito (2007). Biogenic birnessite minerals such as this are typically found enmeshed in an organic matrix of bacterial cells and extracellular polymeric substances (Tebo et al., 2004; Tebo et al., 2005; Toner et al., 2005a), thus forming heterogeneous biomass-mineral assemblages that contain a variety of reactive organic functional groups, such as -COOH, -CHOH, - $\text{PO}_4\text{H}_3$ , -SH, and - $\text{NH}_2$  (Fein et al., 2001; Warren and Haack, 2001; Toner et al., 2005b; Sposito, 2008), as well as mineral sorption sites.

Besides the retention of Ni on birnessite precipitated in soils or sediments of metal-impacted ecosystems, ferromanganese nodules can accumulate up to percent levels of Ni by mass (Manceau et al., 1987; Bodei et al., 2007; Manceau et al., 2007a). In nodules from marine (Bodei et al., 2007; Peacock and Sherman, 2007a), freshwater (Manceau et al., 2007a), and soil environments (Manceau et al., 2002b; Manceau et al., 2003), Ni was present as a divalent cation incorporated (inc) into the octahedral sheets of layer-type Mn(IV) oxide minerals (**Fig. 1a**). Analysis of the Ni K-edge extended X-ray absorption fine structure (EXAFS) spectra of various nodule samples (Manceau et al., 2002a; Bodei et al., 2007; Peacock and Sherman, 2007a) showed that Ni is in an edge-sharing configuration with respect to Mn(IV) octahedra and has a shell of Mn nearest-neighbors at  $2.9 \text{ \AA}$ .

In contrast to the speciation of Ni in ferromanganese nodules, adsorption—not incorporation—was the dominant mechanism of Ni sorption by birnessite-coated sand grains

in a groundwater filter (Manceau et al., 2007b), where 65 % of the total Ni (0.33 % wt) was bound as a triple-corner-sharing (TCS) surface complex (**Fig. 1b**) at cation vacancy sites, while 25 % was incorporated into the sheet structure, as inferred from EXAFS-derived Ni-Mn interatomic distances of 3.5 and 2.9 Å, respectively. These two coordination environments also were observed by Manceau et al. (2007b) and Peacock and Sherman (2007b) and Peacock (2009) for Ni sorbed by  $\delta$ -MnO<sub>2</sub> and hexagonal birnessite (H<sup>+</sup>-exchanged hexagonal birnessite prepared by acidifying crystalline triclinic Na-birnessite to pH 2), respectively, at very low Ni:Mn molar ratio (< 0.01). At pH 4, Ni was bound predominantly as a TCS complex (> 90 %), whereas at pH 7, variable extents of Ni incorporation (10 – 45 %) were observed in samples with a 0.01 Ni: Mn molar ratio. In support of the hypothesis that increased pH favors incorporation, Peacock (2009) observed that the fraction of Ni-inc increased to 20 % when samples initially equilibrated at pH 4 for 24 h were exposed to an electrolyte solution maintained at pH 7 for either 24 or 120 h. Peacock (2009) also showed that as the contact time increased from 24 h to 408 h in samples prepared at pH 7, the fraction of Ni-inc increased from 10 % to 30%. However, greater Ni incorporation (45 %) was observed after a short equilibration time of 12 h in a  $\delta$ -MnO<sub>2</sub> sample prepared at pH 7 and a 0.01 Ni:Mn molar ratio (Manceau et al., 2007b). The birnessite investigated by Manceau et al. (2007b) was synthesized according to the method described by Villalobos et al. (2003) for  $\delta$ -MnO<sub>2</sub>, but the large vacancy content and presence of layer and interlayer trivalent Mn in this specimen proposed from recent X-ray diffraction simulations (Grangeon et al., 2008) contrast with the structural formula ([Na<sub>0.24</sub>H<sub>2</sub>O<sub>0.72</sub>[Mn<sup>4+</sup><sub>0.94</sub>□<sub>0.06</sub>]O<sub>2</sub>) proposed by Villalobos et al. (2006) by use of the same method.

Based on the literature reviewed above, at low Ni:Mn molar ratios, Ni sorbs to hexagonal birnessite either by becoming incorporated into the MnO<sub>2</sub> sheet (Ni-inc, **Fig. 1a**) or by forming triple-corner-sharing surface complexes at vacancy sites (Ni-TCS, **Fig. 1b**), with the former sorption mechanism found to be dominant in ferromanganese nodules and the latter dominant in laboratory-synthesized hexagonal birnessite samples that often are equilibrated with Ni-containing solutions for relatively short times when compared to the timescales over which ferromanganese nodules accrue. Although decreased proton activity favors Ni-inc, the extent of Ni-inc in chemically-synthesized birnessite samples has been variable (10 – 45 % of the total Ni). Thus, besides pH and contact time, the formation of Ni-TCS versus Ni-inc in hexagonal birnessite may be influenced by structural disorder in the mineral. Differences between the hexagonal birnessite minerals studied by Manceau et al. (2007b) and Peacock (2009) arise with respect to specific surface area and structural disorder, with the  $\delta$ -MnO<sub>2</sub> sample employed by Manceau et al. (2007b) having a greater surface area and lacking sheet-stacking order along the *c*-axis direction. The vacancy content of the two minerals may also differ; crystalline hexagonal birnessite has a vacancy content of 16.7 % (Lanson et al., 2000), whereas that of  $\delta$ -MnO<sub>2</sub> may lie between 6 and 18 % (Villalobos et al., 2006; Grangeon et al., 2008).

For biogenic hexagonal birnessites that occur within heterogeneous microbe-mineral assemblages, we expect that, as for their chemically-synthesized analogs, Ni will sorb mainly as Ni-TCS at vacancy sites, so long as the adsorption mechanism is not impeded or modified by bacterial cell surfaces and extracellular polymeric substances. In addition, the large abundance of vacancy sites, lack of sheet stacking along the *c*-axis direction and large specific surface area of biogenic birnessite may lead to greater Ni-inc than observed in

synthetic hexagonal birnessites. We hypothesize further that, while decreased proton activity favors Ni-inc, the relative absence of this species in studies of short-term Ni sorption by synthetic birnessites may be explained from first principles by a kinetically inhibited reaction leading to Ni-inc, such that Ni-TCS precedes the formation of Ni-inc.

In this paper, we report the results of a systematic investigation of the mechanisms of Ni sorption by biogenic hexagonal birnessite using a synergistic experimental-theoretical approach. The bacteriogenic birnessite precipitated by *Pseudomonas putida* was selected for study because its structure is well characterized and it can be synthesized with good replication (Villalobos et al., 2003; 2006). We performed batch experiments to quantify the Ni sorption characteristics of *P. putida* biomass-birnessite assemblages. To determine the local coordination environment of sorbed Ni, we applied EXAFS spectroscopy to samples prepared with various Ni loadings and at pH 6 – 8. From the interatomic distances ( $R$ ) and coordination numbers ( $CN$ ) obtained by fitting the EXAFS spectra, we were able to infer the presence of Ni-TCS and/or Ni-inc, as well as determine the influence of Ni concentration and proton activity on the distribution of the two species. Finally, we investigated these two “end-member” Ni species using first-principles geometry optimizations based on density functional theory (DFT) (Koch and Holthausen, 2002; Martin, 2004; Kohanoff, 2006). The excellent agreement achieved between the EXAFS- and DFT-derived structural parameters encouraged us to explore the geometry-optimized structures further in relation to the transition from Ni-TCS to Ni-inc under scenarios of low and high proton activity.

## **2. MATERIALS AND METHODS**

### **2.1. Materials**

A.C.S. reagent-grade chemicals were used in all experiments. Solutions were prepared using Milli-Q (MQ) water with a resistivity of 18.2 M $\Omega$ -cm. Birnessite was produced using a *Pseudomonas putida* GB-1 culture (Villalobos et al., 2003; Toner et al., 2005a). Microbiological work was carried out in a sterile laminar flow-hood. The bacterial growth medium (Leptothrix medium) was prepared by dissolving solid components in MQ water, autoclaving the solution for 20 min, cooling the autoclaved solution to room temperature and adding filter-sterilized metal cation solutions to the autoclaved solution. Leptothrix medium is a nutrient-rich growth medium containing 1.0 g L<sup>-1</sup> D-glucose (Acros, Lot no. B0119190), 0.5 g L<sup>-1</sup> yeast extracts (Fisher Chemicals, Lot no. 062199), 0.5 g L<sup>-1</sup> casamino acids (Fisher Chemicals, Lot no. 061582), 2.38 g L<sup>-1</sup> HEPES acid (Enzyme grade, Fisher Chemicals), 0.5 mM CaCl<sub>2</sub>, 0.83 mM MgSO<sub>4</sub>, 3.7  $\mu$ M FeCl<sub>3</sub>, 1.0 mM MnCl<sub>2</sub>, 40 nM CuSO<sub>4</sub>·5H<sub>2</sub>O, 152 nM ZnSO<sub>4</sub>·7H<sub>2</sub>O, 84 nM CoCl<sub>2</sub>·6 H<sub>2</sub>O and 54 nM Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (Tebo et al., 2007). *Pseudomonas putida* cultures were propagated in 250 mL Erlenmeyer flasks containing 125 mL of Leptothrix medium inoculated with a culture grown overnight to achieve a thousandfold dilution factor. Cultures were incubated on a rotary shaker (150 RPM, 27 °C) for 5.7  $\pm$  0.1 days, allowing for 90 – 100 % of the added Mn(II) to be removed from solution by oxidation and precipitation as birnessite and/or sorption (Toner et al., 2005a). At the time of harvesting, the biomass-birnessite suspension had a pH value of 6.0  $\pm$  0.1. To determine the sorbent concentration ( $c_{sorbent}$ ), the solids from 5 mL of each suspension were collected by centrifugation and dried at 70 °C for 24 h. The sorbent concentration was determined to be 0.62  $\pm$  0.06 g dry sorbent L<sup>-1</sup>. The biomass-birnessite assemblage (birnessite + bacterial cells + exopolymer matrix) was separated from the spent growth medium by centrifugation (40 min, 10 °C, 3,700 RCF). It was rinsed once by re-

suspending it in 10 mM NaCl and 10 mM HEPES buffer (initial pH was adjusted to 6.0 – 7.0 using HEPES acid and Na-HEPES) and allowing it to equilibrate with the electrolyte solution for 2 to 3 h. The suspension was centrifuged a second time and then re-suspended in the buffered electrolyte solution such that the final Mn concentration was  $1.0 \pm 0.1$  mM ( $0.087 \pm 0.009$  g L<sup>-1</sup>). Aqueous concentrations of Mn(II) in the suspensions used for sorption experiments were always less than 2  $\mu$ M.

## 2.2. Sorption of Ni

Sorption experiments were conducted in 30 mL opaque high-density polyethylene (HDPE) bottles using  $15 \pm 0.1$  mL of the biomass-birnessite suspension; the suspension was transferred by pipette while under vigorous stirring. Experiments were initiated by adding an aliquot of a 10 mM NiCl<sub>2</sub> solution to each bottle to attain initial Ni concentrations of 0 to 680  $\mu$ M. For each sorption isotherm, a total of 24 experiments was carried out using 10 different initial Ni concentrations, with each experiment performed either in duplicate or triplicate. Additional measurements were made at pH 8: 10  $\mu$ M Ni was added to 0.1 g dry sorbent L<sup>-1</sup> (equivalent to 160  $\mu$ M MnO<sub>2</sub>). Two types of sorption control experiment were conducted: a) biomass-birnessite suspension in the absence of Ni to assess Mn desorption or dissolution and b) Ni or Mn solution in the absence of sorbent to measure loss to the HDPE bottle walls. In the absence of Ni, less than 3  $\mu$ M Mn(II) was released in the suspension after 50 h; in the absence of the sorbent, no significant Mn or Ni was lost to the HDPE bottle walls.

After a 50 h equilibration period on a rotary shaker (150 RPM,  $25 \pm 2$  °C), two aliquots were removed from each bottle to determine aqueous and total Mn and Ni concentrations ( $c_{Mn}$ ,  $c_{MnTOT}$ ,  $c_{Ni}$ ,  $c_{NiTOT}$ ). The equilibration time was chosen based on measurements of aqueous Ni concentrations after 50 and 96 hrs, which differed by less than 3

%, and from saturation kinetics data for Pb sorption on biogenic MnO<sub>2</sub> (Villalobos et al., 2005). The adsorptive solution was separated from the slurry by filtering the suspension immediately through a 0.22 μm polyethersulfone syringe filter (Millex<sup>®</sup>-GP, Millipore). Solution pH was measured using a Thermo-Orion glass combination pH electrode and a Beckman Φ71 pH meter. During the course of the experiments, the pH values of the supernatant solutions decreased by 0.0 – 0.4 pH units. For total metal analysis, 1 mL of the suspension was transferred to a 2 mL Eppendorf centrifuge tube and digested using excess oxalic acid (25 – 50 μL of a 1 M solution) and concentrated nitric acid (25 – 50 μL of a 69 % solution). The samples were then centrifuged to pellet sorbent material. The supernatant solution was diluted in MQ water for subsequent analysis.

A Perkin-Elmer Optima 5300 Inductively-Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) was used to determine metal concentrations. Emission at 257.6, 259.3 and 260.6 nm and 231.6, 232.0 and 221.6 nm was read for Mn and Ni, respectively. Eight standard solutions with concentrations ranging from 1 – 1000 μM for Mn and 0.1 – 100 μM for Ni were prepared using 1 mg mL<sup>-1</sup>, 5 % HNO<sub>3</sub> VHG Labs plasma standards. All samples (except standards) were acidified with a drop of concentrated nitric acid and vortex-mixed prior to analysis. Measurements were conducted in triplicate using Sc as an internal standard.

### **2.3. EXAFS spectroscopy**

Fluorescence-yield Ni K-edge EXAFS spectra were obtained for selected samples as listed in **Table 1**. Absorption spectra of the reference materials NiCl<sub>2</sub>(aq) (50 mM, pH < 4) and Ni(II)EDTA(aq) (50 mM, pH ≈ 7) were collected in transmission mode; a spectrum for α-Ni(OH)<sub>2</sub>(s) was obtained from Scheinost and Sparks (2000). Sorption samples used for

EXAFS spectroscopy were prepared as described in § 2.2, but using a larger suspension volume (200 mL). Wet pastes obtained by centrifugation (40 minutes, 10 °C, 3,700 RCF) were stored in the absence of light at -20 °C until analysis. At the beamline, samples were thawed and the pastes transferred to polycarbonate sample holders. After loading a sample, the sample holder was covered with a polycarbonate window and Kapton tape on each side. Samples were kept moist and in the absence of light until EXAFS spectral measurements were made.

All EXAFS studies were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 11-2 using a Si (220)  $\phi = 90^\circ$  double crystal monochromator. The incident beam was detuned to 70 % of maximum incident intensity to suppress higher-order harmonic X-rays. Samples were positioned at a  $45^\circ$  angle with respect to the incident beam. The monochromator energy was calibrated using a Ni foil; the maximum of the first derivative of the absorption spectrum was set at 8333 eV. Data were acquired at room temperature using a 30-element Ge detector or Lytle ion-chamber detector. Detectors were used with Co and V X-ray filters and soller slits. On average, up to seven consecutive spectral scans up to wavenumbers of  $12 - 13 \text{ \AA}^{-1}$  were made for individual samples.

The EXAFS spectra were analyzed with SixPack (Webb, 2004), a graphical user interface that incorporates several algorithms from the IFEFFIT library (Newville, 2001). In the data reduction step, replicate spectra were aligned to a common energy scale, dead-time corrected, and averaged. Averaged spectra were background-subtracted using the following parameters:  $E0 = 8347 \text{ eV}$ ,  $Rbkg = 1.0 \text{ \AA}$  (Kelly et al., 2008), no clamps, Gaussian pre-edge

function, quadratic post-edge function, default number of spline knots, a Kaiser-Bessel window function, and  $k$ -weight = 3.

Structural parameters ( $R$ ,  $CN$ , and Debye-Waller factor,  $\sigma^2$ ) describing the local coordination environment of Ni sorbed on birnessite were obtained by fitting the experimental  $k^3$ -weighted EXAFS spectra to the standard EXAFS equation (Sposito, 2004). Phase and amplitude functions for single- and multiple-scattering paths were calculated using FEFF61 (Rhehr et al., 1992; Newville, 2001). The CrystalMaker (Crystal Maker Software Limited, 2006) software package was used both to visualize possible metal-sorbent coordination environments and to obtain atomic coordinates for FEFF calculations (**Fig. 1**). Clusters of atoms utilized in the analysis of Ni K-edge EXAFS spectra were based on the crystal structure of hexagonal birnessite published by Lanson et al. (2002). An amplitude reduction factor ( $S_0^2$ ) of 0.96 was determined by fitting the Ni-O shell of NiCl<sub>2</sub>(aq) and Ni(II)EDTA(aq) EXAFS spectra. The parameter  $\Delta E0$ , which accounts for the misalignment in energy between experimental and theoretical spectra (Kelly et al., 2008), was allowed to vary during fitting, but the same value was applied to all paths. Unless specified otherwise,  $R$ ,  $CN$ , and  $\sigma^2$  were varied for each shell during spectral fitting. All EXAFS spectra were fit in  $R$ -space over the  $k$ -range 3 – 11.6 Å<sup>-1</sup> and  $R$ -range 1 – 6 Å, which yielded a total of 27 independent points ( $n_{independent}$ ). In some instances, the least squares fitting module in SixPack was used to analyze  $k^3$ -weighted EXAFS spectra directly in  $k$ -space by linear combination of spectra of Ni in defined coordination environments in order to estimate the fractional contribution of each component to the experimental spectrum (Webb, 2004; Kelly et al., 2008).

Four criteria were used to evaluate goodness of fit: 1) two statistical parameters calculated by IFEFFIT (Kelly et al., 2008), *R-factor* (a value of 0.05 reflects a reasonable fit) and *reduced chi square* (abbreviated as *red chi2*; a decrease in *red chi2* between two candidate structural models by a factor of about two indicates significant improvement in a fit); 2) uncertainties in fitted structural parameters as estimated by FEFF6l (Kelly et al., 2008); 3) visual inspection of the spectral fit in *k*-space and the Fourier-transform fit in *R*-space, including the imaginary part, which is sensitive to phase shift, thus can be helpful in determining the identity of a backscattering atom (Sarret et al., 1998); 4) structural reasonableness of results based on the known chemistry of the sorbate and sorbent.

#### **2.4. Geometry optimizations**

All geometry optimizations were performed with the CASTEP code (Clark et al., 2005), which implements DFT in a plane-wave basis set to represent wavefunctions and uses ultrasoft pseudopotentials (Vanderbilt, 1990). Eigenstates and eigenvalues of the Kohn-Sham equations (Payne et al., 1992) were calculated with electron exchange and correlation described using the spin-polarized generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerhof functionals (Perdew et al., 1996).

To obtain the most accurate description of the electronic structure, the Mn pseudopotential was constructed with the semi-core 3s and 3p states excluded from the core and treated explicitly as valence states. Valence-electron configurations for Mn and O were  $3s^2 3p^6 3d^5 4s^2$  and  $2s^2 2p^4$ , respectively. The core radius ( $r_c$ ) for Mn was  $2.3 a_0$  ( $a_0 = 0.52918 \text{ \AA}$  is the Bohr radius) while that of O was  $1.3 a_0$ . Ultrasoft pseudopotentials were used for H ( $r_c = 0.8 a_0$ ) and Ni ( $3d^8 4s^2$  and  $r_c = 2.0 a_0$ ). The Ni pseudopotential includes a non-linear core correction (Louie et al., 1982) to treat semi-core electrons. The kinetic energy cutoff for the

pseudopotentials was 500 eV. All optimizations were performed with spin polarization (i.e., densities are calculated separately for spin-up and spin-down electrons) under ferromagnetic ordering among Mn ions, but antiferromagnetic ordering between Ni and Mn ions. Details concerning DFT calculations with spin polarization can be found in Kwon et al. (2009).

Geometry optimizations were performed without imposed symmetry using the BFGS procedure (Pfrommer et al., 1997) by fixing supercell parameters while relaxing all internal atoms. The energy tolerance was  $5 \times 10^{-6}$  eV/atom; the maximum tolerance for force and atom displacements along any Cartesian component was 0.03 eV/Å and 0.001 Å, respectively. A  $2 \times 2 \times 2$  *k*-point grid (Monkhorst and Pack, 1976) (i.e., 4 *k*-points) was chosen for the sorbed Ni species at a Mn vacancy, achieving a high force convergence (i.e., 0.005 eV/Å or better) in our tests.

To create the two sorbed Ni structures under conditions of low pH, layer-type MnO<sub>2</sub> with the negative charge from a Mn(IV) vacancy balanced by four protons (structural formula H<sub>0.13</sub>[Mn<sub>0.967</sub>□<sub>0.033</sub>]O<sub>2</sub>) was geometry-optimized from  $4 \times 4 \times 1$  unit cells based on the atomic coordinates for microcrystalline K-birnessite (Gaillot et al., 2003), which has a two-layer periodicity along the *c* axis. Starting from the protonated supercell (i.e., 11.587 Å x 11.587 Å x 14.001 Å and 90°, 90°, 120°), two H on one side of the vacancy were replaced by Ni to create the singly-occupied Ni-TCS complex, Ni·H<sub>2</sub>[Mn<sub>31</sub>□]O<sub>64</sub>. To create Ni-inc at low pH, Ni was placed inside a vacancy, yielding H<sub>2</sub>[NiMn<sub>31</sub>□]O<sub>64</sub>. An estimate of the energy barrier for the transition from Ni-TCS to Ni-inc then was obtained simply by calculating the total energy of sorbed Ni at a series of Ni positions along the *c*-axis between the position it occupies in Ni-TCS and that in Ni-inc. At each position in the series, the

sorbed-Ni structure was geometry-optimized by relaxing all atoms in the MnO<sub>2</sub> sheet to which Ni was coordinated while constraining the positions of Ni and the atoms in neighboring MnO<sub>2</sub> sheets. To describe Ni incorporation at high pH, a proton at a vacancy site was removed from Ni·H<sub>2</sub>[Mn<sub>31</sub>□]O<sub>64</sub> and H<sub>2</sub>[NiMn<sub>31</sub>□]O<sub>64</sub> to create Ni·H[Mn<sub>31</sub>□]O<sub>64</sub><sup>-</sup> and H[NiMn<sub>31</sub>□]O<sub>64</sub><sup>-</sup>, respectively. A uniform positive background (Leslie and Gillan, 1985) was applied to compensate the charge of Ni·H [Mn<sub>31</sub>□]O<sub>64</sub><sup>-</sup> and H[NiMn<sub>31</sub>□]O<sub>64</sub><sup>-</sup>.

### 3. RESULTS AND DISCUSSION

#### 3.1. Sorption behavior

Sorption isotherms measured at pH 6 (5.6 – 6.0) and 7 (6.7 – 6.9) for the biomass-birnessite assemblage are plotted in **Fig. 2**. The highest surface excess (*q*) values measured were  $0.32 \pm 0.02$  mol Ni kg<sup>-1</sup> and  $0.45 \pm 0.01$  mol Ni kg<sup>-1</sup>, at pH 6 and 7, respectively, indicating increasing Ni sorption capacity with increasing pH. Sorption edges measured over the range of pH 6 to 8 for Ni reacted with the assemblage in both the presence and the absence of its biogenic MnO<sub>2</sub> component (Peña, 2009) confirmed the effect of pH and showed that, while comprising only 12 wt % of the sorbent, the MnO<sub>2</sub> component enhanced Ni removal from solution by up to a factor of 3 to 4 as compared to the biomass component alone.

Plots of the conventional distribution coefficient, *K<sub>d</sub>*, versus the Ni surface excess, *q*, were examined to determine which sorption isotherm model was most appropriate to fit our data (Sposito, 2008). Nonlinearity in these plots and, to some extent, a paucity of data at very low *q*-values, precluded successful application of either a one-site or a two-site

Langmuir model (Peña, 2009). The sorption data could be fit well ( $R^2 > 0.93$ ), however, with the van Bemmelen-Freundlich isotherm (Sposito, 2008)

$$q = Ac^\beta \quad (2)$$

where  $q = (0.045 \pm 0.009)c^{(0.31 \pm 0.04)}$  and  $q = (0.197 \pm 0.018)c^{(0.13 \pm 0.01)}$  at pH 6 and 7, respectively, with  $q$  and  $c$  expressed as in **Fig. 2**. The concentration exponent in the isotherm equation ( $\beta$ ) can be interpreted as a “heterogeneity parameter” which characterizes the spectrum of sorption affinities of a non-homogeneous material, the exponent tending to 0 for a very broad spectrum and to 1.0 for a very narrow spectrum (Sposito, 2004). Thus, the factor of two decrease in the value of the exponent as pH increases from 6 to 7 can be interpreted as a broadening of the spectrum of sorption affinities for Ni in the biomass-birnessite assemblage, which in turn may result from greater variety among the ionized acidic organic functional groups that become available as pH increases.

In the pH 6 sorption experiments, up to 40  $\mu\text{M}$  Mn(II) was detected in solution after equilibration with Ni, whereas a negligible soluble Mn concentration was measured both in the absence of added Ni and in sorption experiments performed above pH 6.5. At very low surface excess,  $q < 0.03 \text{ mol Ni kg}^{-1}$  ( $c_{\text{NiTOT}} < 16 \mu\text{M}$ ), less than 1  $\mu\text{M}$  Mn(II) was detected. However, above this threshold, the concentration of Mn(II) appearing in solution increased linearly with increasing Ni surface excess (Peña, 2009). The release of Mn to solution upon Ni sorption suggests that Ni, which does not undergo redox reactions with Mn(IV), displaced sorbed Mn. Chemical and structural analyses of biogenic MnO<sub>2</sub> samples have routinely indicated that sorbed Mn comprises 5 – 20 % of the total Mn associated with the solid phase (Villalobos et al., 2003; Tani et al., 2004; Toner et al., 2005a; Toner and Sposito, 2005; Webb et al., 2005; Villalobos et al., 2006; Miyata et al., 2007). In addition, through simulations of X-ray diffraction patterns constrained by the composition of the solid phase

and average Mn oxidation number, Grangeon et al. (2008) found that the interlayer occupancy of Mn decreased as the Ni content increased in three  $\delta$ -MnO<sub>2</sub> samples equilibrated with Ni at pH 7 (note that the structural formula proposed for  $\delta$ -MnO<sub>2</sub> by Grangeon et al. (2008) differs significantly from that proposed for  $\delta$ -MnO<sub>2</sub> by Villalobos et al. (2006)).

These considerations, along with the linear relationship observed between Mn(II) in solution and the Ni surface excess, suggested the hypothesis that soluble Mn(II) and Ni(II) compete for binding sites ( $\equiv$ ) on the birnessite component of the sorbent:



In our experiments, soluble Mn(II) could derive from sorbed Mn(II) or Mn(III) since Mn(III) in solution is susceptible to rapid disproportionation unless complexed strongly by a ligand (Morgan, 2000). Hence we designate sorbed Mn without an oxidation number. The cation-exchange reaction in **Eq. 3** can be characterized by a Vanselow selectivity coefficient,  $K_{\text{app}}$  (Sposito, 2008):

$$K_{\text{app}} = \frac{[\equiv \text{Ni(II)}][\text{Mn(II)}]}{[\equiv \text{Mn}][\text{Ni(II)}]} \quad (4)$$

where the surface species concentration is equal to the product of the surface excess ( $q$ ) with the adsorbent solids concentration ( $c_{\text{sorbent}}$ ) and the aqueous species concentration is written as  $c$ , thus

$$K_{\text{app}} = \frac{q_{\text{Ni(II)}} c_{\text{Mn(II)}}}{q_{\text{Mn}} c_{\text{Ni(II)}}} \quad (5)$$

If the birnessite bears a fixed number of sorption sites ( $q_{\text{TOT}}$ ) that can accommodate either Mn or Ni(II), the mass balance expression,

$$q_{TOT} = q_{Ni(II)} + q_{Mn} \quad (6)$$

can be applied to rearrange **Eq. 4** as

$$\frac{q_{Ni(II)}}{c_{Ni(II)}/c_{Mn(II)}} = -K_{app}q_{Ni(II)} + K_{app}q_{TOT} \quad (7)$$

Under our hypothesis, a plot of the left side of **Eq. 6** versus  $q_{Ni(II)}$  should be a straight line.

Such a plot is shown in **Fig. 3** with the surface excess of Ni expressed in units of mol Ni mol<sup>-1</sup> Mn. These units for the Ni surface excess are useful because they facilitate comparison of  $q$ -values with the fraction of birnessite vacancy sites available to bind Ni (**Table 1**). Surface excess with units of mol Ni mol<sup>-1</sup> Mn ( $q'$ ) was calculated by multiplying the conventional expression for surface excess by  $c_{sorberent}/(c_{MnTOT} - c_{Mn})$ , where  $c_{sorberent}$  is the solids concentration of the sorbent and  $c_{MnTOT}$  is measured after complete dissolution of the Mn oxide component by digestion with nitric and oxalic acids and adjustment has been made for any loss in total Mn by desorption ( $c_{Mn}$ ).

The plot in **Fig. 3** is indeed linear ( $R^2 = 0.92$ ,  $n = 12$ ) for  $q$  values  $< 0.13$  mol Ni mol<sup>-1</sup> Mn, and regression analysis of the linear portion yielded  $K_{app}$  and  $q_{TOT}$  values of  $0.36 \pm 0.08$  and  $0.22 \pm 0.05$  mol Ni(II) mol<sup>-1</sup> Mn, respectively. The value of  $K_{app} < 1$  implies selectivity for Mn over Ni in the cation-exchange reaction (Sposito, 2008). This result is consistent with the solid-phase characterization of Ni- $\delta$ -MnO<sub>2</sub> samples equilibrated at pH 7, where XRD simulations showed that an increase in the Ni occupancy from 0.00 to 0.13 followed a relatively small decrease in interlayer Mn occupancy of 0.10 to 0.07 (Grangeon et al., 2008). In addition, there is excellent agreement between the value of  $q_{TOT}$  and the vacancy content of the biogenic MnO<sub>2</sub> component, 0.20 mol vacancy mol<sup>-1</sup> Mn based on the chemical formula in **Eq. 1** (Villalobos et al., 2006). Therefore, it is reasonable to conclude that, at pH 6 and

relatively low values of the surface excess, the biogenic MnO<sub>2</sub> component sorbs Ni<sup>2+</sup> and, for charge balance, two protons on its vacancies, with little or no competition from the biomass component. At higher surface excess values ( $q > 0.13 \text{ mol Ni mol}^{-1} \text{ Mn}$ ) where the cation-exchange model deviates from the data, Ni may be sorbed by the organic component of the sorbent and/or at non-vacancy sites on the mineral component of the sorbent—see Section 3.2.1. In previous studies of metal sorption by composite biomass-mineral assemblages, the biomass component did not inhibit metal sorption by the mineral component, sorbing metal cations significantly only after the mineral component was saturated (Templeton et al., 2003; Toner et al., 2006; Duckworth et al., 2008).

## **3.2. Coordination environments of sorbed Ni**

### *3.2.1. EXAFS spectroscopy*

Nickel K-edge XANES spectra for the biogenic MnO<sub>2</sub> samples showed a relatively symmetric white line near 8350 eV and a weak pre-edge feature 8333 eV, characteristic spectral features of Ni(II) in octahedral coordination (Peña, 2009). The Ni K-edge EXAFS spectra and corresponding Fourier transforms for reference materials and biogenic MnO<sub>2</sub> samples are plotted in **Fig. 4**. The EXAFS spectrum for Ni<sup>2+</sup>(aq) is dominated by a single wave, consequently the Fourier transform (FT) consists of one major peak corresponding to Ni-O scattering at  $R + \Delta R \approx 1.5 \text{ \AA}$ . The EXAFS spectra for  $\alpha$ -Ni(OH)<sub>2</sub>(s) and biogenic MnO<sub>2</sub> are composed of multiple interfering waves, evidenced by multiple, intense peaks in the FT at  $R + \Delta R > 2.0 \text{ \AA}$ . The peaks in the Fourier transforms at 2.0 – 3.6 Å (uncorrected for phase shift) arise mainly from Ni-Mn (or Ni-Ni in  $\alpha$ -Ni(OH)<sub>2</sub>) single scattering interactions, whereas the peaks in the Fourier transforms beyond 3.6 Å (uncorrected for

phase shift) are due to both single and multiple scattering from higher-order O and Mn/ Ni shells.

The Ni K-edge EXAFS spectra and corresponding FT plotted in **Fig. 4** reveal two dominant coordination environments for Ni in samples for which the surface excess (expressed per mole of Mn) is close to or less than the nominal cation vacancy content of our birnessite sample. The Ni-TCS configuration gives rise to a second-shell peak in the Fourier transform at  $R + \Delta R \approx 3.1 \text{ \AA}$ . As Ni becomes incorporated into the sheet, transitioning to Ni-inc, the distance to Mn next-nearest neighbors decreases, giving rise to a peak in the Fourier transform at  $R + \Delta R \approx 2.4 \text{ \AA}$ . Inspection of **Fig. 4** thus shows that Ni-inc was favored at high sorptive concentrations and low proton activity.

For samples equilibrated at pH 6, the amplitude of EXAFS oscillations become attenuated as the surface excess increases from 0.02 to 0.23 mol Ni mol<sup>-1</sup> Mn, indicating greater overall disorder in the coordination environment, such as could be produced by an increase in the variety of binding sites occupied by Ni. These spectral changes are also reflected in the Fourier transforms, where the amplitude of the peak corresponding to Ni adsorption at vacancy sites ( $R + dR \approx 3.1 \text{ \AA}$ ) decreases with increasing Ni loading. At the highest Ni loading, there is a peak in the FT at  $R + \Delta R \approx 2.4 \text{ \AA}$ , but also significant attenuation of the intermediate-range FT structure ( $R + \Delta R > 4.0 \text{ \AA}$ ) observed in samples Ni\_2\_pH6 and Ni\_13\_pH6. To determine whether or not the second peak in the FT arose from Ni-inc, we compared the Fourier-filtered peak at  $R + \Delta R \approx 2.4 \text{ \AA}$  in Ni\_23\_pH6 and Ni\_6\_pH8. We found that while differing in amplitude, the reverse Fourier transforms displayed highly similar phase and wave envelopes. The presence of Ni-inc in this sample is also supported by preliminary fitting of this peak, which yielded a Ni-Mn interatomic

distance of  $2.87 \pm 0.02 \text{ \AA}$ . The FT of the EXAFS spectra for Ni\_6\_pH8, which was equilibrated at pH 8 and a loading between that in samples Ni\_2\_pH6 and Ni\_13\_pH6, shows both a prominent Fourier transform peak at  $R + \Delta R \approx 2.4 \text{ \AA}$  and significant structure at  $R + \Delta R > 4.0 \text{ \AA}$ . Consistent with the speciation of sorbed Ni observed in ferromanganese nodules and chemically-synthesized birnessite samples, discussed in the Introduction, increased pH favored Ni incorporation into biogenic birnessite. In addition, while Ni engages in both corner-sharing and edge-sharing configurations in samples Ni\_6\_pH8 and Ni\_23\_pH6, the average coordination environments beyond the first shell in the two evidently differ. In sample Ni\_23\_pH6, the slight asymmetry in the peak at  $R + \Delta R \approx 2.4 \text{ \AA}$  and diminished structure at  $R + \Delta R \approx 3.5 \text{ \AA}$ , as well as the deviation from the cation exchange model at large surface excess values (Section 3.1), suggest that besides Ni-TCS and Ni-inc, additional Ni surface complexes occur either on the mineral or organic components of the adsorbent. Manceau et al. (2007b) postulated that at high loadings, Ni adsorbs at birnessite particle edges by forming a double-corner sharing (DCS) complex with two singly-coordinated surface oxygen atoms and a Ni-Mn interatomic distance that is indistinguishable from the interatomic distance for Ni adsorption at vacancy sites. For biogenic birnessite, it is not straightforward to distinguish Ni-DCS from a mixture of Ni-TCS and Ni bound to organic surfaces because both configurations would lead to similar Ni-Mn interatomic distances, but reduced coordination numbers. Finally, in samples where the surface excess of Ni greatly exceeded the nominal cation vacancy content of our birnessite (pH > 7), the EXAFS spectra and their Fourier transforms, as well as the XANES spectra, showed some similarity to the spectra and Fourier transforms for macrocrystalline  $\alpha$ -Ni(OH)<sub>2</sub>, which is consistent with polymerization or precipitation of Ni (Peña, 2009).

3.2.1.1 *Structural Analysis of EXAFS spectra.* As suggested by our sorption data, Ni formed predominantly Ni-TCS in samples equilibrated at pH 6 and for a surface excess below 0.13 mol Ni mol<sup>-1</sup> Mn, where at most 65 % of the vacancies are singly-occupied (**Tables 1 and 2, Figs. 5 and 6**). The EXAFS spectra of samples Ni\_13\_pH6 and Ni\_2\_pH6 were described well by the TCS model (**Fig. 1a**, inset table). However, sample Ni\_13\_pH6 was better fit by the TCS model than was Ni\_2\_pH6. A two-fold increase in the uncertainties of the optimized fit parameters for Ni\_2\_pH6 as compared to Ni\_13\_pH6, as well as the appearance of a shoulder in the Fourier transform at  $R + dR \approx 2.5 \text{ \AA}$  and a 0.1  $\text{\AA}$  left-shift in the Ni-Mn<sub>2</sub> peak in Ni\_2\_pH6 as compared to Ni\_13\_pH6, raises the possibility that a minor amount of Ni, although not detectable at higher loadings, may be bound as Ni-inc.

Second-shell O atoms were excluded from the TCS optimization fit due to the weak scattering of O atoms [i.e.,  $Z(\text{O}) = 8$  versus  $Z(\text{Mn}) = 25$ ], as well as the similarity in the interatomic distance for second-shell O (O<sub>2</sub>) and first-shell Mn (Mn<sub>1</sub>) atoms (**Fig. 1b**, inset table). The sensitivity of the fitted Ni-Mn<sub>1</sub>  $R$  and  $CN$  to a Ni-O<sub>2</sub> shell was evaluated by adding a Ni-O path to the model with all parameters constrained [ $CN = 6$ ,  $\sigma^2(\text{Ni-O}_2) = \sigma^2(\text{Ni-O}_3) = 0.011 \text{ \AA}^2$  and  $R = 3.54 \text{ \AA}$ ] and the Ni-O<sub>2</sub> distance fixed at the average value obtained from our DFT geometry optimizations. The addition of a Ni-O<sub>2</sub> shell to the structural model did not result in a significant change in neither the Ni-Mn<sub>1</sub>  $R$  nor the Ni-Mn<sub>1</sub>  $CN$ . However, we found that the Ni-Mn<sub>1</sub>  $CN$  was strongly correlated with the Ni-O<sub>2</sub> distance. For example, setting  $R(\text{Ni-O}_2) = 3.40 \text{ \AA}$  yielded  $CN(\text{Ni-Mn}_1) = 3.4 \pm 0.49$ , whereas setting  $R(\text{Ni-O}_2) = 3.60 \text{ \AA}$  yielded  $CN(\text{Ni-Mn}_1) = 7.4 \pm 0.88$ . When this fitting exercise was repeated with  $\sigma^2(\text{Ni-O}_2) = 0.02 \text{ \AA}^2$ , the  $CN(\text{Ni-Mn}_1)$  was found to deviate by 16 - 24 % from the fitted  $CN$  obtained with the Ni-O<sub>2</sub> shell excluded from the optimization. Under all scenarios tested, the

EXAFS-derived structural parameters obtained for the Ni-Mn<sub>1</sub> shell were in closest agreement with the TCS structural model (**Fig. 1b**) when the distance of second-shell O atoms was fixed at the average distance obtained by geometry optimization.

Although the features in the Fourier transform beyond  $R + dR > 3.6 \text{ \AA}$  are due to single and multiple scattering from higher-order O and Mn shells, we only considered the Ni-O<sub>3</sub> and Ni-Mn<sub>2</sub> shells in the TCS optimization fits. Interatomic distances of  $4.48 \pm 0.016 \text{ \AA}$  (Ni-O<sub>3</sub>) and  $5.44 \pm 0.009 \text{ \AA}$  (Ni-Mn<sub>2</sub>) were estimated by constraining the *CN* of Ni-O<sub>3</sub> to 9.0 and the *CN* of Ni-Mn<sub>2</sub> to 6.0, as expected from the structural model (**Fig. 1b**, inset table). The addition of each of these paths to the spectral fit resulted in a reduction of the *R*-factor by at least a factor of two. However, the relatively large uncertainties in *R* and  $\sigma^2$  for shells fitted at  $R > 3.6 \text{ \AA}$  reflect scattering interactions excluded from the model, such as Ni-O<sub>4</sub> and Ni-Mn<sub>3</sub> and multiple scattering between Ni-O-O (degeneracy = 6;  $\theta \approx 166^\circ$ ;  $R \approx 4.5 \text{ \AA}$ ) and Ni-Mn-O (degeneracy = 12;  $\theta \approx 169^\circ$ ;  $R \approx 5.4 \text{ \AA}$ ). Also, the *CN* assigned to Ni-Mn<sub>2</sub> does not take into account the reduction in the fitted *CN* expected from the presence of cation vacancies in the MnO<sub>2</sub> sheet. Thus, the  $\sigma^2$  values obtained for Ni-O<sub>3</sub> and Ni-Mn<sub>2</sub> are useful for comparing between spectra from similar samples, but their scaling to “absolute” values is limited.

At pH 8 and a loading intermediate to the pH 6 samples containing Ni predominantly in the TCS binding mode, Ni both capped and filled the vacancy sites (**Table 3, Figs. 5 and 6**). The large amplitude of the peak at  $2.86 \text{ \AA}$ , as well as the evident structure between 4.5 and  $6.0 \text{ \AA}$  indicate that Ni in sample Ni\_6\_pH8 is bound at a well-defined site. In the EXAFS fitting, a two-site model was developed by constraining the *CNs* for Ni-Mn<sub>1,TCS</sub> and Ni-Mn<sub>1,inc</sub> at their structural model values (**Fig. 1**) and including a species abundance scaling

parameter to estimate the fraction of Ni adsorbed ( $f$ ) or incorporated ( $1 - f$ ) at vacancy sites. In addition, the  $\sigma^2$  parameters for the Ni-Mn shells were linked to a common floated value. The fit results indicated that about 30 % of the total sorbed Ni, or 0.02 mol Ni mol<sup>-1</sup> Mn (**Table 1**), is incorporated into the MnO<sub>2</sub> sheet (**Table 3**). Thus, about 10 % of the vacancy sites are filled by Ni in sample Ni\_6\_pH8. A variation in  $f$  by  $\pm 5$  % of the optimized fit value yielded visibly worsened fits, as well as an increase by about a factor of two in the IFEFFIT *red chi2* statistic and *R-factor*.

Similarities between the difference the EXAFS spectrum of Ni\_6\_pH8 and the difference EXAFS spectrum of Ni\_2\_pH6 and Ni\_13\_pH6 (Peña, 2009) suggested that a small fraction of Ni in sample Ni\_2\_pH6 is in an edge-sharing configuration with respect to Mn(IV) octahedra. Linear combination fitting of the spectrum for Ni\_2\_pH6 using those for Ni\_13\_pH6 and Ni\_6\_pH8 as components [ $\Sigma(\text{components}) = 1.06$ , *red chi2* = 0.45] yielded an estimate of about 10 % Ni-inc (< 0.002 mol Ni mol<sup>-1</sup> Mn). A similar estimate was obtained from optimization fitting, although the addition of Ni-inc only lead to a decrease in *red chi2* by a factor of 1.6 (**Table 3**). This mediocre improvement in the fit underscores the point that only a trace amount of Ni is incorporated into the MnO<sub>2</sub> sheet at a loading of 0.02 mol Ni mol<sup>-1</sup> Mn (10 % of vacancy sites singly-occupied). Our finding is consistent with a study of Manceau et al. (2007b) in which Ni incorporation was detected in a sample equilibrated at pH 4 having a Ni:Mn molar ratio of 0.002, but not in a sample equilibrated at pH 4 having a Ni:Mn molar ratio of 0.01. Finally, the optimized distance for Ni-Mn<sub>1,inc</sub> in Ni\_2\_pH6 was 2.90 Å, about 0.04 Å longer than in Ni\_6\_pH8. This slight elongation in the Ni-Mn distance with decreasing pH may be attributed to electrostatic repulsion from protons adsorbed at the vacancy site to compensate charge not compensated by Ni<sup>2+</sup>.

### 3.2.2. DFT geometry optimizations

Average structural parameters obtained from geometry optimizations of Ni-TCS and Ni-inc were in excellent agreement with those obtained from EXAFS spectroscopy (**Table 4**). For example, an average Ni-O<sub>1,TCS</sub> distance of 2.05 Å was obtained from both geometry optimizations and EXAFS spectral analysis. Average Ni-Mn distances of 3.46 Å and 2.91 Å in the geometry optimized structures are very similar to the Ni-Mn<sub>1,TCS</sub> and Ni-Mn<sub>1,inc</sub> of 3.48 Å and 2.86 – 2.91 Å obtained from EXAFS optimization fitting. On average, the distance between Mn atoms nearest to Ni [ $R(\text{Mn}_1\text{-Mn}_1)$ ] is larger in Ni-inc than in Ni-TCS by 0.06 Å. This expansion in the Mn-Mn distance for the first-shell Mn neighbors follows from the much larger ionic radius of Ni<sup>2+</sup> (0.69 Å) as compared Mn<sup>4+</sup> (0.53 Å). Visualizations of the geometry-optimized structures (**Fig. 7**) showed that, in Ni-TCS, where the effect of Ni<sup>2+</sup> repulsion is less, the protons are oriented approximately at an 8 ° angle with respect to the *ab* plane of MnO<sub>2</sub> sheet, whereas in Ni-inc, the protons point away from Ni at about an 109 ° angle relative to the *ab* plane.

The agreement between these DFT results for the geometry-optimized structures and the experimental structural parameters encouraged us to undertake reaction-path calculations to probe the transition from Ni-TCS to Ni-inc. The total energy of sorbed Ni at a series of Ni positions was calculated along the *c*-axis between the position it occupies in Ni-TCS and Ni-inc. Our calculations revealed a pH-dependent energy barrier between the two species (**Fig. 8**). The energy barrier for Ni-TCS to transform into H<sub>2</sub>[NiMn<sub>31</sub>□]O<sub>64</sub>, representing sorption at low pH, was 50.0 kJ/mol, whereas the energy barrier to form H[NiMn<sub>31</sub>□]O<sub>64</sub>, representing sorption at higher pH, was only 36.6 kJ/mol. In addition, gradual changes in the proton

orientations—which also exhibited pH dependence—were observed as Ni invaded a vacancy site, implying that the energy barrier for Ni incorporation is closely related to the energy required to overcome repulsion between the invading  $\text{Ni}^{2+}$  and the charge-compensating protons bound on the other side of the vacancy. The GGA exchange-correlation functional is known to underestimate the height of transition-state and reaction barriers. Although the absolute values of the Ni-TCS to Ni-inc barrier from our calculations are almost certainly lower than the true barriers, a probable cancellation of error means that the differential decrease in the energy barrier with pH remains a valid result.

Our reaction-path calculations provide insight into the sorption mechanisms of Ni at vacancy sites. First, the existence of a relatively large energy barrier explains the abundance of Ni-TCS species in Ni-birnessite samples equilibrated in the laboratory under ambient conditions on a time scale of days, as well as the predominance of Ni-inc in birnessite phases found in marine nodules. The greater energy barrier for the reverse reaction in both the low- and high-pH scenarios (83.8 and 103.5 kJ/mol, respectively) suggests that the reverse reaction may not be as favorable as the forward reaction. Second, the decreased energy barrier found for the transition from Ni-TCS to Ni-inc in the high pH scenario confirms that decreasing proton activity indeed facilitates the incorporation of Ni into the vacancy sites. The 14.4 kJ/mol reduction in the energy barrier upon the loss of a proton at a vacancy site corresponds to a 200-fold increase in the rate coefficient at room temperature according to the conventional Arrhenius equation (Sposito, 2008). This lower energy barrier, thus larger rate coefficient, at high pH implies that the ratio of Ni-inc to Ni-TCS should increase with increasing pH in Ni-sorbed birnessite, as is indeed observed experimentally (Manceau et al., 2007b; Peacock and Sherman, 2007b; Peacock, 2009). Lastly, the structural distortion

induced among the Mn atoms surrounding the invading Ni atom in Ni-inc may impose a limit on the maximum amount of Ni incorporation that is possible. In fact, incorporated Ni occupied at most 10 % (this study and Manceau et al. (2007b)) and 2 % (Peacock and Sherman, 2007b) of the total vacancy sites in laboratory hexagonal birnessite samples, with comparisons made across pH (7 – 8) and equilibration times (12 – 408 h).

### **3.3. Conclusions**

Our study shows that biogenic birnessite nanoparticles are highly effective scavengers of Ni, reaching surface excess values of up to  $0.13 \text{ mol Ni mol}^{-1} \text{ Mn}$  at pH 6. In addition, we found that bacterial surfaces and extracellular polymeric substances do not contribute significantly to Ni complexation at surface excess values well below the octahedral vacancy content. The release of Mn to solution upon Ni(II) sorption at pH 6 suggested that these divalent cations compete for the same sorption sites on the oxide surface and that the oxide surface is selective for Mn. A cation-exchange sorption mechanism was valid for surface excess values below  $0.13 \text{ mol Ni mol}^{-1} \text{ Mn}$ , coinciding with the loading below which the EXAFS spectra were modeled entirely by Ni adsorption at vacancy sites as triple-corner-sharing complexes. Our EXAFS spectra also showed that the incorporation of Ni into the birnessite sheet was favored at high sorptive Ni concentrations (pH 6) and high pH values (pH 8). In addition, the biogenic hexagonal birnessite studied herein has a greater capacity to sorb Ni at vacancy sites (up to  $0.13 \text{ mol Ni mol}^{-1} \text{ Mn}$  at pH 6) than the synthetic hexagonal birnessite studied by Manceau et al. (2007b), where samples with Ni:Mn molar ratios  $<0.01$  contained Ni sorbed at vacancy and samples with Ni:Mn molar ratios  $>0.05$  contained Ni sorbed at particle edges. The reaction energy barriers for the transition from Ni-TCS to Ni-inc identified through our DFT-based geometry optimizations confirmed the pH dependence

of the sorption mechanism. In addition, the existence of the energy barriers resolved the differences in observed coordination environments of Ni in laboratory sorption samples and in nodule samples from freshwater and marine environments. The synergistic application of density functional theory and EXAFS spectroscopy in this study has provided direct and quantitative insights regarding the controls on the mechanism of Ni sorption in birnessite, an important scavenger of nutrient and toxicant metals in many aquatic systems. This combined experimental and theoretical approach may be helpful in developing a molecular-scale understanding of metal sorption within complex, heterogeneous microbe-mineral assemblages.

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### **REFERENCES**

- Bargar J. R., Fuller C. C., Marcus M. A., Brearley A. J., De la Rosa M. P., Webb S. M., and Caldwell W. A. (2009) Structural characterization of terrestrial microbial Mn oxides from Pinal Creek, AZ. *Geochimica et Cosmochimica Acta* 73, 889-910.
- Bodei S., Manceau A., Geoffroy N., Baronnet A., and Buatier M. (2007) Formation of todorokite from vernadite in Ni-rich hemipelagic sediments. *Geochimica et Cosmochimica Acta* 71, 5698-5716.
- Crystal Maker Software Limited. (2006) Crystal Maker, pp. Real Time Interactive Crystallography. Crystal Maker Software Limited.
- Duckworth O. W., Bargar J. R., and Sposito G. (2008) Sorption of ferric iron from ferrioxamine B to synthetic and biogenic layer type manganese oxides. *Geochimica et Cosmochimica Acta* 72, 3371-3380.
- Duckworth O. W. and Sposito G. (2007) Siderophore-promoted dissolution of synthetic and biogenic layer-type Mn oxides. *Chemical Geology* 242, 497-508.
- Fein J. B., Martin A. M., and Wightman P. G. (2001) Metal adsorption onto bacterial surfaces: Development of a predictive approach. *Geochimica et Cosmochimica Acta* 65, 4267-4273.
- Friedl G., Wehrli B., and Manceau A. (1997) Solid phases in the cycling of manganese in eutrophic lakes: New insights from EXAFS spectroscopy (vol 61, pg 275, 1997). *Geochimica Et Cosmochimica Acta* 61, 3277-3277.
- Fuller C. C. and Harvey J. W. (2000) Reactive uptake of trace metals in the hyporheic zone of a mining-contaminated stream, Pinal Creek, Arizona. *Environmental Science and Technology* 34, 1150-1155.
- Gaillot A. C., Flot D., Drits V. A., Manceau A., Burghammer M., and Lanson B. (2003) Structure of synthetic K-rich birnessite obtained by high-temperature decomposition of  $\text{KMnO}_4$ . I. Two-layer polytype from 800 °C experiment. *Chemistry of Materials* 15, 4666-4678.
- Grangeon S., Lanson B., Lanson M., and Manceau A. (2008) Crystal structure of Ni-sorbed synthetic vernadite: a powder X-ray diffraction study. *Mineralogical Magazine* 72, 1279-1291.
- Haack E. A. and Warren L. A. (2003) Biofilm hydrous manganese oxyhydroxides and metal dynamics in acid rock drainage. *Environmental Science and Technology* 37, 4138-4147.
- Hochella M. F., Kasama T., Putnis A., Putnis C. V., and Moore J. N. (2005) Environmentally important, poorly crystalline Fe/Mn hydrous oxides: Ferrihydrite and a possibly new vernadite-like mineral from the Clark Fork River Superfund Complex. *American Mineralogist* 90, 718-724.
- Kay J. T., Conklin M. H., Fuller C. C., and O'Day P. A. (2001) Processes of nickel and cobalt uptake by a manganese oxide forming sediment in Pinal Creek, Globe Mining District, Arizona. *Environmental Science and Technology* 35, 4719-4725.
- Kelly S. D., Hesterberg D., and Ravel B. (2008) Analysis of Soils and Minerals Using X-ray Absorption Spectroscopy. In *Methods of Soil Analysis, Part 5-Mineralogical Methods* (eds. A. L. Ulrey and R. L. Drees). Soil Science Society of America.
- Koch W. and Holthausen M. C. (2002) *A Chemist's Guide to Density Functional Theory*. Wiley-VCH.
- Kohanoff J. (2006) *Electronic Structure Calculations fro Solids and Molecules: Theory and Computational Methods*. University Cambridge Press.

- Lanson B., Drits V. A., Feng Q., and Manceau A. (2002) Structure of synthetic Na-birnessite: Evidence for a triclinic one-layer unit cell. *American Mineralogist* 87, 1662-1671.
- Lanson B., Drits V. A., Silvester E., and Manceau A. (2000) Structure of H-exchanged hexagonal birnessite and its mechanism of formation from Na-rich monoclinic busserite at low pH. *American Mineralogist* 85, 826-838.
- Leslie M. and Gillan M. J. (1985) The Energy and Elastic Dipole Tensor of Defects in Ionic-Crystals Calculated by the Supercell Method. *Journal of Physics C-Solid State Physics* 18, 973-982.
- Louie S. G., Froyen S., and Cohen M. L. (1982) Non-Linear Ionic Pseudopotentials in Spin-Density-Functional Calculations. *Physical Review B* 26, 1738-1742.
- Manceau A., Kersten M., Marcus M. A., Geoffroy N., and Granina L. (2007a) Ba and Ni speciation in a nodule of binary Mn oxide phase composition from Lake Baikal. *Geochimica et Cosmochimica Acta* 71, 1967-1981.
- Manceau A., Lanson M., and Geoffroy N. (2007b) Natural speciation of Ni, Zn, Ba, and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. *Geochimica et Cosmochimica Acta* 71, 95-128.
- Manceau A., Llorca S., and Calas G. (1987) Crystal-chemistry of cobalt and nickel in lithiophorite and asbolane from New Caledonia. *Geochimica et Cosmochimica Acta* 51, 105-113.
- Manceau A., Marcus M. A., and Tamura N. (2002a) Quantitative Speciation of Heavy Metals in Soils and Sediments by Synchrotron X-ray Techniques. In *Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Sciences*, Vol. 49 (eds. P. A. Fenter, M. L. Rivers, Sturchio, and S. R. Sutton). Mineralogical Society of America.
- Manceau A., Tamura N., Celestre R. S., MacDowell A. A., Geoffroy N., Sposito G., and Padmore H. A. (2003) Molecular-scale speciation of Zn and Ni in soil ferromanganese nodules from loess soils of the Mississippi Basin. *Environmental Science and Technology* 37, 75-80.
- Manceau A., Tamura N., Marcus M. A., MacDowell A. A., Celestre R. S., Sublett R. E., Sposito G., and Padmore H. A. (2002b) Deciphering Ni sequestration in soil ferromanganese nodules by combining X-ray fluorescence, absorption, and diffraction at micrometer scales of resolution. *American Mineralogist* 87, 1494-1499.
- Martin R. M. (2004) *Electronic Structure: Basic Theory and Practical Methods*. Cambridge University Press.
- Miyata N., Sugiyama D., Tani Y., Tsuno H., Seyama H., Sakata M., and Iwahori K. (2007) Production of biogenic manganese oxides by repeated-batch cultures of laboratory microcosms. *Journal of Bioscience and Bioengineering* 103, 432-439.
- Monkhorst H. J. and Pack J. D. (1976) Special Points for Brillouin-Zone Integrations. *Physical Review B* 13, 5188-5192.
- Morgan J. J. (2000) Manganese in natural waters and earth's crust: Its availability to organisms. In *Metal Ions in Biological Systems: Iron Transport and Storage in Microorganisms, Plants, and Animals*, Vol. 37 (eds. A. Siegel and H. Siegel), pp. 1-34. Marcel Dekker.
- Newville M. (2001) EXAFS analysis using FEFF and FEFFIT. *Journal of Synchrotron Radiation* 8, 96-100.

- Payne M. C., Teter M. P., Allan D. C., Arias T. A., and Joannopoulos J. D. (1992) Iterative Minimization Techniques for Abinitio Total-Energy Calculations - Molecular-Dynamics and Conjugate Gradients. *Reviews of Modern Physics* 64, 1045-1097.
- Peacock C. L. (2009) Physiochemical controls on the crystal-chemistry of Ni in birnessite: genetic implications for ferromanganese precipitates. *Geochimica et Cosmochimica Acta*, 3568-78.
- Peacock C. L. and Sherman D. M. (2007a) Crystal-chemistry of Ni in marine ferromanganese crusts and nodules. *American Mineralogist* 92, 1087-1092.
- Peacock C. L. and Sherman D. M. (2007b) Sorption of Ni by birnessite: Equilibrium controls on Ni in seawater. *Chemical Geology* 238, 94-106.
- Peña J. (2009) Contaminant Metal Immobilization by Biogenic Manganese Oxide Nanoparticles: Implications for Natural Attenuation and Bioremediation. PhD, University of California.
- Perdew J. P., Burke K., and Ernzerhof M. (1996) Generalized gradient approximation made simple. *Physical Review Letters* 77, 3865-3868.
- Pfrommer B. G., Cote M., Louie S. G., and Cohen M. L. (1997) Relaxation of crystals with the quasi-Newton method. *Journal of Computational Physics* 131, 233-240.
- Rhehr J. J., Zabinsky S. I., and Albers R. C. (1992) High-order multiple scattering calculations of X-ray-absorption fine structure. *Physical Review Letters* 69, 3397.
- Sarret G., Manceau A., Spadini L., Roux J. C., Hazemann J. L., Soldo Y., Eybert-Berard L., and Menthonnex J. J. (1998) Structural determination of Zn and Pb binding sites in *Penicillium chrysogenum* cell walls by EXAFS spectroscopy. *Environmental Science and Technology* 32, 1648-1655.
- Scheinost A. C. and Sparks D. L. (2000) Formation of layered single- and double-metal hydroxide precipitates at the mineral/water interface: A multiple-scattering XAFS analysis. *Journal of Colloid and Interface Science* 223, 167-178.
- Sposito G. (2004) *The Surface Chemistry of Natural Particles*. Oxford University Press.
- Sposito G. (2008) *The Chemistry of Soils*. Oxford University Press.
- Tani Y., Ohashi M., Miyata N., Seyama H., Iwahori K., and Soma M. (2004) Sorption of Co(II), Ni(II), and Zn(II) on biogenic manganese oxides produced by a Mn-oxidizing fungus, strain KR21-2. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances and Environmental Engineering* 39, 2641-2660.
- Tebo B. M., Bargar J. R., Clement B. G., Dick G. J., Murray K. J., Parker D., Verity R., and Webb S. M. (2004) Biogenic manganese oxides: Properties and mechanisms of formation. *Annual Review of Earth and Planetary Sciences* 32, 287-328.
- Tebo B. M., Clement B. G., and Dick G. J. (2007) Biotransformations of manganese. In *Manual of Environmental Microbiology* (eds. C. J. Hurst, R. L. Crawford, J. L. Garland, D. A. Lipson, A. L. Mills, and L. D. Stetzenbach), pp. 1223-1238. ASM Press.
- Tebo B. M., Johnson H. A., McCarthy J. K., and Templeton A. S. (2005) Geomicrobiology of manganese(II) oxidation. *Trends in Microbiology* 13, 421-428.
- Templeton A. S., Spormann A. M., and Brown G. E. (2003) Speciation of Pb(II) sorbed by *Burkholderia cepacia*/goethite composites. *Environmental Science and Technology* 37, 2166-2172.

- Toner B., Fakra S., Villalobos M., Warwick T., and Sposito G. (2005a) Spatially resolved characterization of biogenic manganese oxide production within a bacterial biofilm. *Applied and Environmental Microbiology* 71, 1300-1310.
- Toner B., Manceau A., Marcus M. A., Millet D. B., and Sposito G. (2005b) Zinc sorption by a bacterial biofilm. *Environmental Science and Technology* 39, 8288-8294.
- Toner B., Manceau A., Webb S. M., and Sposito G. (2006) Zinc sorption to biogenic hexagonal-birnessite particles within a hydrated bacterial biofilm. *Geochimica et Cosmochimica Acta* 70, 27-43.
- Toner B. and Sposito G. (2005) Reductive dissolution of biogenic manganese oxides in the presence of a hydrated biofilm. *Geomicrobiology Journal* 22, 171-180.
- Vanderbilt D. (1990) Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Physical Review B* 41, 7892-7895.
- Villalobos M., Lanson B., Manceau A., Toner B., and Sposito G. (2006) Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *American Mineralogist* 91, 489-502.
- Villalobos M., Toner B., Bargar J., and Sposito G. (2003) Characterization of the manganese oxide produced by *Pseudomonas putida* strain MnB1. *Geochimica et Cosmochimica Acta* 67, 2649-2662.
- Warren L. A. and Haack E. A. (2001) Biogeochemical controls on metal behaviour in freshwater environments. *Earth-Science Reviews* 54, 261-320.
- Webb S. M. (2004) SIXPack: a Graphical User Interface for XAS Analysis Using IFEFFIT. *Physica Scripta* T115, 1011-1014.
- Webb S. M., Tebo B. M., and Bargar J. R. (2005) Structural characterization of biogenic Mn oxides produced in seawater by the marine *Bacillus sp.* strain SG-1. *American Mineralogist* 90, 1342-1357.

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