



# Copper sorption by the edge surfaces of synthetic birnessite nanoparticles



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## ABSTRACT

We investigated the sorption of Cu by  $\delta$ -MnO<sub>2</sub>, 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 Mn<sup>3+</sup>. The synthetic  $\delta$ -MnO<sub>2</sub> 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 m<sup>2</sup> g<sup>-1</sup> and a 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<sup>-1</sup> Mn far exceeded the nominal vacancy content for  $\delta$ -MnO<sub>2</sub> (ca. 6–11% mol vacancy mol<sup>-1</sup> 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  $\delta$ -MnO<sub>2</sub> samples differ with respect to the EXAFS spectra for Cu(OH)<sub>2</sub>, CuO, and Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> and Cu-sorbed by biogenic MnO<sub>2</sub>. 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  $\delta$ -MnO<sub>2</sub> as dimers or polynuclear surface species. This sorption mechanism is consistent with the moderate vacancy content of  $\delta$ -MnO<sub>2</sub> and explains the similarity in the EXAFS spectra from samples having surface loadings of 0.01 to 0.26 mol Cu mol<sup>-1</sup> 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 discreet precipitate, making the surface sites at the particle edges the dominant sorption site for Cu.

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## 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<sub>2</sub> can control the speciation of Cu through adsorption at the water–mineral interface (Jenne, 1968; McLaren and Crawford, 1973; Davies-Colley et al., 1984).

Birnessite (layer-type MnO<sub>2</sub>) may bind Cu via three general mechanisms: adsorption at cation vacancy sites, incorporation into the MnO<sub>2</sub> 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, 2007b). In birnessite suspensions equilibrated with Cu at low pH values (pH ≈ 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 (Manceau et al., 2002; Sherman and Peacock, 2010; Arai, 2011). The occurrence of up to 20% Cu-incorporation (Cu-INC) at high pH values (pH ≈ 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  $\delta$ -MnO<sub>2</sub> sample with a loading of 0.068 mol Cu mol<sup>-1</sup> 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

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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 (Villalobos et al., 2005; Manceau et al., 2007b; Takahashi et al., 2007).

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 (Tebo et al., 2004; Learman et al., 2011) or surface-catalyzed (Morgan, 2005) oxidation of Mn(II), leads to disordered nanocrystalline birnessite minerals with high specific surface areas (Marcus et al., 2004; Hochella et al., 2005; Webb et al., 2005; Manceau et al., 2007a,b; Peacock and Sherman, 2007a; Bargar et al., 2009; Grangeon et al., 2010; Tan et al., 2010; Santelli et al., 2011). 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  $\delta$ -MnO<sub>2</sub> is characterized by curled MnO<sub>2</sub> nanosheets with hexagonal sheet symmetry and a small to moderate vacancy content (Villalobos et al., 2006; Grangeon et al., 2008; Manceau et al., 2013). 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 MnO<sub>2</sub> (Sherman and Peacock, 2010; Kwon et al., 2013). 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 (Manceau et al., 2002; Sherman and Peacock, 2010; Arai, 2011).

In the present study we combine sorption isotherm measurements with EXAFS spectroscopy to identify the mechanism of Cu sorption by  $\delta$ -MnO<sub>2</sub> over a broad range of surface loadings and at circumneutral pH. The specific surface area of the  $\delta$ -MnO<sub>2</sub> used in our experiments is 254 m<sup>2</sup> g<sup>-1</sup> (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.

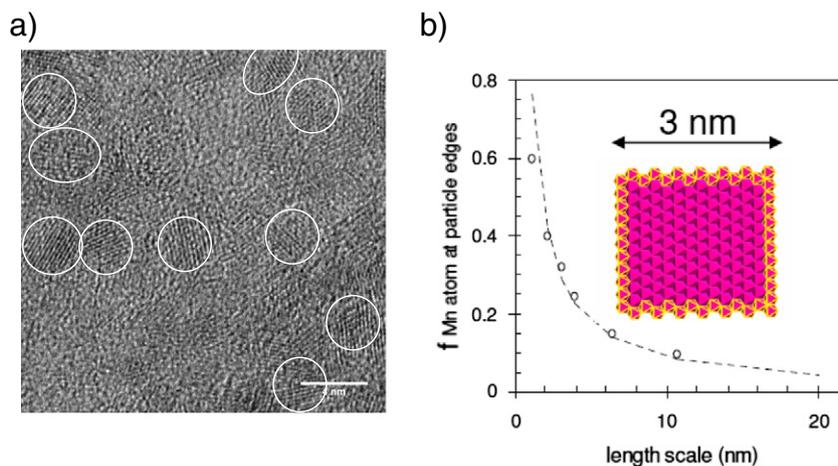
## 2. Materials and methods

### 2.1. Mineral samples

Delta-MnO<sub>2</sub> was synthesized according to the “redox” method, which involves mixing a solution of MnCl<sub>2</sub>·4H<sub>2</sub>O with a solution of KMnO<sub>4</sub> in excess NaOH and with a Mn(VII):Mn(II) molar ratio of 0.67 (Villalobos et al., 2003). The  $\delta$ -MnO<sub>2</sub> powder used in this study has a specific surface area of 254 ± 2 m<sup>2</sup> g<sup>-1</sup>, 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 to 200 °C (Metler Toledo TGA 851e). High-resolution TEM (Philips CM300 FEG/UT) images of a  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> given by Villalobos et al. (2006) and Webb et al. (2005).

### 2.2. Sorption experiments

Copper sorption and Mn desorption from  $\delta$ -MnO<sub>2</sub> 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<sup>-1</sup> solid to the background electrolyte solution. The MnO<sub>2</sub> concentration determined from total digestion of the slurry with a mixture of nitric acid and oxalic acid to measure Mn<sub>TOT</sub> and assuming an *M<sub>w</sub>* for MnO<sub>2</sub> of 87 g mol<sup>-1</sup> was 0.2 g L<sup>-1</sup> MnO<sub>2</sub>. 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 CuCl<sub>2</sub> solution. Before Cu addition but after equilibration in the background electrolyte (10 mM NaCl and



**Fig. 1.** a) HR-TEM image of  $\delta$ -MnO<sub>2</sub> 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 sizes. The inset illustrates how *f* was determined for a 3 nm particle (Mn octahedra at particle edges/total number of Mn octahedra = 0.3).

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