Copper sorption by the edge surfaces of synthetic birnessite nanoparticles

Jasquelin Peña^{*1}, John Bargar², Garrison Sposito³

Revised submission to Chemical Geology

¹Institute of Earth Surface Dynamics

University of Lausanne

Lausanne, CH 1015

Email: jasquelin.pena@unil.ch; Tel: +41 21 692 4355

²Stanford Synchrotron Radiation Lightsource Directorate

SLAC National Accelerator Laboratory

Menlo Park, CA 94025

Email: bargar@slac.stanford.edu; Tel: (650) 926-4949

³Geochemistry Department, Earth Sciences Division

Lawrence Berkeley National Laboratory

Berkeley, CA 94720

Email: gsposito@berkeley.edu; Tel: (510) 643-8297

*Corresponding author. Tel: +41 21 692 4355; Fax: +41 21 692 4305;

Email: jasquelin.pena@unil.ch

Keywords: manganese oxide; birnessite; trace metals; copper; sorption; EXAFS spectroscopy

Abstract

We investigated the sorption of Cu by δ -MnO₂, an analog for natural birnessite (layer-type Mn oxide) that is characterized by randomly stacked and curled nanosheets, a low to moderate vacancy content, and variable amounts of layer and interlayer Mn³⁺. The synthetic δ -MnO₂ used in this study had a Na:Mn molar ratio of 0.13, an average manganese oxidation number (AMON) of 3.85 after reaction, a specific surface area of 254 m² g⁻¹ and particle size of 2 – 4 nm in the *ab* plane. The maximum surface excess (q_{max}) value at pH 6 estimated from sorption data of 0.72 (0.64 – 0.83, 95 % confidence interval) mol Cu mol⁻¹ Mn far exceeded the nominal vacancy content for δ -MnO₂ (ca. 6 – 11 % mol vacancy mol⁻¹ Mn), thus implicating multiple binding sites for Cu. The large values of q_{max} and specific surface area of the mineral suggest a major role for surface sites at the particle edges relative to vacancy sites. The extended X-ray absorption fine structure (EXAFS) spectra from δ -MnO₂ samples differ with respect to the EXAFS spectra for Cu(OH)₂, CuO, and Cu₃(CO₃)₂(OH)₂ and Cu-sorbed by biogenic MnO₂. The Cu K-edge EXAFS spectra show two second-shell peaks that can be modeled with Mn and Cu near-neighbors. Copper appears to bind dominantly at particle edges of δ -MnO₂ as dimers or polynuclear surface species. This sorption mechanism is consistent with the moderate vacancy content of δ -MnO₂ and explains the similarity in the EXAFS spectra from samples having surface loadings of 0.01 to 0.26 mol Cu mol⁻¹ Mn. The strong proclivity of Cu to bind on the edge surfaces of nanoparticulate birnessite leads to very large surface excesses of Cu without the formation of a discrete precipitate, making the surface sites at the particle edges the dominant sorption site for Cu.

1. Introduction

Copper is a trace metal of environmental concern due to its widespread use in agriculture and the large quantities of Cu extracted via mining activities (Bradl, 2005). For example, the mass of Cu extracted annually by mining and fossil fuel production is 632 times greater than the mass released annually through crustal weathering and volcanic activity (Klee and Graedel, 2004; Sposito, 2008). This large anthropogenic mobilization factor—the largest among all metals—reflects the significant anthropogenic perturbation of the global biogeochemical cycle of Cu. In soils and sediments receiving anthropogenic inputs, oxide minerals such as layer-type MnO_2 can control the speciation of Cu through adsorption at the water-mineral interface (Davies-Colley et al., 1984; Jenne, 1968; McLaren and Crawford, 1973).

Birnessite (layer-type MnO_2) may bind Cu via three general mechanisms: adsorption at cation vacancy sites, incorporation into the MnO_2 sheet and adsorption at lateral edge surfaces. The adsorption of divalent metals at vacancy sites involves the coordination of the metal to the three surface oxygen atoms surrounding the vacancy site, thus forming a triple-corner-sharing (TCS) complex (Manceau et al., 2002; Manceau et al., 2007b). In birnessite suspensions equilibrated with Cu at low pH values ($\text{pH} \approx 4.0$), Cu-TCS complexes were inferred from the Cu-Mn interatomic distance of 3.39 – 3.43 Å obtained from fitting extended X-ray absorption fine structure (EXAFS) spectra (Arai, 2011; Manceau et al., 2002; Sherman and Peacock, 2010). The occurrence of up to 20 % Cu-incorporation (Cu-INC) at high pH values ($\text{pH} \approx 8.0$) was proposed by Sherman and Peacock (2010) based on the appearance of a peak near 2.9 Å in the Fourier-transformed EXAFS spectrum for $\delta\text{-MnO}_2$ sample with a loading of 0.068 mol Cu mol⁻¹ Mn. However, in a recent density functional theory (DFT) study, Kwon et al. (2013) demonstrated that the incorporation of Cu into a vacancy site strongly inhibits the Jahn-Teller distortion of Cu, destabilizing the Cu-INC species relative to

the Cu-TCS species at any pH value. The formation of Cu-INC thus appears unfavorable. In addition, the Cu-Mn interatomic distance of 2.9 Å may indicate the formation of other surface species. To date there are no reports of Cu adsorption at birnessite edges, but this mode of adsorption has been reported for Ni and Pb, which bind at particle edges in either edge- or corner-sharing configurations with respect to Mn octahedra (Manceau et al., 2007b; Takahashi et al., 2007; Villalobos et al., 2005).

Villalobos et al. (2005) have argued that ion adsorption increases as the specific surface area, and thus the fraction of edge surface sites, increases. Their calculations of residual charges based on bond-valence concepts with all charges expressed as monovalent charges showed that a 5 nm particle with an 8 % vacancy rate would have 70 % of the residual charges located at the particle edges (Villalobos et al., 2005). The formation of Mn oxides in most environments, which occurs predominantly via biological (Learman et al., 2011; Tebo et al., 2004) or surface-catalyzed (Morgan, 2005) oxidation of Mn(II), leads to disordered nanocrystalline birnessite minerals with high specific surface areas (Bargar et al., 2009; Grangeon et al., 2010; Hochella et al., 2005; Manceau et al., 2007a; Manceau et al., 2007b; Marcus et al., 2004; Peacock and Sherman, 2007a; Santelli et al., 2011; Tan et al., 2010; Webb et al., 2005). Consequently, in light of the potentially large fraction of reactive edge sites on birnessite surfaces, we expect particle edges to play an important role in Cu uptake.

The synthetic birnessite δ -MnO₂ is characterized by curled MnO₂ nanosheets with hexagonal sheet symmetry and a small to moderate vacancy content (Grangeon et al., 2008; Manceau et al., 2013; Villalobos et al., 2006). Its high specific surface area and low vacancy content thus make it an optimal choice for studying edge adsorption experimentally. The study of Cu adsorption at birnessite particle edges is particularly relevant in light of the disagreement between experimental and computational findings regarding the incorporation

of Cu into MnO₂ (Kwon et al., 2013; Sherman and Peacock, 2010). Moreover, the inability to explain the observed maximum surface excess of Cu in terms of the nominal vacancy content of the birnessite used (Sherman and Peacock, 2010) implies additional sorption mechanisms. Finally, Cu speciation on birnessite is not well-documented; only a few samples have been characterized to date, three of which were prepared at pH 4 and one at pH 8 (Arai, 2011; Manceau et al., 2002; Sherman and Peacock, 2010).

In the present study we combine sorption isotherm measurements with EXAFS spectroscopy to identify the mechanism of Cu sorption by δ -MnO₂ over a broad range of surface loadings and at circumneutral pH. The specific surface area of the δ -MnO₂ used in our experiments is 254 m²g⁻¹ (Duckworth and Sposito, 2007), indicating nanoparticulate dimensions and thus an overwhelming fraction of residual charges at the particle edges available to bind Cu. We also expect that vacancy sites contribute to Cu adsorption in the TCS geometry but that the incorporation of Cu is unlikely.

2. Materials and methods

2.1 Mineral samples. Delta-MnO₂ was synthesized according to the “redox” method, which involves mixing a solution of MnCl₂·4H₂O with a solution of KMnO₄ in excess NaOH and with a Mn(VII):Mn(II) molar ratio of 0.67 (Villalobos et al., 2003). The δ -MnO₂ powder used in this study has a specific surface area of 254 ± 2 m² g⁻¹, an average manganese oxidation number (AMON) of 4.02 ± 0.06 (prior to reaction), and a Na:Mn content of 26 ± 0.5 % (Duckworth and Sposito, 2007). A water content of 19 % was determined by thermogravimetric analysis using a 10°C/min heating rate from 25 - 200°C (Metler Toledo TGA 851e). High-resolution TEM (Philips CM300 FEG/UT) images of a δ -MnO₂ specimen show a polycrystalline material with an average particle size of 3.2 ± 0.6 nm (10 particles, each measured along *x* and *y* directions) in the *ab* plane (**Fig. 1**). The average Mn-O and Mn-

Mn interatomic distances (R) and coordination numbers (CN) in the birnessite samples obtained from shell-by-shell fits of Mn K-edge EXAFS spectra (**Table A.1** and **Fig. A.1**) are consistent with the structural description of δ -MnO₂ given by Villalobos et al. (2006) and Webb et al. (2005).

2.2 Sorption experiments. Copper sorption and Mn desorption from δ -MnO₂ were measured by equilibrating an oxide slurry with Cu(II) in a 10 mM NaCl and 20 mM MES (2-(N-morpholino)ethanesulfonic acid) solution buffered to pH 6. Mineral samples were ground to a fine powder in an agate mortar and pestle. Stock suspensions were prepared by adding about 0.35 g L⁻¹ solid to the background electrolyte solution. The MnO₂ concentration determined from total digestion of the slurry with a mixture of nitric acid and oxalic acid to measure Mn_{TOT} and assuming an M_w for MnO₂ of 87 g mol⁻¹ was 0.2 g L⁻¹ MnO₂. To ensure that particles were well dispersed, the suspensions were stirred vigorously for 1.5 h, sonicated for 25 min (Branson 3210 sonicator) and returned to the stir plate for 0.5 - 1.0 h. To begin a sorption experiment, 15 mL of the oxide suspension was transferred to a 40 mL Teflon tube by pipette, followed by the addition of Cu(II) from a 50 mM CuCl₂ solution. Before Cu addition but after equilibration in the background electrolyte (10 mM NaCl and 20 mM MES buffer), aliquots were removed for determination of the Na:Mn ratio by ICP-OES and AMON by potentiometric titration using Mohr's salt and Na pyrophosphate. The potentiometric titration method used gives the AMON with a 0.05 uncertainty (Lingane and Karplus, 1946; Vetter and Jaeger, 1966).

Experiments were conducted in duplicate at six concentrations ranging from 0 to 1500 μ M Cu. Aqueous speciation calculations including hydrolysis, carbonate and chloride species, and determinations of the relative saturation with respect to various solids ($\Omega = IAP/K_{so}$) were made using stability constants from the MINEQL+ thermodynamic database (Schecher and McAvoy, 2001) and initial Cu concentrations corrected for ionic strength.

Over the range of concentrations used in sorption experiments, Cu^{2+} accounts for 96-97% of the total Cu. All samples were initially undersaturated with respect to the homogeneous precipitation of $\text{Cu}(\text{OH})_2(\text{s})$ [$\Omega = 0.08 - 0.69$] and CuCO_3 [$\Omega = 0.003 - 0.03$], but not with respect to $\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$ [$\Omega = 1.2 - 8.0$ for $\text{Cu} > 285 \mu\text{M}$ (pH 5.9)] or $\text{CuO}(\text{s})$ [$\Omega = 1.1 - 8.6$ for $\text{Cu} > 86 \mu\text{M}$ (pH 6.0)].

After 50 h of equilibration on a tabletop shaker (150 RPM), two samples were taken from each tube. A 1 mL sample of the slurry was digested with nitric acid (50 μL of a 69 % solution) and oxalic acid (50 μL of a 1 N solution) to determine the total concentrations of Cu and Mn. A 5 mL sample of the solution was obtained by filtration through a 0.22 μm polyethersulfone syringe filter (Millex[®]-GP, Millipore) and acidified with nitric acid to determine the aqueous concentrations of Cu and Mn. A Perkin-Elmer Optima 5300 Inductively-Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) was used to determine Cu and Mn concentrations, using Sc as an internal standard (**Table A.2**). The pH of the filtered solution (pH_{eq}) was also measured at the time of sampling using a Thermo-Orion glass combination pH electrode and a Beckman $\Phi 71$ pH meter (**Table A.2**).

2.3 Sorption isotherms. Surface excess (q) was expressed as the moles of Cu accumulated on the sorbent, with the sorbent concentration expressed in terms of the total moles of Mn in solid phase, as determined by total digestion of the slurry. We chose to express q as a Cu:Mn molar ratio, rather than using the standard units of mol Cu kg^{-1} sorbent, to facilitate the interpretation of q in terms of sorbent properties such as the vacancy content and number of Mn octahedra at particle edges. Plots of the distribution coefficient ($K_d = q / c$ [=] L mol^{-1} , where c is the concentration of the adsorptive species) against q were examined to determine which sorption model best fit the data (Sposito, 2008).

2.4 X-ray absorption spectroscopy. All XAS studies were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL) at Beam Line 4-1 using a Si (220) double crystal

monochromator, calibrated to 8979 eV using a Cu(0) foil. Copper K-edge X-ray absorption spectra were obtained for various samples as outlined in **Table 1**. A liquid N₂ (T = 77 K) cryostat was used to prevent beam-induced changes in the samples. At the beam line, samples were filtered onto Millipore Type HA membranes, which were fixed onto the sample holder using Kapton tape. Samples were kept moist in the dark until the time for XAS measurements. Fluorescence-yield (FY) spectra were measured with a Lytle-type gas ionization chamber detector to values of 12 Å⁻¹, with samples positioned at a 45° angle with respect to the incident beam. The peak heights of X-ray absorption near edge structure (XANES) features in fluorescence mode matched those in transmission mode, suggesting that self-absorption of the FY spectra were insignificant. X-ray absorption spectra of Cu²⁺(aq) (50 mM CuCl₂) and Cu(OH)₂(s) were also measured. The EXAFS spectrum measured for Cu(OH)₂(s) is similar to that published by Cheah et al. (2000). Reference X-ray absorption spectra were obtained from the XAFS Model Compound Data Library for CuO(s) and Cu(CO₃)₂OH(s) (Newville et al., 1999). Finally, a biogenic birnessite sample with 0.02 mol Cu mol⁻¹ Mn adsorbed at vacancy sites [$R_{\text{Cu-Mn}} = 3.44 \text{ Å}$; (Peña, 2009)] is included as a reference.

Both the near edge (XANES) and fine structure (EXAFS) portions of the X-ray absorption spectra were analyzed to determine the Cu coordination geometry and local bonding environment, respectively. X-ray absorption spectra were averaged and background subtracted using SixPack (Webb, 2004). The XANES spectra [$\mu(E)$] included the signal up to 100 eV above the absorption edge. The Cu K-edge XANES spectra from the sorption samples were compared with those measured for reference materials. The EXAFS spectra [$\chi(k)$] were k^3 -weighted and converted to R -space by fast Fourier transform [$\text{FT}(\chi(k)*k^3)$] over the k range of 2.5 - 12 Å⁻¹ using a Kaiser-Bessel window with the windowing parameter (dk) set to 3 Å⁻¹.

2.5 Structural modeling of EXAFS spectra. The d^9 electronic configuration of Cu(II) leads to the Jahn-Teller distortion of the first coordination shell. This structural distortion leads two distinct Cu-O subshells, where the equatorial sub-shell dominates the EXAFS signal, but the axial sub-shell cannot be fitted reliably due to its anisotropic disorder (Cheah et al., 2000). The range of interatomic distances between Cu and first neighbors is also propagated to the second-shell neighbors. To best constrain the bonding environment of sorbed Cu, we developed a list of diagnostic Cu-X (X = O, Mn, Cu) second-shell interatomic distances for a range of Cu-MnO₂ surface complexes (**Fig. 2**): For outer sphere (O.S.) surface complexes, we estimated the shortest-possible second-shell Cu-O interatomic distances assuming a 0.135 nm ionic radius for O(-II) and a 0.27 nm distance between O atoms (Shannon, 1976; Xia et al., 1997). For inner-sphere surface complexes at vacancy sites and/or particle edges, we estimated the Cu-Mn distances from sorption studies of Cu (Arai, 2011; Manceau et al., 2002; Sherman and Peacock, 2010) or other trace metals on birnessite (Duckworth et al., 2008; Manceau et al., 2007b; Villalobos et al., 2005). For Cu polymerization or precipitation, we obtained Cu-Cu distances by fitting reference compounds or from reports of polynuclear Cu surface complexes (Cheah et al., 2000).

Shell-by-shell fits of the EXAFS spectra were made using SixPack (Webb, 2004) or Artemis (Ravel and Newville, 2005). Phase and amplitude functions were obtained with FEFF6l (Rhehr et al., 1992) for Cu(OH)₂(s) (Downs and Hall-Wallace, 2003), geometry-optimized Cu-MnO₂ clusters with Cu coordinated to the surface oxygen atoms at a vacancy site (Kwon et al., 2013), and single scattering paths of varying interatomic distances to represent second-shell neighbors for Cu sorbed via outer-sphere (X = O), inner-sphere (X = Mn) or precipitation mechanisms (X = Cu), following **Fig. 2**. The amplitude reduction factor (S_0^2) was set to 0.9 in all fits, based on analysis of the EXAFS spectra obtained from 50 mM CuCl₂ and 50 mM Cu-EDTA solutions. Final fits were made in Artemis in *R*-space with all

data sets fit simultaneously using a k -range of 2.5 - 12 Å⁻¹, which gives a spatial resolution of $\Delta R = \pi / 2 \Delta k = 0.17$ Å (Kelly et al., 2008), k -weights of 2 and 3, and a Kaiser-Bessel window with a dk value of 3 Å⁻¹. Fits of multiple k -weights simultaneously reduce errors in fitted parameters and correlations between variables (Kelly et al., 2008).

3. Results

3.1 Copper sorption. As shown by **Fig. 3**, Cu was sorbed extensively by δ -MnO₂ in suspensions equilibrated to pH values of 6 (10 mM NaCl and 20 mM MES buffer). Plots of K_d against q showed that K_d extrapolated to a finite value as q approached zero and tended to zero at a finite value of q (**Fig. 3, inset**). A maximum surface excess value of 0.72 (0.64 – 0.83, 95 % confidence interval) mol Cu mol⁻¹ Mn was determined from the x -intercepts of K_d versus q plots for δ -MnO₂. If each linear segment in the K_d versus q plots is assumed to correspond to a class of sorption sites with different affinities, the corresponding maximum surface excess values are 0.19 (0.18 - 0.20) and 0.53 (0.43 - 0.64) mol Cu mol⁻¹.

The sorption of Cu by δ -MnO₂ was accompanied by the concomitant accumulation of Mn(II) in solution (**Fig. 4**). At the highest loadings (ca. 0.5 - 0.6 mol Cu mol⁻¹ Mn), concentrations of 110 - 130 µM Mn were measured in solution. These Mn(II) concentrations, which were adjusted by the fraction of Mn(II) released from Cu-free suspensions (28 µM Mn or 1.23 % of the total Mn at pH 6.03), represent about 5 % of the total initial Mn in the solid phase. The Mn released to solution derives from Mn(II,III) associated with the δ -MnO₂ particles. Although the unreacted δ -MnO₂ powder had an AMON of 4.0 and Na:Mn content of 26 %, the AMON value of δ -MnO₂ equilibrated to pH 6.0 (10 mM NaCl, 20 mM HEPES) decreased to 3.85 and the Na:Mn content to 13 % before the addition of Cu(II). This decrease in AMON suggests that the buffer used to control solution pH may interact with the Mn oxide particles through Mn(IV) reduction. This AMON value indicates that δ -MnO₂ contains up to

15 % Mn(III) or 7 % Mn(II), which may be distributed within the MnO₂ sheets or in the interlayer (Manceau et al., 2013). The decrease in the Na:Mn content is consistent with the increase in H⁺ activity and accumulation of layer Mn(III) and interlayer Mn(II, III) in δ -MnO₂ as pH is lowered from the synthesis pH of 8 to the experimental pH of 6 (Manceau et al., 2013).

The concentration of aqueous Mn increased in proportion to the Cu surface excess for $q < 0.4 \text{ mol Cu mol}^{-1} \text{ Mn}$, with 1 mol of Mn measured in solution for every 7.4 mol of Cu sorbed ($R^2 = 0.97$). Based on this correlation, we determined the apparent cation-exchange constant, K_{app} , for the reaction.

by regressing $q / (c_{\text{Cu}} / c_{\text{Mn(II)}})$ against q for $q < 0.4 \text{ mol Cu mol}^{-1} \text{ Mn}$ (**Fig. A.2**) following the approach described in Peña et al. (2010). On the left side of equation (2), both Mn(II) and Mn(III) are indicated as surface-bound species. However, Mn³⁺, which disproportionates readily to Mn(IV) and Mn(II) unless complexed by a high-affinity ligand (Morgan, 2000), is not included on the right-hand side of equation (2). The apparent cation-exchange constant of 1.67 ± 0.80 , which is not statistically different from 1.0, suggests no preference of δ -MnO₂ for neither Cu(II) nor Mn(II,III) (Sposito, 2008).

3.2 X-ray absorption near edge structure spectra. The XANES spectra from experimental samples are plotted together with the spectra from CuCl₂(aq), Cu(OH)₂(s) and CuO(s) in **Fig. 5**. The presence of Cu as Cu(II) is confirmed by the absorption edge position of 8998 eV and very weak pre-edge feature around 8981 eV (Kau et al., 1987). The shoulder in the XANES spectra near 8990 eV, manifest as distinct peaks near 8987 and 8993 eV in the first derivative of the XANES spectra (**Fig. 5b**), indicates significant distortion of the Cu(II) polyhedron in the sorption samples. This feature arises from the destabilization of the 4p_z orbitals that causes the elongation of the axial bonds relative to the equatorial ones (Alcacio et al., 2001;

Frenkel et al., 2000; Garcia et al., 1989). In tetrahedral coordination, the pre-edge feature in the Cu K-edge XANES should show greater intensity and be shifted towards slightly lower energies (Dupont et al., 2002; Shimizu et al., 2001). The XANES spectra from the sorption samples show additional differences relative to the reference compounds as indicated by the arrowheads in **Fig. 5a**. The intensity of the shoulder near 9010 eV in the sorption samples is intermediate to that in aqueous Cu(II) and the Cu solids. Furthermore, the shape and position of the oscillation around 9040 eV in the XANES spectra from the δ -MnO₂ samples differ from that in Cu(OH)₂(s). These differences between the experimental and reference XANES spectra support the adsorption rather than the precipitation of Cu(II) in the δ -MnO₂ samples.

3.3 Qualitative interpretation of the EXAFS spectra. The Cu K-edge EXAFS spectra and corresponding FTs obtained from δ -MnO₂ samples are presented in **Fig. 6**. The EXAFS spectra for samples with loadings ranging from 1 to 26 % (mol Cu mol⁻¹ Mn) show only small sample-to-sample variations. Principal component analysis (Toner et al., 2006) returns one component, which can describe 73 % of the variance in the entire data set or 82 % of the variance in the data set when Cu_01a and Cu_02a were excluded from the analysis due to high noise at large k -values. In **Fig. 7**, the EXAFS spectra from samples Cu_02b (**Fig. 7A**) and Cu_12b (**Fig. 7B**) are overlain with the reference spectra from Cu²⁺(aq), Cu-biogenic MnO₂, Cu(OH)₂(s), CuO(s) and Cu(CO₃)₂OH(s). The EXAFS spectra from the sorption samples differ from both the EXAFS spectrum for Cu²⁺(aq), which consists of one major frequency, and the EXAFS spectra for Cu-biogenic MnO₂ and Cu(OH)₂(s), which show distinct splitting of the oscillations around 8.0 Å⁻¹ and 10 Å⁻¹. The EXAFS spectra from the experimental samples also match poorly with those from CuCO₃OH and CuO. Target transform analysis (Toner et al., 2006) for all Cu minerals returned spoil values greater than 5, confirming the poor match between the EXAFS spectra from the reference Cu solids and the sorption samples. None of the reference compounds tested provides a close match to the

experimental samples, suggesting that these phases were not present in the samples at fractions above the detection limit of EXAFS spectroscopy.

The FTs of the EXAFS spectra (**Fig. 6b**) show a major peak near 1.5 Å ($R + dR$), corresponding to the first shell of oxygen atoms surrounding Cu. The absence of a prominent second-shell peak near 3 Å ($R + dR$) contrasts the FT EXAFS spectra from Cu- δ -MnO₂ [pH 4, (Manceau et al., 2007b)], Cu-biogenic MnO₂ [pH 6, (Peña, 2009)], and Ni and Zn-MnO₂ [pH 4 – 8, (Manceau et al., 2007b; Peacock and Sherman, 2007b; Peña et al., 2010; Toner et al., 2006)] where the metal adsorbs mainly as a TCS species at the vacancy sites. Instead, the FTs of our EXAFS spectra show two small second-shell peaks at ca. 2.5 and 3.5 Å ($R + dR$) that are separated by 0.4 – 0.5 Å. Due to geometric constraints, a second-shell O atom could be no closer than about 3.4 Å (**Fig. 2**). Oxygen second neighbors thus can only contribute amplitude to the 2nd of these two second-shell peaks. Copper is unlikely to contribute amplitude to the 2nd second-shell peak based on the Cu-Cu distances in oxide and hydroxide minerals, which range from 2.91 to 3.10 Å (Cheah et al., 2000). Manganese, however, could be present over the entire range of 2.5 and 3.5 Å ($R + dR$). At distances greater than 3.6 Å ($R + dR$), small amplitude peaks are present but we cannot ascertain whether they arise from scattering from neighboring atoms or artifacts from Fourier transformation.

The preceding qualitative analysis provides three insights into the sorption mechanism of Cu equilibrated with δ -MnO₂ at pH 6: 1) a discreet Cu precipitate is unlikely; 2) Cu-TCS complexes are not a major surface species; and 3) Cu appears to show no preference in the average bonding environment at low surface loading relative to high surface loading.

3.4 Shell-by-shell fits of EXAFS spectra. We fit the first-shell peak in the FT of the EXAFS spectra with 3.6 - 4.0 oxygen atoms at 1.94 Å (**Table 2**). The *CN* for the Cu-O shell at 1.94 Å was higher for samples with lower loadings and lower pH values. The decrease in *CN* as the

Cu loading increases indicates an increase in the *average* structural disorder around Cu, which is consistent with an increase in the number of surface complex geometries.

While we expect the presence of one or two axial ligands in the first coordination shell, they are far from the Cu center and have high structural disorder (Cheah et al., 2000). Manceau et al. (2002) obtained an improved fit and more physically reasonable model by adding 1 - 2 oxygen atoms at 2.23 Å, along with 4 the oxygen atoms at 1.96 Å. Consistent with this result, the 6 eV separation between the α - and β - peaks in the 1st derivative of the XANES spectra (**Fig. 5b**) indicates that the axial ligand(s) are located at about $1.9 + 0.4$ Å or 2.3 Å (Frenkel et al., 2000). We cannot confirm whether Cu has one or two axial ligands but, in principle, both outcomes are reasonable because Cu in aqueous solution prefers a 5-fold elongated square pyramidal coordination that is likely to be competitive with a 6-fold distorted octahedral coordination (Bryantsev et al., 2008; Frenkel and Korshin, 2001).

To test the coordination geometries shown in **Fig. 2**, we fit the ca. 2.0 Å ($R + dR$) peak with Cu-Mn and Cu-Cu paths and the ca. 3.5 Å ($R + dR$) peak with Cu-Mn and Cu-O scattering paths (**Figs. 8** and **9**). Fits to the ca. 2.0 Å peak using either Cu-Cu or Cu-Mn scattering paths yielded similar results in terms of the R -factor and uncertainties in estimated parameters (**Table 2**). However, the optimized distances representing edge-sharing and corner-sharing linkages between Cu and Mn polyhedra varied slightly depending on the backscatter included in the fit: Cu-Cu 2.88 Å or Cu-Mn 2.90 Å with Cu-Mn at 3.39 Å. Our attempts to include a Cu-O path to fit 2nd second-shell peak were not successful, suggesting that Cu-Cu/Mn scattering contribute most of the amplitude to the second-shell peaks. Finally, the fitted second-shell CNs , which ranged from 0.50 ± 0.23 to 1.47 ± 0.39 , indicate that on average Cu has few near neighbors.

4. Discussion

4.1 Copper coordination environment

The XANES spectra obtained from Cu sorbed δ -MnO₂ indicate that Cu is present as Jahn-Teller distorted Cu(II) with either one or two axial ligands. In our analysis of the EXAFS spectra, we fit approximately 4 Cu atoms with a low Debye Waller factor ($0.005 \pm 0.0003 \text{ \AA}^2$), indicating relatively low local structural disorder in the four Cu-O bond distances. Presumably, these four Cu-O bonds are the equatorial bonds of the Jahn-Teller distorted Cu polyhedron. The Cu-O interatomic distance of $1.94 \pm 0.002 \text{ \AA}$ found for our samples is slightly shorter by $0.01 - 0.02 \text{ \AA}$ relative to the Cu-O distance reported for Cu(OH)₂ and Cu sorbed δ -MnO₂ samples (Arai, 2011; Cheah et al., 2000; Manceau et al., 2002). A Cu-O distance of $1.94 \text{ \AA}$ was observed for Cu complexed by NOM (Manceau and Matynia, 2010). This ideal or strain-free metal-ligand bond length is achieved when Cu lies in the plane formed by two ring chelates (Manceau and Matynia, 2010). By analogy, this result together with the low fit-derived CNs for the Cu-Cu/Mn shells ($\text{CN} < 2$) and the similarity in fits where Cu or Mn was used as the second-shell backscatter suggests that at least a fraction of the total Cu sorbs as Cu-dimers at the particle edges in the DES geometry, with one pair of equatorial oxygen atoms in Cu coordinated to Cu and the other pair coordinated to Mn.

The Fourier transformed Cu K-edge EXAFS spectra acquired from δ -MnO₂ displayed two small second-shell peaks due to scattering from Mn and Cu second-shell neighbors. We attempted to establish the polyhedral connectivity between Cu and Mn polyhedra (**Fig. 2**) based on the Cu-Mn and Cu-Cu interatomic distances obtained from fitting the EXAFS spectra. However, for the ca. $2.0 \text{ \AA}$ ($R + dR$) FT peak, the goodness of fit criteria and uncertainties in fitted parameters were similar regardless of whether Cu or Mn was used as the backscattering atom. In addition, in all fits the coordination numbers of the Cu-Cu and/or Cu-Mn shells ranged from 0.52 ± 0.14 to 1.47 ± 0.38 , with Debye-Waller factors less than $0.008 \text{ \AA}^2$. These structural parameters together with the low amplitude of FT peaks at $R + dR$

$> 4 \text{ \AA}$ suggest that on average Cu has a relatively small number of Mn and Cu near neighbors. Evidently, the surface complex geometries are not well defined. However, our data indicate that the formation of a discrete Cu precipitate and the incorporation of Cu at vacancy sites are unlikely.

Several lines of evidence indicate that the formation of a discrete precipitate is unlikely. First, the XANES spectra show distinct differences in the samples versus the Cu precipitates, especially in the oscillation near 9040 eV. Second, the fitted Cu-Cu distance of $2.88 \pm 0.006 \text{ \AA}$ for the samples is shorter by $0.03 - 0.08 \text{ \AA}$ than the Cu-Cu distances observed in Cu solids such as $\text{Cu(OH)}_2(\text{s})$ and $\text{CuO}(\text{s})$. Target transform analysis showed that the EXAFS spectra from various Cu solids could not be reconstructed based on the principle components identified in the data set. Third, the EXAFS spectra measured from the sorption samples were similar irrespective of the Cu surface loading, even at the lowest surface loading (Cu_01a) where the saturation index with respect to the Cu solids ranged from 0.01 – 0.36.

Our EXAFS spectra also do not provide strong evidence in support of the incorporation of Cu at vacancy sites. In a previous study, a small extent of Cu incorporation (ca. 20 % of the total sorbed Cu or $0.01 \text{ mol Cu mol}^{-1} \text{ Mn}$) has been reported to occur at pH 8 (Sherman and Peacock, 2010). However, the Cu K-edge EXAFS spectrum acquired from a sample at pH 8 was rather similar to the EXAFS spectrum acquired from a sample at pH 4, where Cu was assigned to bind exclusively to vacancy sites as Cu-TCS. In the current study, in addition to the low fitted CNs and to the lack of structure at R -values greater than $3 \text{ \AA}$, we exclude the significant incorporation of Cu at vacancy sites based on the strongly distorted first shell of Cu^{2+} polyhedron and the highly-ordered bonding environment imposed by the triangular cavity formed by the three surface oxygen atoms at a vacancy site. Our interpretation is consistent with a recent DFT study, which showed that Cu incorporation

strongly inhibited the Jahn-Teller distortion of Cu and thus destabilized this species relative to the Cu-TCS species.

Instead, we suggest that Cu forms multiple surface species, including inner-sphere complexes and dimeric or polynuclear surface species (*i.e.*, containing multiple Cu atoms). The large measured surface excess values support the formation of Cu dimers or polynuclear surface species. In addition, these complexes should occur in all samples based on the similarity in the Cu K-edge EXAFS spectra at the lowest and highest surface loadings.

If Cu dimers sorbed at the δ -MnO₂ particle edges in an edge-sharing configuration with respect to Mn octahedra, then both Cu and Mn near-neighbors would be located at similar interatomic distances and photoelectron backscattering from both elements would contribute to the 2.0 Å ($R + dR$) peak in the FT-EXAFS spectra. When a Cu shell was fit to the second-shell peak at ca. 2.5 Å ($R + dR$), we obtained a Cu-Cu distance of 2.88 ± 0.006 Å. This distance is within 0.03 - 0.08 Å of the Cu-Cu distances observed in Cu(OH)₂ and CuO. The contracted Cu-Cu distance in our sorption samples may be caused by the underlying mineral substrate, which is known to influence the distance between Cu atoms in polynuclear surface complexes (Cheah et al., 2000; Karthikeyan et al., 1999; Morton et al., 2001; Peacock and Sherman, 2004; Rodda et al., 1996; Strawn et al., 2004). When a Mn shell was fit to this peak, we obtained a Cu-Mn distance of 2.90 ± 0.006 Å. This Cu-Mn distance is similar to the average Mn-Mn (2.87 Å) and Ni-Mn (2.86 Å) distances between edge-sharing octahedra in birnessite (Peña et al., 2010; Villalobos et al., 2006).

The longer second-shell interatomic distance of 3.39 Å does not appear in Cu solids (Cheah et al., 2000). Therefore, this distance likely arises from Mn second neighbors. The average Cu-Mn distance of 3.39 Å may be due to the adsorption of Cu at vacancy sites. Manceau et al. (2002) and Sherman and Peacock (2010) each collected an EXAFS spectrum from samples prepared at pH 4 with loadings of 0.156 mol Cu mol⁻¹ Mn and 0.07 mol Cu

mol⁻¹ Mn, respectively. Manceau et al. (2002) proposed a Jahn-Teller distorted octahedral TCS complex with 5.4 Mn atoms fitted at 3.43 Å, whereas Sherman and Peacock (2010) suggested a 4-coordinate TCS complex with 3 Mn atoms fixed at 3.39 Å and 3 Mn atoms fixed at 3.43 Å. Similar to these Cu-Mn distances, Arai (2011) fitted 2 – 3 Mn atoms at 3.42 Å in samples where Cu was adsorbed in kaolinite-birnessite mixtures with a maximum loading of 0.02 mol Cu mol⁻¹ Mn (33 m² g⁻¹ specific surface area) and a solution pH value of 4 or 6. Geometry optimizations of Cu-TCS with Cu in six-fold coordination (octahedral) showed average Cu-O and Cu-Mn distances of 2.02 Å and 3.48 Å, whereas Cu-TCS in four-fold coordination (tetrahedral) with two hydrogen-bonded water molecules showed average Cu-O and Cu-Mn distances of 1.95 Å and 3.40 Å (Kwon et al., 2013). The geometry-optimized structures for both Cu-TCS with Cu in six or four-fold coordination showed highly asymmetric distributions of near-neighbor distances and similar relative stabilities in terms of the total energy of the complex (Kwon et al., 2013). Thus, both coordination geometries may be possible at the vacancy sites.

4.2 Copper sorption capacity

The δ-MnO₂ used in this study showed extensive sorption of Cu. The measured surface excess values of Cu on birnessite agree with previous reports. For example, at pH 4 - 4.5, surface excess values of 0.13 - 0.14 mol Cu mol⁻¹ Mn were obtained for birnessite (McKenzie, 1970; Traina and Doner, 1985b; Wang et al., 2012), whereas at pH 6, in the presence of equimolar solutions of Cu(II) and Co(II), a surface excess of 0.39 mol Cu mol⁻¹ Mn was observed (Traina and Doner, 1985b). In addition, comparable surface excess values ranging from 0.22 - 0.31 mol Pb mol⁻¹ Mn have been reported for Pb sorption by δ-MnO₂ at pH 5 – 6 (Nelson et al., 1999; Villalobos et al., 2005). The surface excess values reported generally increased with the specific surface area of birnessite used, which is consistent with

the increasing proportion of edge sites with decreasing particle size (Villalobos et al., 2005). For example, Catts and Langmiur (1986) showed that as the specific surface area of δ -MnO₂ increased from 143 to 290 m² g⁻¹, the surface excess increased from 0.07 to 0.12 mol Cu mol⁻¹ Mn. However, Wang et al. (2012) showed that variations in the average manganese oxidation number influenced adsorption capacity more strongly than specific surface area, thus the Mn(III) content and distribution within the MnO₂ structure must be considered in order to assess correctly the relative importance of vacancy versus edge sites for metal sorption by birnessite.

Concomitant with the adsorption of Cu, up to 5 % of the total Mn initially in the solid phase was measured in solution as Mn(II), after correction for any Mn released from the Cu-free experiments. Aqueous Mn derives from adsorbed lower-valent Mn that is readily displaced by Cu(II) (McKenzie, 1970; Traina and Doner, 1985a, b). The measured AMON value of 3.85 indicates that δ -MnO₂ equilibrated with 10 mM NaCl and 20 mM MES buffer contains up to 15% Mn(III) or 7% Mn(II) before Cu addition. Thus, at the maximum surface loadings, 30 – 70 % of the lower-valent Mn has been replaced by Cu. While Mn(III) is assumed to migrate from layer to interlayer sites as vacancies are generated (Manceau et al., 2013), it is also plausible that some lower valent Mn is located at the particle edges.

4.3 Distribution of Cu among surface sites

Based on our fit-derived *CN*s normalized to the ideal *CN* of the Cu-Mn shell characteristic for the TCS complex, and based on the correlation between the Mn(II) concentration in solution and the Cu surface excess that may arise from Cu-Mn exchange at vacancy sites, we suggest that 15 - 24 % of the total Cu adsorbed or 0.04 – 0.06 mol Cu mol⁻¹ Mn may be present as Cu-TCS. The remaining Cu (76 - 85 %) would be adsorbed at the δ -MnO₂ particle edges. The fractional contribution of Cu-TCS species corresponds to a 0.06

mol Cu mol⁻¹ Mn loading in the highest loading sample studied EXAFS spectroscopy. This loading is consistent with the moderate vacancy content reported for δ -MnO₂ (Villalobos et al., 2013; Manceau et al., 2013).

The Cu-TCS loading estimated above represents the upper-limit contribution from Cu-TCS species because the Cu-Mn shell at 3.39 Å may also reflect Cu or Cu dimers adsorbed at the δ -MnO₂ particle edges. For example, a Cu atom coordinated to two singly-coordinated oxygen atoms (e.g., Cu-DCS) may have a Cu-Mn interatomic distance similar to the Cu-Mn distance in the Cu-TCS complex, as proposed for Ni-TCS and Ni-DCS species (Manceau et al., 2007b). In addition, Kwon et al. (2010) showed that the metal-Mn distances at the particle edges can overlap with the metal-Mn distances of complexes formed at vacancy sites.

The relative proportions of Cu adsorbed at vacancy sites and particle edges can also be estimated by considering the structure and size of δ -MnO₂ particles. A vacancy content ranging from 6 – 11 % has been proposed for δ -MnO₂ based on modeling of X-ray diffraction and high energy X-ray scattering data (Villalobos et al., 2006; Manceau et al., 2013). However, the “true” vacancy content is likely to be smaller because these estimates do not consider explicitly the under-coordinated Mn atoms at the particle edges (Grangeon et al., 2008; Villalobos et al., 2006). Using the 2 - 4 nm particle size obtained from HR-TEM (**Fig. 1**), we estimated that the proportion of binding sites at the particle edges, normalized to monovalent charges following Villalobos et al. (2005) is greater than the proportion of vacancy sites by at least one order of magnitude. Thus, our identification of the particle edges as the dominant reactive sites from EXAFS spectroscopy is reasonable in terms of surface site density and particle size.

Assuming that Cu adsorbs as dimers and assuming an approximate site density of 18 sites nm⁻² (Catts and Langmuir, 1986) or 1.5 x 10⁻³ mol sites L⁻¹ for a δ -MnO₂ suspension

containing 0.2 g L^{-1} and a specific surface area of $254 \text{ m}^2 \text{ g}^{-1}$, we estimated that Cu occupies 0.7 - 17 % of all surface sites on $\delta\text{-MnO}_2$ in samples with loadings of 0.01 to $0.26 \text{ mol Cu mol}^{-1} \text{ Mn}$. If the loading was adjusted to account for the fraction of Cu that may adsorb as a TCS complex at vacancy sites, then Cu would occupy ca. 14 % of the remaining surface sites in $\delta\text{-MnO}_2$ at the highest loading studied by EXAFS spectroscopy ($0.26 \text{ mol Cu mol}^{-1} \text{ Mn}$). For particles with a 2 - 4 nm diameter (i.e., 20 - 40 % of the Mn atoms at the particle edges), it is reasonable to have up to 20% of the reactive surface sites located at the particle edges. At the q_{max} value of $0.72 \text{ mol Cu mol}^{-1} \text{ Mn}$, we estimate that Cu would occupy ca. 46 % of all surface sites in $\delta\text{-MnO}_2$ and that these reactive surface sites would be located dominantly at the particle edges. In contrast, assuming that only vacancy sites were reactive, Sherman and Peacock (2010) estimated a maximum sorption capacity of $0.013 \text{ mol Cu mol}^{-1} \text{ Mn}$ based on the measured specific surface area of 107 g m^{-2} and estimate of 2.22 vacancies per nm^2 . Their measured a surface excess of $0.068 \text{ mol Cu mol}^{-1} \text{ Mn}$ suggest that either the reactive surface area is not well approximated by specific surface area or that additional binding sites are involved in Cu sorption. The results in this study help to resolve this paradox.

4.4 Environmental implications

The manganese oxide used in the study, $\delta\text{-MnO}_2$, has been proposed as a synthetic analog for birnessite found in natural environments (Villalobos et al., 2003). The maximum sorption capacity of $0.72 \text{ mol Cu mol}^{-1} \text{ Mn}$ (pH 6), derived from plots of the distribution coefficient against surface excess, greatly exceeds the vacancy content expected for birnessite minerals. Our EXAFS analysis shows that Cu has a strong proclivity for adsorbing on the edge surfaces of nanoparticulate birnessite. The large tendency of Cu to sorb at the edges can be rationalized in terms of its Jahn-Teller distorted coordination and the ease with which it dimerizes. Both of these properties render the adsorption of Cu to geometrically-constrained

sorption sites on the basal surface of MnO_2 (i.e., triangular cavity formed by three surface oxygen atoms at a vacancy site) less favorable than adsorption at edge surface sites. For these same reasons, Cu may sorb more favorably at the particle edges than trace metals such as Ni and Zn, which display significantly less distortion in the first coordination shell relative to Cu^{2+} and do not tend to polymerize. Nonetheless, Ni and Zn adsorption at edge surfaces may occur under conditions where vacancy sites are not available for sorption or where an overwhelming fraction of the reactive surface sites are located at the particle edges. In summary, the contribution of the edge surfaces to metal sorption by birnessite will be controlled by i) the preferred bonding geometry of the metal cation, ii) the relative proportions of edge to vacancy surface sites and iii) the presence of competing ligands that may block surface sites at the particle edges (e.g., organic ligands present in the biofilm matrix surrounding biogenic birnessite particles). Our findings suggest that in the absence of a biofilm matrix and/or in the case of vanishingly small particles, metal sorption at birnessite particle edges may be the dominant mode of metal attenuation.

Acknowledgements

This research was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. HR-TEM images were acquired at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory. J. Peña acknowledges support from the Sandoz Family Foundation. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.

References

Alcacio, T.E., Hesterberg, D., Chou, J.W., Martin, J.D., Beauchemin, S., Sayers, D.E., 2001. Molecular scale characteristics of Cu(II) bonding in goethite-humate complexes. *Geochim. Cosmochim. Acta* 65, 1355-1366.

Arai, Y., 2011. Aqueous interfacial chemistry of kaolinite for the removal of Cu(II) in the presence of birnessite: Kinetic and spectroscopic studies. *Appl. Clay Sci.* 53, 572-580.

Bargar, J.R., Fuller, C.C., Marcus, M.A., Brearley, A.J., De la Rosa, M.P., Webb, S.M., Caldwell, W.A., 2009. Structural characterization of terrestrial microbial Mn oxides from Pinal Creek, AZ. *Geochim. Cosmochim. Acta* 73, 889-910.

Bradl, H.B., 2005. *Heavy Metals in the Environment*, Interface Science and Technology. Elsevier Academic Press, New York, p. 269.

Bryantsev, V.S., Diallo, M.S., van Duin, A.C.T., Goddard, W.A., III, 2008. Hydration of copper(II): New insights from density functional theory and the COSMO solvation model. *Journal of Physical Chemistry A* 112, 9104-9112.

Catts, J.G., Langmuir, D., 1986. Adsorption of Cu, Pb and Zn by δ -MnO₂: applicability of the site binding-surface complexation model. *Appl. Geochem.* 1, 25-264.

Cheah, S.F., Brown, G.E., Parks, G.A., 2000. XAFS study of Cu model compounds and Cu²⁺ sorption products on amorphous SiO₂, gamma-Al₂O₃, and anatase. *Am. Mineral.* 85, 118-132.

Davies-Colley, R.J., Nelson, P.O., Williamson, K.J., 1984. Copper and cadmium uptake by estuarine sedimentary phases. *Environ. Sci. Technol.* 18, 491-499.

Downs, R.T., Hall-Wallace, M., 2003. The American mineralogist crystal structure database. *Am. Mineral.* 88, 247-250.

Duckworth, O.W., Bargar, J.R., Sposito, G., 2008. Sorption of ferric iron from ferrioxamine B to synthetic and biogenic layer type manganese oxides. *Geochim. Cosmochim. Acta* 72, 3371-3380.

Duckworth, O.W., Sposito, G., 2007. Siderophore-promoted dissolution of synthetic and biogenic layer-type Mn oxides. *Chem. Geol.* 242, 497-508.

Dupont, L., Guillon, E., Bouanda, J., Dumonceau, J., Aplincourt, M., 2002. EXAFS and XANES studies of retention of copper and lead by a lignocellulosic biomaterial. *Environmental Science & Technology* 36, 5062-5066.

Frenkel, A.I., Korshin, G.V., 2001. Studies of Cu(II) in soil by X-ray absorption spectroscopy. *Canadian Journal of Soil Science* 81, 271-276.

Frenkel, A.I., Korshin, G.V., Ankudinov, A.L., 2000. XANES study of Cu²⁺-binding sites in aquatic humic substances. *Environmental Science & Technology* 34, 2138-2142.

Garcia, J., Benfatto, M., Natoli, C.R., Bianconi, A., Fontaine, A., Tolentino, H., 1989. The quantitative Jahn-Teller distortion of the Cu²⁺ site in aqueous-solution by XANES spectroscopy. *Chem. Phys.* 132, 295-307.

Grangeon, S., Lanson, B., Lanson, M., Manceau, A., 2008. Crystal structure of Ni-sorbed synthetic vernadite: a powder X-ray diffraction study. *Mineralogical Magazine* 72, 1279-1291.

Grangeon, S., Lanson, B., Miyata, N., Tani, Y., Manceau, A., 2010. Structure of nanocrystalline phyllomanganates produced by freshwater fungi. *Am. Mineral.* 95, 1608-1616.

Hochella, M.F., Kasama, T., Putnis, A., Putnis, C.V., 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. *Am. Mineral.* 90, 718-724.

Jenne, E.A., 1968. Controls on Mn Fe Co Ni Cu and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe Oxides. *Advances in Chemistry Series*, 337-387.

Karthikeyan, K.G., Elliott, H.A., Chorover, J., 1999. Role of surface precipitation in copper sorption by the hydrous oxides of iron and aluminum. *J. Colloid Interface Sci.* 209, 72-78.

Kau, L.S., Spirasolomon, D.J., Pennerhahn, J.E., Hodgson, K.O., Solomon, E.I., 1987. X-Ray absorption-edge determination of the oxidation-state and coordination-number of copper: Application to the type-3 Site in *Rhus vernicifera* laccase and its reaction with oxygen. *J. Am. Chem. Soc.* 109, 6433-6442.

Kelly, S.D., Hesterberg, D., Ravel, B., 2008. Analysis of Soils and Minerals Using X-ray Absorption Spectroscopy, in: Ulrey, A.L., Drees, R.L. (Eds.), *Methods of Soil Analysis, Part 5-Mineralogical Methods*. Soil Science Society of America, Madison.

Klee, R.J., Graedel, T.E., 2004. Elemental cycles: A status report on human or natural dominance. *Annual Review of Environment and Resources* 29, 69-107.

Kwon, K.D., Refson, K., Sposito, G., 2010. Surface complexation of Pb(II) by hexagonal birnessite nanoparticles. *Geochim. Cosmochim. Acta* 74, 6731-6740.

Kwon, K.D., Refson, K., Sposito, G., 2013. Understanding the trends in transition metal sorption by vacancy sites in birnessite. *Geochim. Cosmochim. Acta* 101, 222-232.

Learman, D.R., Voelker, B.M., Vazquez-Rodriguez, A.I., Hansel, C.M., 2011. Formation of manganese oxides by bacterially generated superoxide. *Nature Geoscience* 4, 95-98.

Lingane, J.J., Karplus, R., 1946. NEW METHOD FOR DETERMINATION OF MANGANESE. Industrial and Engineering Chemistry-Analytical Edition 18, 191-194.

Manceau, A., Kersten, M., Marcus, M.A., Geoffroy, N., Granina, L., 2007a. Ba and Ni speciation in a nodule of binary Mn oxide phase composition from Lake Baikal. Geochim. Cosmochim. Acta 71, 1967-1981.

Manceau, A., Lanson, B., Drits, V.A., 2002. Structure of heavy metal sorbed birnessite. Part III: Results from powder and polarized extended X-ray absorption fine structure spectroscopy. Geochim. Cosmochim. Acta 66, 2639-2663.

Manceau, A., Lanson, M., Geoffroy, N., 2007b. Natural speciation of Ni, Zn, Ba, and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. Geochim. Cosmochim. Acta 71, 95-128.

Manceau, A., Marcus, M.A., Grangeon, S., Lanson, M., Lanson, B., Gaillot, A.C., Skanthakumar, S., Soderholm, L., 2013. Short-range and long-range order of phyllomanganate nanoparticles determined using high-energy X-ray scattering. J. Appl. Crystallogr. 46, 193-209.

Manceau, A., Matynia, A., 2010. The nature of Cu bonding to natural organic matter. Geochim. Cosmochim. Acta 74, 2556-2580.

Marcus, M.A., Manceau, A., Kersten, M., 2004. Mn, Fe, Zn, and As speciation in a fast-growing ferromanganese marine nodule. Geochim. Cosmochim. Acta 68, 3125-3136.

McKenzie, R.M., 1970. Reaction of cobalt with manganese dioxide minerals. Australian Journal of Soil Research 8, 97-106.

McLaren, R.G., Crawford, D.V., 1973. Studies on soil copper .II. Specific adsorption of copper by soils. Journal of Soil Science 24, 443-452.

Morgan, J.J., 2000. Manganese in natural waters and earth's crust: Its availability to organisms, in: Siegel, A., Siegel, H. (Eds.), Metal Ions in Biological Systems: Iron Transport and Storage in Microorganisms, Plants, and Animals. Marcel Dekker, New York, pp. 1-34.

Morgan, J.J., 2005. Kinetics of reaction between O₂ and Mn(II) species in aqueous solutions. Geochim. Cosmochim. Acta 69, 35-48.

Morton, J.D., Semrau, J.D., Hayes, K.F., 2001. An X-ray absorption spectroscopy study of the structure and reversibility of copper adsorbed to montmorillonite clay. Geochim. Cosmochim. Acta 65, 2709-2722.

Nelson, Y.M., Lion, L.W., Ghiorse, W.C., Shuler, M.L., 1999. Production of biogenic Mn oxides by *Leprothrix discophora* SS-1 in a chemically defined growth medium and evaluation of their Pb adsorption characteristics. Appl. Environ. Microbiol. 65, 175-180.

Newville, M., Carroll, S., O'Day, P., Waychunas, G., Ebert, M., 1999. A web-based library of XAFS data on model compounds. *J. Synchrotron Radiat.*, 276-277.

Peacock, C.L., Sherman, D.M., 2004. Copper(II) sorption onto goethite, hematite and lepidocrocite: A surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy. *Geochim. Cosmochim. Acta* 68, 2623-2637.

Peacock, C.L., Sherman, D.M., 2007a. Crystal-chemistry of Ni in marine ferromanganese crusts and nodules. *Am. Mineral.* 92, 1087-1092.

Peacock, C.L., Sherman, D.M., 2007b. Sorption of Ni by birnessite: Equilibrium controls on Ni in seawater. *Chem. Geol.* 238, 94-106.

Peña, J., 2009. Contaminant Metal Immobilization by Biogenic Manganese Oxide Nanoparticles: Implications for Natural Attenuation and Bioremediation, Department of Civil and Environmental Engineering. University of California, Berkeley, p. 304.

Peña, J., Kwon, K.D., Refson, K., Bargar, J.R., Sposito, G., 2010. Mechanisms of nickel sorption by a bacteriogenic birnessite. *Geochim. Cosmochim. Acta* 74, 3076-3089.

Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* 12, 537-541.

Rhehr, J.J., Zabinsky, S.I., Albers, R.C., 1992. High-order multiple scattering calculations of X-ray-absorption fine structure. *Phys. Rev. Lett.* 69, 3397.

Rodda, D.P., Wells, J.D., Johnson, B.B., 1996. Anomalous adsorption of copper(II) on goethite. *J. Colloid Interface Sci.* 184, 564-569.

Santelli, C.M., Webb, S.M., Dohnalkova, A.C., Hansel, C.M., 2011. Diversity of Mn oxides produced by Mn(II)-oxidizing fungi. *Geochim. Cosmochim. Acta* 75, 2762-2776.

Schecher, W.D., McAvoy, D.C., 2001. MINEQL+, in: Schecher, W.D., McAvoy, D.C. (Eds.), 4.5 ed. Environmental Research Software, Hallowell, ME.

Shannon, R.D., 1976. Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A* 32, 751-767.

Sherman, D.M., Peacock, C.L., 2010. Surface complexation of Cu on birnessite (δ -MnO₂): Controls on Cu in the deep ocean. *Geochim. Cosmochim. Acta* 74, 6721-6730.

Shimizu, K., Maeshima, H., Yoshida, H., Satsuma, A., Hattori, T., 2001. Ligand field effect on the chemical shift in XANES spectra of Cu(II) compounds. *Physical Chemistry Chemical Physics* 3, 862-866.

Sposito, G., 2008. *The Chemistry of Soils*, 2nd ed. Oxford University Press, New York.

Strawn, D.G., Palmer, N.E., Furnare, L.J., Goodell, C., Amonette, J.E., Kukkadapu, R.K., 2004. Copper sorption mechanisms on smectites. *Clays and Clay Minerals* 52, 321-333.

Takahashi, Y., Manceau, A., Geoffroy, N., Marcus, M.A., Usui, A., 2007. Chemical and structural control of the partitioning of Co, Ce, and Pb in marine ferromanganese oxides. *Geochim. Cosmochim. Acta* 71, 984-1008.

Tan, H., Zhang, G.X., Heaney, P.J., Webb, S.M., Burgos, W.D., 2010. Characterization of manganese oxide precipitates from Appalachian coal mine drainage treatment systems. *Appl. Geochem.* 25, 389-399.

Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004. Biogenic manganese oxides: Properties and mechanisms of formation. *Annu. Rev. Earth Planet. Sci.* 32, 287-328.

Toner, B., Manceau, A., Webb, S.M., Sposito, G., 2006. Zinc sorption to biogenic hexagonal-birnessite particles within a hydrated bacterial biofilm. *Geochim. Cosmochim. Acta* 70, 27-43.

Traina, S.J., Doner, H.E., 1985a. Copper manganese(II) exchange on a chemically reduced birnessite. *Soil Sci. Soc. Am. J.* 49, 307-313.

Traina, S.J., Doner, H.E., 1985b. Heavy-metal induced releases of manganese(II) from a hydrous manganese-dioxide. *Soil Sci. Soc. Am. J.* 49, 317-321.

Vetter, K.J., Jaeger, N., 1966. Potentialausbildung an der Mangandioxid-Elektrode als oxidelektrode mit nichtstöchiometrischem oxid. *Electrochim. Acta*, 401-419.

Villalobos, M., Bargar, J., Sposito, G., 2005. Mechanisms of Pb(II) sorption on a biogenic manganese oxide. *Environ. Sci. Technol.* 39, 569-576.

Villalobos, M., Lanson, B., Manceau, A., Toner, B., Sposito, G., 2006. Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *Am. Mineral.* 91, 489-502.

Villalobos, M., Toner, B., Bargar, J., Sposito, G., 2003. Characterization of the manganese oxide produced by *Pseudomonas putida* strain MnB1. *Geochim. Cosmochim. Acta* 67, 2649-2662.

Wang, Y., Feng, X., Villalobos, M., Tan, W., Liu, F., 2012. Sorption behavior of heavy metals on birnessite: Relationship with its Mn average oxidation state and implications for types of sorption sites. *Chem. Geol.* 292, 25-34.

Webb, S.M., 2004. SIXPack: a Graphical User Interface for XAS Analysis Using IFEFFIT. *Phys. Scr.* T115, 1011-1014.

Webb, S.M., Tebo, B.M., Bargar, J.R., 2005. Structural characterization of biogenic Mn oxides produced in seawater by the marine *Bacillus sp.* strain SG-1. *Am. Mineral.* 90, 1342-1357.

Xia, K., Blears, W., Helmke, P.A., 1997. Studies of the nature of binding sites of first row transition elements bound to aquatic and soil humic substances using X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* 61, 2223-2235.

A.

B.

Figure 1. A) HR-TEM image of δ -MnO₂ particles acquired near Scherzer defocus using a Philips CM300 microscope; average particle size is 3.2 ± 0.6 nm (10 particles, each measured along x and y directions); approximate particle boundaries are circled in white. B) Fraction (f) of Mn octahedra located at particle edges for square birnessite particles with varying particle size. The inset illustrates how f was determined for a 3 nm particle (Mn octahedra at particle edges / total number of Mn octahedra = 0.3).

O.S.	TCS	DCS / DES	INC	PPT	Cu(OH) ₂
	3.43 ^{*, [1]} 3.44 ^{*, [2]}				
3.41 ⁺ 4.65 ⁺	3.39 (3), 3.43 (3) ^{*, [3]} 3.41-3.47 (4), 3.54-3.55 (2) ^{#, [5]}	n.a.	2.81-2.94 ^{*, [3]} 2.84 (2), 2.95 (2), 2.98 (2) ^{#, [5]}	2.6 – 3.0 ^{*, [4]}	2.97 [*]

Figure 2. Schematic of Cu sorbate configurations and corresponding interatomic distances for second-shell neighbors: Cu-O (outer-sphere surface complex, O.S.), Cu-Mn (inner-sphere surface complex, I.S.), or Cu-Cu (precipitate). The abbreviations TCS, DCS, DES, and INC indicate different Cu sorbate configurations: triple-corner sharing, double-corner sharing, double-edge sharing, and incorporated, respectively. Interatomic distances are based on experimental values (*) from Manceau et al. (2002)¹, Peña (2009)², Sherman and Peacock (2010)³, and Cheah et al. (2000)⁴; geometric considerations (+); or theoretical values from DFT geometry optimizations (#) from Kwon et al. (2013)⁴. The number in parentheses refers to the fitted coordination number.

Figure 3. Sorption of Cu by δ -MnO₂ at pH 6. Surface excess (q) expressed as a molar ratio of adsorbed Cu to Mn oxide adsorbent (mol Cu mol⁻¹ Mn) is plotted against aqueous Cu concentration (μM). The inset shows a plot of the distribution coefficient, K_d against surface excess, q . Dashed lines are intended as guides to the eye.

Figure 4. Concentration of aqueous Mn(II) (μM) released upon Cu sorption plotted against surface excess ($\text{mol Cu mol}^{-1} \text{ Mn}$); Mn(II) concentrations were adjusted by the fraction of Mn(II) released in Cu-free $\delta\text{-MnO}_2$ suspensions.

a.

b.

Figure 5. Normalized Cu K-edge XANES spectra (a) and their first derivatives (b) for reference materials and Cu- δ -MnO₂ samples. Arrowheads point to features present in the XANES spectra of Cu solids that are absent in those from the experimental samples.

Figure 6. Cu K-edge EXAFS spectra and corresponding Fourier transforms for samples listed in Table 2: Cu_01a (top); Cu_02; Cu_02a; Cu_06; Cu_12; Cu_12a; Cu_26 (bottom).

Figure 7a. Cu K-edge EXAFS spectrum from sample Cu_02a (grey line) overlain with various reference materials (black lines): Cu^{2+} (top), Cu-biogenic MnO_2 , $\text{Cu}(\text{OH})_2$, CuCO_3OH , and CuO (bottom).

Figure 7b. Cu K-edge EXAFS spectrum from sample Cu_12a (grey line) overlain with the EXAFS spectra from various reference materials (black lines): Cu^{2+} (top), Cu-biogenic MnO_2 , $\text{Cu}(\text{OH})_2$, CuCO_3OH , and CuO (bottom).

Figure 8. Cu K-edge EXAFS spectra (solid lines) from sample Cu_2a (solid line; top two spectra) and Cu_12a (solid line, bottom two spectra) plotted with best-fit curves (dashed line) for structural models described in the text (see Table 2).

Figure 9. Fourier transforms (magnitude and imaginary part) of the Cu K-edge EXAFS spectra from samples Cu_2a (a, b) and Cu_12a (c, d) (solid lines) plotted with best-fit curves (dashed lines) for the structural models described in Table 2: Cu-O, Cu-Cu and Cu-Mn (a,c) and Cu-O, Cu-Mn and Cu-Mn (b, d).

Table 1. Samples investigated by EXAFS spectroscopy. Sample ID indicates the Cu:Mn molar ratio $\times 100$. The difference between the initial and final aqueous Cu concentrations (Δc_{Cu}) and final aqueous Mn concentration are reported in the third and fourth columns. The Cu surface excess is expressed as a Cu:Mn molar ratio in the fifth column (q). Finally, saturation index values (Ω) are reported for CuO(s) and Cu(OH)₂CO₃(s) in the sixth and seventh columns, respectively.

Sample ID	pH _{eq}	Δc_{Cu} (μM)	c_{Mn} ¹ (μM)	q ² (mol Cu mol ⁻¹ Mn)	$\Omega_{\text{CuO(s)}}$	$\Omega_{\text{Cu(OH)2CO3(s)}}$
Cu_01a	5.99	25	26	0.011	0.36	0.01
Cu_02a	5.99	50	26	0.023	0.70	0.05
Cu_12a	5.95	257	31	0.112	3.00	0.98
Cu_02	6.13	37	8	0.019	0.99	0.11
Cu_06	6.12	108	8	0.055	2.76	0.83
Cu_12	6.08	208	17	0.115	4.44	2.14
Cu_26	6.02	444	51	0.258	7.34	5.83

¹Concentrations of 28 and 9 μM Mn were measured in the absence of Cu at pH 6.03 and 6.15, respectively.

²The concentration of Mn in the solid phase was 2.29 ± 0.05 mM (pH 6.0) and 1.85 ± 0.08 (pH 6.1).

Table 2. Representative fit parameters obtained from shell-by-shell fits to the EXAFS spectra presented in Figure 6. EXAFS-derived fitting uncertainties are reported in parenthesis.

3 path fit: Cu-O, Cu-Cu, and Cu-Mn						3 path fit: Cu-O, Cu-Mn, and Cu-Mn				
		R (Å)	σ^2 (Å ²)	CN	$E0$ (eV)		R (Å)	σ^2 (Å ²)	CN	$E0$ (eV)
Global parameters	Cu-O	1.94 (0.002)	0.005 (0.0003)			Cu-O	1.94 (0.002)	0.005 (0.0003)		
	Cu-Cu	2.88 (0.006)	0.007 (0.002)	Varied	-4.22	Cu-Mn	2.90 (0.006)	0.004(0.002)	varied	-4.08
	Cu-Mn	3.39 (0.007)	0.008 (0.002)		(0.39)	Cu-Mn	3.39 (0.007)	0.008(0.002)		(0.39)
Cu_01a			Cu-O	3.98 (0.41)				Cu-O	3.95 (0.39)	
			Cu-Cu	0.80 (0.53)				Cu-Mn	0.60 (0.36)	
			Cu-Mn	1.17 (0.77)				Cu-Mn	1.14 (0.79)	
Cu_02			Cu-O	3.78 (0.21)				Cu-O	3.74 (0.20)	
			Cu-Cu	0.83 (0.31)				Cu-Mn	0.54 (0.20)	
			Cu-Mn	0.90(0.40)				Cu-Mn	0.90 (0.41)	
Cu_02a			Cu-O	4.00 (0.41)				Cu-O	3.98 (0.39)	
			Cu-Cu	0.91 (0.53)				Cu-Mn	0.61 (0.34)	
			Cu-Mn	1.19 (0.78)				Cu-Mn	1.17 (0.79)	
Cu_06			Cu-O	3.80 (0.27)				Cu-O	3.78 (0.25)	
			Cu-Cu	0.77 (0.37)				Cu-Mn	0.50 (0.23)	
			Cu-Mn	0.98 (0.51)				Cu-Mn	0.99 (0.53)	
Cu_12			Cu-O	3.67 (0.24)				Cu-O	3.64 (0.23)	
			Cu-Cu	0.85 (0.35)				Cu-Mn	0.56 (0.22)	
			Cu-Mn	1.05 (0.48)				Cu-Mn	1.05 (0.50)	
Cu_12a			Cu-O	3.78 (0.13)				Cu-O	3.75 (0.12)	
			Cu-Cu	0.78 (0.24)				Cu-Mn	0.52 (0.14)	
			Cu-Mn	1.47 (0.38)				Cu-Mn	1.46 (0.39)	
Cu_26			Cu-O	3.58 (0.14)				Cu-O	3.56 (0.13)	
			Cu-Cu	0.81 (0.25)				Cu-Mn	0.53 (0.14)	
			Cu-Mn	1.05 (0.48)				Cu-Mn	0.94 (0.30)	

Note: *R* = interatomic distance; σ^2 = Debye-Waller factor; *CN* = coordination number; *E0* = energy shift; the R-factor is a goodness of fit parameter. All Cu K-edge EXAFS spectra were fit simultaneously with *R*, σ^2 , and *E0* varied globally and the *CN* varied for each spectrum, over a *k*-range 2.5 to 12 Å⁻¹ and with *k*-weights of 2 and 3 Å⁻¹. Both fits had 108 independent points and 28 variables. The R-factor was 0.003.

Annex

Table A.1. Optimized fit parameters for Mn K-edge EXAFS spectra of birnessite sample collected in transmission mode. The dry, unreacted mineral sample was diluted in powdered sugar.

Sample ID	Mn-X	CN	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R-factor
δ -MnO ₂	O	5.45 ± 0.93	1.91 ± 0.008	0.005 ± 0.001	7.39 ± 1.73	0.010
	Mn	4.39 ± 0.90	2.87 ± 0.010	0.006 ± 0.001		

Note: The backscattering atom (X) used in the fit is listed in the second column. Fits were done in *R*-space from 1 – 3.0 Å and using a *k*-range of 3 – 11.7 Å⁻¹. Fit parameters [interatomic distance *R* (Å), coordination number *CN*, and mean-square displacement of bond length σ^2 (Å²)] are reported together with their IFEFFIT-derived uncertainties.

Table A.2. Data for Cu sorption on δ -MnO₂

pH	c _{Mn_TOT} (μM)	c _{Cu_TOT} (μM)	c _{Mn_FIN} (μM)	c _{Cu_FIN} (μM)	q (mol mol ⁻¹)	c _{Mn_FIN} / c _{MnTOT} (-)	Kd (L mol ⁻¹)
5.78	1975.72	n.a.	35.42	n.a.	n.a.	0.02	n.a.
6.03	2343.28	n.a.	28.36	n.a.	n.a.	0.01	n.a.
5.98	1343.84	68.79	33.32	0.81	0.05	0.02	63890
5.99	1736.89	85.63	33.11	0.77	0.05	0.02	64621
5.97	1713.61	166.01	43.93	2.42	0.10	0.03	40554
5.97	1805.80	176.96	43.90	2.48	0.10	0.02	39944
5.93	1947.85	280.13	71.93	6.97	0.15	0.04	20899
5.96	2039.65	284.57	64.43	6.07	0.14	0.03	23234
5.89	1958.09	369.21	87.95	12.89	0.19	0.04	14779
5.89	1990.58	375.32	83.31	11.87	0.19	0.04	16050
5.86	2022.32	899.61	143.43	125.52	0.41	0.07	3282
5.86	1977.62	903.87	143.18	130.66	0.42	0.07	3226
5.80	2454.52	1531.71	148.87	282.65	0.54	0.06	1917
5.77	2281.67	1499.75	150.58	312.61	0.56	0.07	1782

Note: The pH averaged over all samples was 5.90 ± 0.07; the solid concentration averaged over all samples was 1.94 ± 0.28 mM Mn (0.17 ± 0.02 g L⁻¹ assuming M_r = 87 g MnO₂ L⁻¹ and excluding mass contribution from exchangeable Na⁺ or adsorbed water).

Figure A.1. Mn K-edge EXAFS spectrum (a) and Fourier transform (b) from $\delta\text{-MnO}_2$ powder (solid line) plotted with best-fit curve for Mn-O and Mn-Mn near neighbors (dashed line). Fit parameters are summarized in Table A.1.

Figure A.2. Plot of $q / (c_{\text{Cu}}/c_{\text{Mn(II)}})$ versus q at pH 6. Solid line shows the least-squares fit for q -values $< 0.4 \text{ mol Cu mol}^{-1} \text{ Mn}$.