Effect of Zn coprecipitation on the structure of layered Mn oxides

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Manganese (Mn) oxides (MnO\textsubscript{x}) are a group of ubiquitous metal oxides in the environment and can significantly affect the biogeochemical cycles of metals, nutrients, and contaminants. Due to their negative surface charge across a wide range of environmental conditions, metal cations have strong affinities for MnO\textsubscript{x}, and the presence of metal cations during or after the formation of MnO\textsubscript{x} might significantly affect their structure and reactivity. This study systematically investigates the effects of Zn\textsuperscript{2+} presence during mineral formation (i.e. coprecipitation) on the structure of acid birnessite and δ-MnO\textsubscript{2}, two synthetic analogs that are structurally similar to fresh biogenic MnO\textsubscript{x}, but with different crystallinity. For both acid birnessite and δ-MnO\textsubscript{2}, Zn\textsuperscript{2+} existed as surface adsorbed species at vacancy sites, interrupted layer stacking along c axis, and caused reductions of the lateral particle size. Zn\textsuperscript{2+} also reduced Mn(III) contents in δ-MnO\textsubscript{2} layers, leaving more vacancy sites (capped by adsorbed Zn\textsuperscript{2+}). The reduction of layer stacking was more obvious for acid birnessite, while the modification of layer structure was more significant for δ-MnO\textsubscript{2}. These structural changes will likely lead to modified reactivity of MnO\textsubscript{x} in natural systems.

1. Introduction

Manganese (Mn) oxides (MnO\textsubscript{x}) are a group of metal oxides that are ubiquitous in nearly all environmental settings, such as fresh waters, marine nodules, soils, and sediments (Bargar et al., 2009; Bodel et al., 2007; Lanson et al., 2008). MnO\textsubscript{x} can form through the oxidation of Mn (II) and this process is much faster when catalyzed by mineral surfaces, species at vacancy sites, interrupted layer stacking along c axis, and caused reductions of the lateral particle size. Metal cations such as Ni\textsuperscript{2+}, Co\textsuperscript{2+}, Cu\textsuperscript{2+}, Pb\textsuperscript{2+}, and Zn\textsuperscript{2+} can either adsorb onto and/or incorporate into the layer vacancies and edge sites of birnessite (Drits et al., 2002; Hinkle et al., 2017; Lanson et al., 2002b; Manceau et al., 2002; Manceau et al., 1997; Peña et al., 2015; Peña et al., 2010; Silvester et al., 1997; Simanova et al., 2015; Villalobos et al., 2005). Adsorption of non-redox sensitive metals on MnO\textsubscript{x} was shown to have limited effects on MnO\textsubscript{x} layer structure (Power et al., 2005; Villalobos et al., 2014b) (except a recent study on Zn\textsuperscript{2+} sorption (Grangeon et al., 2012), as discussed later). Although numerous studies have examined the sorption and/or incorporation of metal cations on pre-formed MnO\textsubscript{x} (i.e. sorption system), much remain unknown on the impact of metal cation presence during MnO\textsubscript{x} formation (i.e. coprecipitation system) on the oxide structure, reactivity, and transformation,
despite the obvious relevance in complex environmental settings. Several recent studies demonstrated significant impacts of metal coprecipitation on the structural properties of MnOx, such as Mn(II, III) contents, vacancy site density, crystallinity, thermal stability, and surface area (Kamimura et al., 2013; Yin et al., 2011a; Yin et al., 2015b; Yin et al., 2014; Yin et al., 2013; Yin et al., 2011b; Yin et al., 2015c; Yin et al., 2012). For biogenic phyllomanganates, the presence of Ni²⁺ can enhance vacancy site formation while Ca²⁺ and Na⁺ were shown to stabilize layer Mn(III) (Zhu et al., 2010). For abiotic hexagonal birnessite, coprecipitation of Ni, Co, Fe, and V were found to modify the surface area, layer stacking, oxidation state, and coherent scattering domain size of MnOx (Yin et al., 2011a; Yin et al., 2015b; Yin et al., 2014; Yin et al., 2012). These influences were shown to be metal specific and dependent on the compatibility of foreign metal ions with the MnOx structure (e.g. size/charge similarities to the structural Mn(III)/IV ions, crystal field stability energy), which was previously suggested to be reflected in the ratio of incorporated vs. surface complexed metal (i.e. incorporation / (incorporation + complexation)) (Yin et al., 2011a; Yin et al., 2015b; Yin et al., 2013; Yin et al., 2015c; Yin et al., 2012).

The degree of compatibility and amount of metal ion incorporation was found to increase in the order of Zn²⁺ < Cu²⁺ < Ni²⁺ < Co³⁺, with the metal impact on structure modification in the reverse order (Yin et al., 2011a; Yin et al., 2013; Yin et al., 2012). These modified structural properties were shown to lead to differences in adsorptive capacities towards metal cations (e.g. Pb²⁺, Zn²⁺) (Li et al., 2015; Yin et al., 2015b; Yin et al., 2014; Yin et al., 2011b; Yin et al., 2012) and anions (e.g. arsenate) (Villalobos et al., 2014b), oxidative capability, as well as catalytic (Wang et al., 2016; Yin et al., 2015a) and electrochemical properties (Liu et al., 2015).

Among the transition metals (e.g. Co, Ni, Cu, Fe, Zn) that are commonly found to associate with MnOx in natural environments, Zn shows the least structural compatibility (Kwon et al., 2013; Yin et al., 2011a; Yin et al., 2012). Zn²⁺ has not been found to incorporate into the layer vacancy sites of synthetic or biogenic birnessite, but instead predominantly adsorbs above/below the vacancy sites. Interestingly, the coordination environment of Zn²⁺ on MnOx is dependent on Zn²⁺ concentration as well as MnOx crystallinity (Grangeon et al., 2012). Tetrahedrally coordinated Zn²⁺ (ZnIV) at low Zn²⁺ concentrations can change to octahedral coordination (ZnVI) with increasing Zn²⁺ loading (Manceau et al., 2002; Toner et al., 2006; Trivedi et al., 2001). A recent study showed that adsorbed Zn²⁺ can reduce the amount of Mn(III) ions in δ-MnO₂ layers, leaving more vacancy sites (capped by adsorbed Zn²⁺) (Grangeon et al., 2012). Zn²⁺ adsorption can also cause the dissolution of birnessite and result in smaller coherent scattering domain size in the a-b plane as calculated by X-ray diffraction (XRD) fitting (Grangeon et al., 2012). Only two previous studies have examined the effect of Zn²⁺ coprecipitation on MnOx structure, but no consensus was reached. Yu et al. found that the presence of Zn²⁺ during the formation of fungal MnOx inhibited the crystal growth and modified the layer stacking of MnOx (Yu et al., 2013). Boonfug et al. found that the presence of Zn²⁺ during biogenic MnOx formation resulted in large Zn²⁺ sequestration (likely due to surface sorption), but with no obvious changes in MnOx local structure (Boonfug et al., 2009). Given the low compatibilities of Zn²⁺ with phyllomanganate structure, as well as its unique dependence of coordination environment on phyllomanganate crystallinity, a systematic study is highly desired to reveal the impact of this environmentally abundant element on the composition, surface properties, morphology, structural properties, as well as subsequent reactivity (e.g. sorptive, redox) of MnOx.

This study examines the impact of Zn²⁺ coprecipitation on the structural properties of two phyllomanganates with different structural order, acid birnessite and δ-MnO₂. Zn²⁺ association with natural MnOx was found to be 0–0.5% (Zn/Mn molar ratio) in marine nodules (Childs, 1975; Jenkins, 1970; Marcus et al., 2004) and soils (Manceau et al., 2003). This ratio can reach 3% in coal mine drainage treatment systems where Mn(II)-oxidizing microbes thrive (Tan et al., 2010), and can be as high as 46% in contaminated sediments (Lanson et al., 2008). This ratio can be even higher locally (Manceau et al., 2007). Since Zn²⁺ sequestration is known to be affected by phyllomanganate structure and crystallinity, this study compared acid birnessite and δ-MnO₂. Two structurally similar phyllomanganate phases but with different structural order. Compared to δ-MnO₂, acid birnessite has better crystallinity, more layer stacking along c axis, larger layer dimension, and lower surface area (Manceau et al., 2013; Villalobos et al., 2003). Because Zn²⁺ stabilization is weaker between incoherently stacked and laterally smaller layers (Kwon et al., 2009), its prevalence on δ-MnO₂ was shown to be two times lower than on acid birnessite at similar Zn/Mn loadings (Grangeon et al., 2012; Yu et al., 2013). Therefore, it is possible that Zn²⁺ coprecipitation can have different effects on the structural properties of these two MnO phases with different crystallinity.

Compared to previous studies on Zn sorption on pre-formed MnOx (Boonfug et al., 2009; Drits et al., 2002; Grangeon et al., 2012; Lanson et al., 2002b; Manceau et al., 2002; Silvester et al., 1997; Toner et al., 2006), in this study Zn was added during the formation of Mn oxides (i.e. Zn coprecipitation). Although Zn was also found to exist as surface adsorbed species in this coprecipitation system (details in results section), more significant effects were observed on MnOx structure compared to Zn sorption system. By exploring two synthetic MnO phases with similar structure but different structure order, our system eliminated the potential toxicity effects associated with biogenic MnO systems, and allowed thorough investigation on the effect of MnOx structure order. We conducted systematic characterization of the Zn-coprecipitated MnO₃ phases, by combining a suite of complementary techniques that are capable of probing mineral surface properties, morphology, and structure order at varied ranges, including BET surface area analysis, zeta-potential measurements, Zn and Mn X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), pair distribution function (PDF) analysis of X-ray total scattering, and high resolution transmission electron microscopy (HRTEM). Information obtained from this study provides a better understanding of the impacts of Zn²⁺ co-precipitation on the structural properties of two environmentally relevant MnO phases, and points to the importance of considering metal coprecipitation effects for studies centered on MnO₃ reactivity in natural systems.

2. Methods

2.1. Synthesis of δ-MnO₂ and acid birnessite in the presence of Zn²⁺

Both δ-MnO₂ and acid birnessite phases were synthesized in the absence or presence of a range of Zn²⁺ concentrations. δ-MnO₂ synthesis followed a previous procedure (Zhu et al., 2012) where 160 mL MnSO₄ solution (0.30 mol L⁻¹) was pumped into a mixture of 160 mL KMnO₄ (5.0 g) and 180 mL NaOH (3.5 g) solutions at a speed of 25 mL min⁻¹ under vigorous stirring. Calculated amounts of ZnSO₄ was dissolved in the MnSO₄ solution to achieve Zn:total Mn molar ratio of 0–20%. For acid birnessite synthesis, ZnSO₄ was dissolved in 45 mL of 6 mol L⁻¹ HCl solution to achieve Zn:total Mn molar ratio of 0–20%. This solution was then pumped at 1 mL min⁻¹ into 300 mL of boiling 0.667 mol L⁻¹ KMnO₄ solution under vigorous stirring (Villalobos et al., 2003). Previous studies on Mn oxide formation in the presence of Zn²⁺ used Zn/Mn ratios of ~1–22% (Yu et al., 2013). After synthesis, the suspensions were allowed to cool down (for birnessite) and the solid precipitates vacuum filtered (0.2 μm), rinsed with deionized (DI) water, dialyzed, and freeze-dried. Samples were labeled according to the starting Zn/Mn molar ratio and are referred to as pure or Zn-coprecipitated samples (see Table 1 for details). A portion of the dried solids was digested by aqua regia and analyzed for elemental composition using inductively coupled plasmas – mass spectrometry (ICP-MS). Samples were also characterized for their morphology, surface, and
structure properties using BET surface area analysis, zeta potential analysis, HRTEM, XRD, PDF, and XAS, as detailed below and in Supporting Information (SI) Text S1–S5.

2.2. X-ray absorption spectroscopy analysis

Mn and Zn K-edge XAS data were collected on both pure and Zn-coprecipitated birnessite and δ-MnO₂ samples to investigate their structural characteristics. Suspensions containing MnO₂ were vacuum filtered through 0.2 μm polycarbonate membranes and rinsed with DI water. The moist filter membranes loaded with MnO₂ wet pastes were mounted in an acrylic sample holder covered with Kapton tape. Samples were stored at ~20 °C and thawed prior to analysis. XAS data were collected at Beamline 4-1 of the Stanford Synchrotron Radiation Lightsource (SSRL; Menlo Park, CA) using Si(220) monochromator and Beamlines 5-BM-D and 12-BM-B at the Advanced Photon Source (APS; Argonne National Laboratory, Lemont, IL) using Si(111) monochromators, all with 40% detuning to avoid higher order harmonics. Energy calibration used Mn or Zn foil. XAS data were collected in both fluorescence mode using a Lytle detector (Beamlines 4-1 at SSRL; Menlo Park, CA) and using a detector (Beamline 5-BM-D at APS). Both XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure) data were collected. Two to six scans were collected and averaged. Analysis of the Mn XANES spectra for each sample showed no photo-reduction of MnO₂ under the X-ray beam.

XAS data analysis was performed using the programs SIXPACK (Webb, 2005), Iffiffi (Ravel and Newville, 2005), and WINXAS (Ressler, 1998). Shell by shell fitting was conducted for both Mn and Zn EXAFS spectra to elucidate local coordination structures. Linear combination fitting (LCF) of the Mn XANES region was conducted to determine the relative percentage of Mn(II), Mn(III), and Mn(IV) species and the average oxidation state (AOS) following the method described in Manceau et al. (2012). Manceau et al. (2012) compared the LCF results of Mn K-edge XANES with different reference sets and pointed out that reference sets with different structures might result in errors when determining AOS. Therefore, two reference compound sets with different Mn(II)/(III)/(IV) compounds were tested. The first set included MnSO₄δM, MnPO₄δ, ramsdellite, and K-birnessite, and the second set included MnSO₄δ, Mn₂O₃δ, and pyrolusite (δ-MnO₂).

2.3. Pair distribution function (PDF) analysis of X-ray total scattering

Synchrotron high-energy X-ray total scattering data of the synthesized MnO₂ samples were collected at beamline 11-ID-B (~58.6 keV, λ = 0.2117 Å) of the Advanced Photon Source (APS), Argonne National Laboratory, IL. Conversion of data from 2D to 1D was performed using the program Fit2D (Hammersley, 1998; Hammersley et al., 1996). The experimental total scattering structure function S(Q), reduced experimental structure function f(Q), and PDF, or G(r), were obtained using PDFget2X (Qiu et al., 2004). The PDFs were calculated from the Fourier transforms of these data truncated at 26 Å⁻¹.

3. Results

3.1. Chemical compositions

Composition analysis of the Zn-coprecipitated MnO₂ showed significant amount of Zn2⁺ sequestration by the oxides (Table 1). Zn/Mn molar ratio in the final solids increased with increasing value of initial Zn/Mn ratio. However, under 20% Zn/Mn starting condition, acid birnessite was only able to sequester ~16% Zn/Mn, as compared to ~21% for δ-MnO₂. This higher Zn2⁺ uptake capacity of δ-MnO₂ might be due to its intrinsic structural properties, as discussed later.

The presence of Zn2⁺ significantly decreased the interlayer cation (K⁺) content for birnessite, but has little impact on the content of interlayer cations (K⁺ and Na⁺) of δ-MnO₂ (Table 1). Total Mn content was similar for birnessite or δ-MnO₂ samples with different Zn2⁺ loadings, except for a slight decrease at 20% Zn/Mn loading for acid birnessite. This suggests that Zn2⁺ might have preferably replaced the interlayer cations in acid birnessite instead of substituting for Mn(III, IV) ions within the MnO₂ layers. This is consistent with previous studies where no Zn2⁺ substitution into the layer structure was observed when Zn2⁺ was sorbed on Mn oxides or was present during biogenic Mn oxide formation (Manceau et al., 2002; Toner et al., 2006; Yu et al., 2013).

3.2. Morphology of Mn oxides as revealed by HRTEM

HRTEM images revealed significant morphological modifications of Zn-coprecipitated birnessite and δ-MnO₂ phases, as compared to their pure phases (Figs. 1 and S1). In general, birnessite samples contain larger particles with multiple layer stacking, while δ-MnO₂ samples show much limited layer stacking and smaller lateral particle size. All phases aggregate heavily with curling features, and the aggregation was enhanced by Zn-coprecipitation, consistent with BET surface area measurements showing decreased surface area with increasing Zn/Mn ratio (Table 1). All δ-MnO₂ samples showed more intense curling morphology compared to acid birnessite samples.

In general, Zn-coprecipitation caused less layer stacking and smaller lateral layer size. The average number of stacking layers (along c axis) for each sample is summarized in Table 1. Pure δ-MnO₂ sample contained 5 ± 1 layers and acid birnessite 11 ± 3 layers. With increasing Zn/Mn ratio, the number of stacking layers decreased significantly from 11 ± 3 to 5 ± 1 for acid birnessite and from 5 ± 1 to 4 ± 1 for δ-
MnO₂. It was difficult to quantitatively measure the lateral particle size from HRTEM images due to strong aggregation, but a general decrease in lateral particle size was observed for all Zn-coprecipitated acid birnessite and δ-MnO₂ samples (Figs. 1 and S1).

3.3. Surface properties

BET specific surface area (SSA) is a commonly used parameter for evaluating Mn oxide adsorption and oxidation capabilities. In this study, the SSAs of pure acid birnessite and δ-MnO₂ were 27.4 and 221.9 m²/g, respectively (Table 1), consistent with previously reported values of 19–40.5 m²/g for acid birnessite and 114–274 m²/g for δ-MnO₂ (Power et al., 2005; Villalobos et al., 2014b; Wang et al., 2016; Yin et al., 2013). For acid birnessite, with increasing Zn/Mn ratio, SSA first increased from 27.4 (p-bir) to 32.5 (5Zn-bir), then decreased to 19.3 m²/g (20Zn-bir). SSA can be affected by many factors including crystallite size and aggregation. Reduction in both layer stacking and lateral layer size decreases crystallite size and increases surface area. However, surface area also decreases with increasing aggregation (Cismasu et al., 2011; Wang et al., 2016; Yin et al., 2011a; Yin et al., 2013). As previously observed (Lee et al., 2007; Yin et al., 2011a) and discussed above, Zn-coprecipitation caused greater aggregation and decreased crystallinity. The net effect of these two competing factors likely accounted for the overall trend of SSA in acid birnessite. For δ-MnO₂, increasing Zn/Mn ratio caused a continuous decrease of the SSA from 221.9 (p-dMn) to 131.6 m²/g (20Zn-dMn), suggesting aggregation to be the dominant factor affecting SSA in the δ-MnO₂ system.

Zn-coprecipitation also affected the surface charge of Mn oxides (Fig. S2), a critical factor controlling the sorption and redox reactions of metals, metalloids, and organics with Mn oxides (Patil et al., 2007; Power et al., 2005; Villalobos et al., 2014b). Mn oxides synthesized in this study had negative zeta potential values even at pH as low as 2–3. Zn-coprecipitation caused these values to become less negative, likely at least partially due to the formation of Zn²⁺ inner-sphere complexes on the oxide surfaces, because Zn²⁺ has strong tendency to sorb on MnOₓ and low compatibility for structural incorporation into MnOₓ. Similar effects on surface charge were also previously observed during Zn²⁺ adsorption onto birnessite (Power et al., 2005).

3.4. X-ray diffraction

XRD analysis was conducted to characterize the long-range order of
all acid birnessite and δ-MnO₂ samples (Fig. 2). The XRD patterns of pure acid birnessite and δ-MnO₂ both agreed well with previous studies (Chen et al., 2002; Drits et al., 1997; Lanson et al., 2000; Zhu et al., 2012) and showed no presence of any additional phases. For all acid birnessite and δ-MnO₂ phases (pure and Zn-coprecipitated), the d-spacing ratio of the peaks at 2.41 Å (11, 20) and 1.41 Å (31, 02) was 1.71, close to \( \sqrt{3} \), indicating a hexagonal layer symmetry (Drits et al., 2007; Drits et al., 1997). Full width at half maximum (FWHM) of the (001) peaks for all acid birnessite samples was measured and the crystallite size along c axis was calculated using the Scherrer equation (Table 1). All δ-MnO₂ phases showed no obvious peak at ~7.23 Å (001) and only a broad peak at ~3.68 Å (002), due to the weaker layer stacking of δ-MnO₂ along c axis compared to acid birnessite phases. This is consistent with previous studies (Grangeon et al., 2012; Villalobos et al., 2006) and our HRTEM observations. Overall, Zn-coprecipitation had more impacts on vertical layer stacking for birnessite phases, while δ-MnO₂ phases are more affected in lateral layer size, as detailed below.

For birnessite phases, Zn-coprecipitation caused significant reduction in layer stacking. With increasing Zn²⁺ content, XRD showed decreased peak height and increased peak width at 7.23 Å (001) and/or 3.62 (002) reflections, suggesting decreased crystallinity and less layer stacking along the c axis, consistent with HRTEM observations. The vertical crystallite size calculated using Scherrer’s equation also showed decreasing values with increasing Zn²⁺ contents (Table 1). Such effect on layer stacking was a result from the coprecipitation process, as Zn²⁺ sorption (during mineral formation) on the vacancy sites disrupted layer formation. In contrast, when Zn²⁺ was equilibrated with hexagonal birnessite (orderly stacked) and exchanged for H⁺, the 3D periodicity along c axis was preserved, although with the transformation to a different symmetry (monoclinic) (Lanson et al., 2002b). Reduced layer stacking was also previously observed for Ni, Co, Fe, and P coprecipitated birnessite samples (Wang et al., 2016; Yin et al., 2011a; Yin et al., 2013; Yin et al., 2012). As shown in the zoomed view (Fig. 2C), the hump at 1.6–1.9 Å were previously suggested to reflect heavy metal adsorption on vacancy sites (Drits et al., 2007; Grangeon et al., 2008; Villalobos et al., 2006). With increasing Zn²⁺ content, this hump became more significant due to vacancy site occupation by Zn²⁺ (Drits et al., 2007; Grangeon et al., 2008).

For δ-MnO₂ phases, Zn-coprecipitation did not cause significant changes in layer stacking, likely due to the already low numbers of layer stacking as shown in HRTEM and the weak intensity of XRD peaks at 7.23 and 3.62 Å (Fig. 2B). At lower d-spacing range (Fig. 2D), significantly decrease in peak intensities and increase in peak width were observed with increasing Zn²⁺ content, suggesting decreased lateral coherent scattering domain (CSD) size (Wang et al., 2016) caused by Zn coprecipitation, which was also observed in Fe (Yin et al., 2013) and P coprecipitated MnOₓ (Wang et al., 2016). This phenomenon is not obvious in the Zn coprecipitated acid birnessite samples.

3.5. X-ray absorption spectroscopy

3.5.1. Mn K-edge XANES spectroscopy

Linear combination fitting (LCF) of Mn K-edge XANES spectra was applied to determine the average oxidation state (AOS) and relative contribution of Mn(II), Mn(III), and Mn(IV) species in each sample (Fig. 3, Fitting 1 using reference set 1). In several previous studies, δ-MnO₂ is a common standard with an AOS close to 4.0 (Jürgensen et al., 2004; Villalobos et al., 2006; Villalobos et al., 2003). Lower values were
also reported (3.84 in Webb et al. (2005a), 3.76 in Grangeon et al. (2012), 3.74 in Grangeon et al. (2008)), indicating the presence of mixed valences of Mn, i.e., adsorbed Mn(II,III) at vacancy sites and Mn (III) within layers. In this study, pure δ-MnO₂ has an AOS of 3.77 and ~15% Mn(III), both similar to the values in Grangeon et al. (2012). Compared to δ-MnO₂, pure acid birnessite has a higher AOS (3.92), which is close to previously reported values of 3.9–4.0 (Toner et al., 2006; Villalobos et al., 2006; Villalobos et al., 2003; Wang et al., 2012a). Less Mn(II,III) contents was observed in acid birnessite compared to δ-MnO₂. For δ-MnO₂ samples, increasing Zn²⁺ content resulted in the significant decrease of Mn(II) and Mn(III) and increase of Mn(IV), thus an overall increase of AOS. The replacement of interlayer Mn(II, III) by foreign cations was also observed during Zn, Pb, and Cd sorption on synthetic phyllomanganates (Grangeon et al., 2012; Lanson et al., 2002b). The AOS of acid birnessite showed no significant change with increasing Zn²⁺, likely due to the already low Mn(II, III) contents in pure acid birnessite thus the replacement effects were not significant.

A second fitting of the Mn XANES data (Fitting 2) was conducted using reference set 2 (Fig. S5). The AOS of pure acid birnessite (3.79) and δ-MnO₂ (3.71) from Fitting 2 are lower than Fitting 1, confirming that LCF fitting method to achieve Mn AOS largely depends on the reference compounds. Based on the results of Fitting 2, Mn AOS of acid birnessite had no significant change with increasing Zn²⁺, as compared to an increase of AOS for δ-MnO₂ samples, similar to the trend obtained from Fitting 1.

### 3.5.2. Mn K-edge EXAFS spectroscopy

Mn EXAFS spectroscopy was used to elucidate the local coordination environment (e.g. layer structure) of the oxide samples. K²-weighted EXAFS spectra of pure and Zn-coprecipitated oxides and corresponding Fourier transforms (FT) are shown in Fig. 4. For Mn EXAFS spectra, the “indicator region” at ~8–9.2 Å⁻¹ (vertical dashed lines in Fig. 4A and C) is sensitive to the layer symmetry of Mn oxides (Gaillot et al., 2007; Gaillot et al., 2003; Marcus et al., 2004). The amplitude of the two peaks at ~8.1 and 9.2 Å decreased while Mn oxides aged and transformed from hexagonal to triclinic symmetry (Learman et al., 2011b; Tang et al., 2014; Zhao et al., 2016). Peak broadening (and even splitting) is due to Mn(III) enrichment and ordering in triclinic birnessite (Manceau et al., 2004; Manceau et al., 2005; Marcus et al., 2004). Zhu et al. also used the sharpness of the two peaks to estimate the layer Mn(III) contents in biogenic Mn oxides (Zhu et al., 2010). Pure δ-MnO₂ has hexagonal symmetry with low Mn(III) content and ordering, and showed sharp peaks in this region (Fig. 4C) (Zhu et al., 2010). Pure acid birnessite (Fig. 4A) showed even sharper peaks compared to pure δ-MnO₂, suggesting the least amount of layer Mn(III) among all samples, which is consistent with the highest AOS measured by Mn XANES analysis (Fig. 3). With increasing Zn²⁺ content, the peak at 9.2 Å⁻¹ of δ-MnO₂ samples became sharper, suggesting a decrease of layer Mn(III) content and ordering. For Zn-birnessite samples, no obvious changes were observed in this region, and all samples showed sharp peaks indicating low Mn(III) content and ordering.

FT spectra of all samples showed two dominant peaks at ~1.5 and 2.5 Å, corresponding to the Mn-O and Mn-Mn edge-sharing (Mn-Mnedge) shells, respectively (Manceau and Combes, 1988). Previous studies suggested that the peak height ratio H₄₄/H₆₆ reflects several factors, such as layer vacancy site occupation fraction (f_vac) and particle size (Saratovsky et al., 2006; Zhu et al., 2010). Saratovsky et al. found the ratios in layered Mn oxides increase with a larger layer cation occupation fraction (f_c) and particle size (Saratovsky et al., 2006). However, several studies found different results from the trend above when it comes to vacancy occupation by Mn(III) incorporation into layer structure. For example, trilinic birnessite has large amount of layer Mn(III) occupation vacancy sites (Lanson et al., 2002a) and a low ratio of 0.73 (Fig. 4D). This ratio was 0.82 in pure δ-MnO₂ and 1.01 in pure acid birnessite, both with less layer Mn(III) and more unoccupied
vacancies compared to triclinic birnessite (Tebo et al., 2004; Zhao et al., 2016). The aging of abiotic (Zhao et al., 2016) and biogenic (Learman et al., 2011b; Tang et al., 2014) Mn oxides in the presence of Mn(II) results in more vacancy occupation by Mn(III) and decreased HMn-Mn/HMn-o ratio. Zhu et al. found the inverse proportionality between focc and HMn-Mn/HMn-o ratio and used this relationship to estimate layer Mn (III) contents in biogenic Mn oxides (Zhu et al., 2010). The decreased ratio can be probably attributed to Jahn-Teller distortion caused by layer Mn(III), which was suggested to split the Mn-Mn peak and decrease the amplitude (Drits et al., 1997; Gaillot et al., 2003; Lanson et al., 2002b; Marcus et al., 2004; Webb et al., 2005b).

For Zn-coprecipitated δ-MnO2, decreased particle size could reduce the relative amplitude of Mn-Mnedge peak (Kawashima et al., 1986; Wang et al., 2016; Webb et al., 2005a) while less layer Mn(III) in Zn-coprecipitated δ-MnO2 samples could increase the amplitude (Sherman and Peacock, 2010; Webb et al., 2005a; Zhu et al., 2010). In this study, H_{Mn-Mn,edge}/H_{Mn-o} increased slightly from 0.82 (pure δ-MnO2) to 0.91 (20Zn-dMn). This indicates that the dominating factor is layer Mn(III) decreased by Zn coprecipitation as shown both in the k space (Fig. 4C) and EXAFS fitting results below. The ratio remained relatively unchanged with increasing Zn2⁺ content for acid birnessite samples, suggesting little changes to the vacancy site density and layer/interlayer Mn(III) contents. This is consistent with no changes in the 8 – 9.2 Å⁻¹ indicator region in the EXAFS spectra (Fig. 4C), as well as the small changes in Mn(III) content and AOS as determined by the Mn XANES spectra. For Zn-coprecipitated birnessite samples, increasing Zn2⁺ content did not result in significant changes in the CNs and distances of these two Mn-Mn shells (except for the slight decrease of the Mn-Mn_{core} distance at 10 and 20% Zn2⁺ contents), suggesting little changes to the vacancy site density and layer/interlayer Mn(III) contents. This is consistent with no changes in the 8 – 9.2 Å⁻¹ indicator region in the EXAFS spectra (Fig. 4C), as well as the small changes in Mn(III) content and AOS as determined by the Mn XANES spectra. For δ-MnO2, with increasing Zn2⁺ content, the Mn-Mnedge path showed a decrease in distance from 2.884 (pure δ-MnO2) to 2.871 – 2.872 Å (all the Zn-coprecipitated δ-MnO2 samples), suggesting less layer Mn(III) content. This was also observed in Ni2⁺ coprecipitated biogenic Mn oxides (Zhu et al., 2010).

The CN for the Mn-Mn_{edge} path also decreased from 6.2 (pure δ-MnO2)
Based on Zn EXAFS analysis (Fig. S3, Table S1), Zn exists as octahedral coordination and consistent with TEM and XRD results. The attenuation of intensity can be used to estimate the size of coherent scattering domains (i.e., bending and fault-stacked particles are less accounted for) (Manceau et al., 2013). In this study, all the oxide samples showed significant bending and stacking faults of the MnO2 layers (and more significant with Zn coprecipitation); therefore, we used HRTEM to estimate the numbers of stacked layers.

Both birnessite and δ-MnO2 showed decreases in layer stacking with increasing Zn content. Disturbed layer stacking has also been previously observed during Ni, Co, Fe, and V coprecipitation with acid birnessite and Zn coprecipitation with biogenic Mn oxides (Liu et al., 2015; Yin et al., 2014; Yin et al., 2013; Yin et al., 2011a; Yin et al., 2015b; Yin et al., 2014; Yin et al., 2013; Yin et al., 2012), and were attributed to the replacement of interlayer alkaline cations (Na+, K+) by foreign metals (Yu et al., 2013). With increasing Zn content, we observed significant disruption of layer stacking for birnessite as compared to the small changes in layer stacking for δ-MnO2 (HRTEM and XRD). Meanwhile, significant decrease of K content was also observed for acid birnessite (Table 1), while no obvious changes were observed for the overall alkaline cation content (K and Na) for δ-MnO2.

4. Discussion

4.1. Layer stacking

Based on HRTEM observations, pure δ-MnO2 had 5 ± 1 layers and pure acid birnessite had 11 ± 1 layers. Both numbers are higher than previously reported values obtained by XRD (3–4 layers for δ-MnO2 and ~6 layers for acid birnessite) (Grangeon et al., 2012; Manceau et al., 2013; Villalobos et al., 2006). Other studies have also observed higher layer numbers from TEM than XRD (Grangeon et al., 2012), likely because XRD is sensitive to coherent scattering domains (i.e., bending and fault-stacked particles are less accounted for) (Manceau et al., 2013). In this study, all the oxide samples showed significant bending and stacking faults of the MnO2 layers (and more significant with Zn coprecipitation); therefore, we used HRTEM to estimate the numbers of stacked layers.

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4.2. Interlayer structure

Zn EXAFS spectra (Fig. S3) and fitting results (Table S1) revealed that Zn2+ formed inner-sphere sorption complexes (ZnIV or ZnVII) above/below the vacancy sites, consistent with the coordination environments during its adsorption onto biogenic and synthetic birnessite phases as well as coprecipitation with biogenic Mn oxides (Manceau et al., 2002; Silvester et al., 1997; Toner et al., 2006; Yu et al., 2013). No previous studies have observed Zn2+ substitution at vacancy sites, likely due to the large size difference between octahedrally coordinated Zn2+ (ionic radius 0.60 Å) and Mn(III) (more likely to exist as low-spin state (Yin et al., 2012), 0.58 Å) or Mn(IV) (0.53 Å) (Shannon, 1976), as well as the large crystal field stabilization energy required for Zn2+ to enter vacancy sites (Kwon et al., 2013). As discussed above, the interlayer alkali cation content was much higher for acid birnessite (~2.7 mmol g−1 in pure birnessite) than δ-MnO2 (~1.1 mmol g−1 in pure δ-MnO2), and showed more obvious decrease with increasing Zn2+ contents (Table 1), suggesting more Zn2+ replacement. Compared to alkali cations, the release of Mn(II)/Mn(III) by surface adsorbed Zn2+ was more significant in the δ-MnO2 system. This was confirmed

Table 2

<table>
<thead>
<tr>
<th>Sample label</th>
<th>R</th>
<th>Shell</th>
<th>CN</th>
<th>Distance (Å)</th>
<th>σ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid birnessite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-bir</td>
<td>0.0049</td>
<td>Mn-O</td>
<td>6.0</td>
<td>1.919 (0.006)</td>
<td>0.007 (0.001)</td>
</tr>
<tr>
<td>1Zn-bir</td>
<td>0.0094</td>
<td>Mn-O</td>
<td>6.0 (1.1)</td>
<td>1.916 (0.009)</td>
<td>0.006 (0.002)</td>
</tr>
<tr>
<td>5Zn-bir</td>
<td>0.0032</td>
<td>Mn-O</td>
<td>6.0 (3.7)</td>
<td>1.914 (0.005)</td>
<td>0.007 (0.001)</td>
</tr>
<tr>
<td>10Zn-bir</td>
<td>0.0183</td>
<td>Mn-O</td>
<td>7.0 (1.5)</td>
<td>1.913 (0.013)</td>
<td>0.008 (0.002)</td>
</tr>
<tr>
<td>20Zn-bir</td>
<td>0.0081</td>
<td>Mn-O</td>
<td>6.7 (1.1)</td>
<td>1.914 (0.008)</td>
<td>0.007 (0.001)</td>
</tr>
<tr>
<td>δ-MnO2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-dMn</td>
<td>0.0077</td>
<td>Mn-O</td>
<td>5.6 (0.9)</td>
<td>1.921 (0.008)</td>
<td>0.005 (0.001)</td>
</tr>
<tr>
<td>1Zn-dMn</td>
<td>0.0049</td>
<td>Mn-O</td>
<td>6.0 (0.8)</td>
<td>1.914 (0.006)</td>
<td>0.005 (0.001)</td>
</tr>
<tr>
<td>5Zn-dMn</td>
<td>0.0034</td>
<td>Mn-O</td>
<td>6.0 (0.9)</td>
<td>1.928 (0.007)</td>
<td>0.008 (0.001)</td>
</tr>
<tr>
<td>20Zn-dMn</td>
<td>0.0075</td>
<td>Mn-O</td>
<td>6.9 (1.0)</td>
<td>1.910 (0.007)</td>
<td>0.006 (0.001)</td>
</tr>
</tbody>
</table>

The PDF, G(r), for all pure and Zn-coprecipitated birnessite and δ-MnO2 samples are shown in Fig. 5. Compared to δ-MnO2, acid birnessite has sharper peaks extending to longer R range, indicating better crystallinity and consistent with TEM and XRD results. The attenuation of intensity can be used to estimate the size of coherent scattering domains (i.e., bending and fault-stacked particles are less accounted for) (Manceau et al., 2013). In this study, all the oxide samples showed significant bending and stacking faults of the MnO2 layers (and more significant with Zn coprecipitation); therefore, we used HRTEM to estimate the numbers of stacked layers.

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by the consistent decrease in Mn(II)/Mn(III) contents and increase in AOS from XANES fitting (Fig. 3), as well as the decrease of Mn-Mn_{corner} CN in Mn EXAFS fitting (Table 2). The slight decrease in the Mn-Mn_{corner} path distance suggests that the ratio of Mn(II)/Mn(III) is lower in Zn-coprecipitated δ-MnO_2 samples. This indicates that Mn(II) is less strongly bound to layers and the expelling effect of Mn(II) is more significant compared to Mn(III).

4.3. Layer structure

Based on previous studies and the results above, Zn^{2+} repelling of layer Mn(III) is more likely to happen in phyllosilicate phases with low AOS and high Mn(III). Grangeon et al. found that Zn^{2+} expelled Mn(III) during its adsorption on δ-MnO_2 with an AOS of 3.76 with ~13% layer Mn(III) (Grangeon et al., 2012). Similar effects were also observed in our Zn-coprecipitated δ-MnO_2 systems with an AOS of 3.77 and ~15% Mn(III) contents. However, our EXAFS fitting results showed no change of the Mn-Mn_{edge} CN and distance for the acid birnessite system, suggesting that Zn^{2+} addition did not significantly affect layer Mn(III) contents in acid birnessite phases. This is possibly due to the already low content of layer Mn(III) in acid birnessite (AOS 3.92, ~6% Mn(III)), causing the Mn(III) expelling effect by Zn^{2+} to be not as obvious as the δ-MnO_2 system. Natural biogenic Mn oxides are typically nanocrystalline phases with lower AOS and more Mn(III) contents than synthetic phyllosilicate analogs (i.e., acid birnessite and δ-MnO_2) (Toner et al., 2006; Villalobos et al., 2006; Villalobos et al., 2003; Webb et al., 2005a; Zhu et al., 2010), therefore, one might expect that Zn^{2+} can cause significant modifications of biogenic MnOx layer structure. Boonfueng et al. studied Zn^{2+} coprecipitation with biogenic MnOx and found modifications to the 8–9 Å^{-1} EXAFS indicator region, although the authors concluded no structural changes (Boonfueng et al., 2009).

The reduction of lateral layer size can be attributed to pH change and/or crystal growth inhibition caused by Zn^{2+} coprecipitation. First, metal doping/coprecipitation during phyllosilicate synthesis is a common method for producing MnOx materials with desired properties, though the pH change caused by metal hydrolysis were rarely measured or discussed in previous studies (Yin et al., 2015a; Yin et al., 2015b; Yin et al., 2011b; Yin et al., 2015c; Yin et al., 2012). In this study, the presence of Zn^{2+} during mineral formation slightly decreased the pH in the synthesis suspensions (Fig. S7). Yu et al. also found that Zn^{2+} addition decreased the pH of fungi growth media during the formation of biogenic MnOx (Yu et al., 2013). Grangeon et al. found that acidic condition caused the dissolution and smaller layer size when preformed δ-MnO_2 was equilibrated at low pH (Grangeon et al., 2014). Secondly, previous studies have indicated that addition of foreign oxyanions (phosphate, silicate, and sulfate) can inhibit the layer growth of acid birnessite. These oxyanions should not significantly change the pH of the synthesis environment but still reduced the layer size by inhibiting crystal growth (Wang et al., 2016; Yin et al., 2015b). Experiments on Zn coprecipitation with biogenic Mn oxides in well-buffered media are ongoing to investigate the significance of these two factors.

4.4. Particle size

Particle size can significantly change the electrochemical (Gao et al., 2001; Li et al., 2016; Wang et al., 2016), catalytic (Wang et al., 2016), adsorptive, and redox properties of phyllosilicates (Villalobos et al., 2014a; Villalobos et al., 2014b). BET Surface area (Villalobos et al., 2014b; Villalobos et al., 2006; Webb et al., 2005a), TEM (Grangeon et al., 2012; Villalobos et al., 2003), XRD (Grangeon et al., 2012; Zhang...
Estimation of acid birnessite and δ-MnO₂ particle size by TEM is also difficult due to strong aggregation. Lateral particle size (along the a-b plane) of ~50–200 nm for acid birnessite and ~20–100 nm for δ-MnO₂ were observed previously (Villalobos et al., 2003) and in our HRTEM analysis. With increasing Zn content, our HRTEM analysis observed a general decrease of layer stacking and lateral particle size. Curling and faults of the MnO₆ nanosheets can lead to less periodicity in the a-b plane and less layer stacking consistency along c axis (Grangeon et al., 2012; Post and Veblen, 1990; Zhu et al., 2012). Along with texture effects (Mancau et al., 2013), this might be the reason that the CSD size calculated by XRD and PDF were much smaller than the particle size observed by HRTEM. Indeed, the CSD size revealed by PDF is around 5 nm for acid birnessite and 2–3 nm for δ-MnO₂ (Fig. 5). The XRD calculated birnessite CSD size along c axis is 4–7 nm, agreeing well with the PDF results, but both smaller than HRTEM measured size.

Interestingly, with increasing Zn content, the PDF CSD size barely changed for both acid birnessite and δ-MnO₂ samples (Fig. 5), while broadened peaks in XRD (Fig. 2) indicated decreasing CSD size along c axis (especially acid birnessite samples) and in a-b plane (especially δ-MnO₂ samples) (Wang et al., 2016). Zn coprecipitation caused more incoherence in both phyllomanganates, e.g. layer collapse, curling, stacking faults, and heavy aggregation, which significantly broadened XRD Bragg peaks and decreased crystallite sizes. However, for PDF analysis, which detects both Bragg and diffuse scattering contributions, decreased crystallinity and formation of sub-domains, although decreasing the peak sharpness, would not affect the longest atomic pair distances which determined the signal attenuation and CSD size.

5. Conclusions

This systematic study demonstrated that the impact of Zn²⁺ during phyllomanganate (acid birnessite and δ-MnO₂) formation are much more significant than by Zn²⁺ adsorption alone (Grangeon et al., 2012). Zn²⁺ neutralized the negative surface charge of phyllomanganates and caused great particle aggregation. Zn-coprecipitation with acid birnessite expelled interlayer alkali cations and water molecules and interrupted the layer stacking along c axis. The AOS of δ-MnO₂ increased due to Mn(II)/Mn(III) expelling by Zn²⁺, while such effect was not obvious in Zn-coprecipitated acid birnessite samples due to the already high AOS and little Mn(II, III) in acid birnessite. Zn²⁺ existed as inner-sphere surface complexes (ZnO₂⁻ or Zn(II)⁺) above/below vacancy sites as adsorbed species instead of substitution at vacancy sites. Zn²⁺ decreased Mn(III) contents within MnO₂ layers, leaving more vacancy sites available for future reactions (e.g. sorption of other cations). For acid birnessite, layer stacking and interlayer cations/water molecules are significantly affected with minimal modulation of the layer structure. The modification of layer structure (e.g. crystallinity and layer Mn (III) contents) is much more significant in Zn-coprecipitated δ-MnO₂ samples.

Previous studies have shown that birnessite structure interruption caused by foreign metals is in the reverse relationship with the compatibility (Co > Ni > Fe) of metals in birnessite layers (Yin et al., 2013). This study provides insights on the possible prediction of structural changes caused by Zn²⁺ and other similar incompatible cations on natural and synthetic phyllomanganates with different crystallinity. The sorptive ability of these metal coprecipitated oxides are expected to change significantly due to the less negative surface charge, decreased particle size, and increased vacancy site density (Villalobos et al., 2014a; Villalobos et al., 2014b; Wang et al., 2012b; Yin et al., 2011a; Yin et al., 2012; Zhao et al., 2010). Zn²⁺ also decreased Mn(II, III) contents and increased AOS in the oxides with high Mn(II, III) contents, which, together with the modified sorptive reactivity, can potentially have great influences on the oxidative reactivity, transformation, and microbial anaerobic respiration of Mn oxides (Nico and Zasoski, 2000; Tebo et al., 2004; Villalobos et al., 2014a; Villalobos et al., 2014b). These factors can also potentially change the band gap and other catalytic properties of Mn oxides (Kang et al., 2017; Lee et al., 2007; Lucht and Mendoza-Cortes, 2015).

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Appendix A. Supplementary data

Details of BET surface area, zeta potential, HRTEM, XRD, Zn XAS, and PDF analysis; Zn EXAFS shell-by-shell fitting results; stacking layer observations by HTREM; HRTEM images; zeta potential data; Zn EXAFS shell-by-shell fitting results; PDF data; Mn XANES spectra and LCF results; change of solution pH during MnO₂ synthesis. Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2018.05.044.

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monoclinic Na-rich birnessite and hexagonal birnessite. I. Results from X-ray diffraction and selected-area electron diffraction. Am. Mineral. 82 (9–10), 946–961.