



## Effect of Zn coprecipitation on the structure of layered Mn oxides

Shiliang Zhao<sup>a</sup>, Qian Wang<sup>b</sup>, Jingying Sun<sup>c</sup>, Olaf J. Borkiewicz<sup>d</sup>, Rixiang Huang<sup>a</sup>, Emily M. Saad<sup>a</sup>, Benjamin Fields<sup>a</sup>, Shuo Chen<sup>c</sup>, Mengqiang Zhu<sup>b</sup>, Yuanzhi Tang<sup>a,\*</sup>

<sup>a</sup> School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, United States

<sup>b</sup> Department of Ecosystem Science and Management, University of Wyoming, Laramie, WY 82071, United States

<sup>c</sup> Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, TX 77204, United States

<sup>d</sup> Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, United States

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### ABSTRACT

Mn oxides (MnO<sub>x</sub>) 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<sub>x</sub>, and the presence of metal cations during or after the formation of MnO<sub>x</sub> might significantly affect their structure and reactivity. This study systematically investigates the effects of Zn<sup>2+</sup> presence during mineral formation (i.e. coprecipitation) on the structure of acid birnessite and δ-MnO<sub>2</sub>, two synthetic analogs that are structurally similar to fresh biogenic MnO<sub>x</sub> but with different crystallinity. For both acid birnessite and δ-MnO<sub>2</sub>, Zn<sup>2+</sup> existed as surface adsorbed species at vacancy sites, interrupted layer stacking along *c* axis, and caused reductions of the lateral particle size. Zn<sup>2+</sup> also reduced Mn(III) contents in δ-MnO<sub>2</sub> layers, leaving more vacancy sites (capped by adsorbed Zn<sup>2+</sup>). The reduction of layer stacking was more obvious for acid birnessite, while the modification of layer structure was more significant for δ-MnO<sub>2</sub>. These structural changes will likely lead to modified reactivity of MnO<sub>x</sub> in natural systems.

### 1. Introduction

Manganese (Mn) oxides (MnO<sub>x</sub>) 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; Bodeř et al., 2007; Lanson et al., 2008). MnO<sub>x</sub> can form through the oxidation of Mn (II) and this process is much faster when catalyzed by mineral surfaces, microorganisms, or reactive oxygen species. Previous studies have shown that the initial biogenic MnO<sub>x</sub> phases produced by bacteria (Learman et al., 2011a; Learman et al., 2011b; Villalobos et al., 2006) and fungi (Bargar et al., 2005; Grangeon et al., 2010; Saratovsky et al., 2009) at circumneutral pHs are typically highly disordered and nanocrystalline phases that are structurally similar to hexagonal phyllo-manganates (e.g. acid birnessite and δ-MnO<sub>2</sub>) (Tebo et al., 2004). Due to their high surface area, large amount of vacancy sites, and negative surface charge across a wide range of pHs, MnO<sub>x</sub> are highly reactive for the adsorption and redox transformation of metals (e.g. Pb, Ni, Cr) (Charlet and Manceau, 1992; Gadde and Laitinen, 1974; Kawashima et al., 1986; Li et al., 2015; Nico and Zasoski, 2000), metalloids (e.g. As, Se) (Chang et al., 2012; Manceau et al., 2007), and organic compounds (Kung and McBride, 1988; Stone and Morgan, 1984), and can exert

significant influences on the biogeochemical cycles of many important elements. From the materials chemistry aspect of view, hexagonal phyllo-manganates are also important layered octahedral molecular sieves (OMS). The design of OMS with specific composition, structure, and morphology is of great interest for environmental, chemical, and material science research, due to their wide applications as catalysts, battery electrodes, adsorbents, and semiconductors (Lee et al., 2007; Li et al., 2006; Poizot et al., 2000; Yin et al., 2011a).

Metal cations such as Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> 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<sub>x</sub> was shown to have limited effects on MnO<sub>x</sub> layer structure (Power et al., 2005; Villalobos et al., 2014b) (except a recent study on Zn<sup>2+</sup> 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<sub>x</sub> (i.e. sorption system), much remain unknown on the impact of metal cation presence during MnO<sub>x</sub> formation (i.e. coprecipitation system) on the oxide structure, reactivity, and transformation,

\* Corresponding author.

E-mail address: [yuanzhi.tang@eas.gatech.edu](mailto:yuanzhi.tang@eas.gatech.edu) (Y. Tang).

despite the obvious relevance in complex environmental settings. Several recent studies demonstrated significant impacts of metal coprecipitation on the structural properties of  $\text{MnO}_x$ , 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 phyllosulfates, the presence of  $\text{Ni}^{2+}$  can enhance vacancy site formation while  $\text{Ca}^{2+}$  and  $\text{Na}^+$  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  $\text{MnO}_x$  (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  $\text{MnO}_x$  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  $\text{Zn}^{2+} < \text{Cu}^{2+} < \text{Ni}^{2+} < \text{Co}^{3+}$ , 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.  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ) (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  $\text{MnO}_x$  in natural environments, Zn shows the least structural compatibility (Kwon et al., 2013; Yin et al., 2011a; Yin et al., 2013; Yin et al., 2012).  $\text{Zn}^{2+}$  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  $\text{Zn}^{2+}$  on  $\text{MnO}_x$  is dependent on  $\text{Zn}^{2+}$  concentration as well as  $\text{MnO}_x$  crystallinity (Grangeon et al., 2012). Tetrahedrally coordinated  $\text{Zn}^{2+}$  ( $\text{Zn}^{\text{IV}}$ ) at low  $\text{Zn}^{2+}$  concentrations can change to octahedral coordination ( $\text{Zn}^{\text{VI}}$ ) with increasing  $\text{Zn}^{2+}$  loading (Manceau et al., 2002; Toner et al., 2006; Trivedi et al., 2001). A recent study showed that adsorbed  $\text{Zn}^{2+}$  can reduce the amount of Mn(III) ions in  $\delta\text{-MnO}_2$  layers, leaving more vacancy sites (capped by adsorbed  $\text{Zn}^{2+}$ ) (Grangeon et al., 2012).  $\text{Zn}^{2+}$  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  $\text{Zn}^{2+}$  coprecipitation on  $\text{MnO}_x$  structure, but no consensus was reached. Yu et al. found that the presence of  $\text{Zn}^{2+}$  during the formation of fungal  $\text{MnO}_x$  inhibited the crystal growth and modified the layer stacking of  $\text{MnO}_x$  (Yu et al., 2013). Boonfueng et al. found that the presence of  $\text{Zn}^{2+}$  during biogenic  $\text{MnO}_x$  formation resulted in large  $\text{Zn}^{2+}$  sequestration (likely due to surface sorption), but with no obvious changes in  $\text{MnO}_x$  local structure (Boonfueng et al., 2009). Given the low compatibilities of  $\text{Zn}^{2+}$  with phyllosulfate structure, as well as its unique dependence of coordination environment on phyllosulfate 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  $\text{MnO}_x$ .

This study examines the impact of  $\text{Zn}^{2+}$  coprecipitation on the structural properties of two phyllosulfates with different structural order, acid birnessite and  $\delta\text{-MnO}_2$ .  $\text{Zn}^{2+}$  association with natural  $\text{MnO}_x$  was found to be 0–0.5% (Zn/Mn molar ratio) in marine nodules (Childs, 1975; Jenkyns, 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  $\text{Zn}^{2+}$  sequestration is known to be affected by phyllosulfate structure and crystallinity, this study compared acid birnessite and  $\delta\text{-MnO}_2$ , two structurally similar phyllosulfate phases but with different structural order. Compared to  $\delta\text{-MnO}_2$ , 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  $\text{Zn}^{\text{VI}}$  stabilization is weaker between incoherently stacked and laterally smaller layers (Kwon et al., 2009), its prevalence on  $\delta\text{-MnO}_2$  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  $\text{Zn}^{2+}$  coprecipitation can have different effects on the structural properties of these two  $\text{MnO}_x$  phases with different crystallinity.

Compared to previous studies on Zn sorption on pre-formed  $\text{MnO}_x$  (Boonfueng 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  $\text{MnO}_x$  structure compared to Zn sorption system. By exploring two synthetic  $\text{MnO}_x$  phases with similar structure but different structure order, our system eliminated the potential toxicity effects associated with biogenic  $\text{MnO}_x$  systems, and allowed thorough investigation on the effect of  $\text{MnO}_x$  structure order. We conducted systematic characterization of the Zn-coprecipitated  $\text{MnO}_x$  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  $\text{Zn}^{2+}$  coprecipitation on the structural properties of two environmentally relevant  $\text{MnO}_x$  phases, and points to the importance of considering metal coprecipitation effects for studies centered on  $\text{MnO}_x$  reactivity in natural systems.

## 2. Methods

### 2.1. Synthesis of $\delta\text{-MnO}_2$ and acid birnessite in the presence of $\text{Zn}^{2+}$

Both  $\delta\text{-MnO}_2$  and acid birnessite phases were synthesized in the absence or presence of a range of  $\text{Zn}^{2+}$  concentrations.  $\delta\text{-MnO}_2$  synthesis followed a previous procedure (Zhu et al., 2012) where 160 mL  $\text{MnSO}_4$  solution (0.30 mol L<sup>-1</sup>) was pumped into a mixture of 160 mL  $\text{KMnO}_4$  (5.0 g) and 180 mL NaOH (3.5 g) solutions at a speed of 25 mL min<sup>-1</sup> under vigorous stirring. Calculated amounts of  $\text{ZnSO}_4$  was dissolved in the  $\text{MnSO}_4$  solution to achieve Zn:total Mn molar ratio of 0–20%. For acid birnessite synthesis,  $\text{ZnSO}_4$  was dissolved in 45 mL of 6 mol L<sup>-1</sup> HCl solution to achieve Zn/total Mn molar ratio of 0–20%. This solution was then pumped at 1 mL min<sup>-1</sup> into 300 mL of boiling 0.667 mol L<sup>-1</sup>  $\text{KMnO}_4$  solution under vigorous stirring (Villalobos et al., 2003). Previous studies on Mn oxide formation in the presence of  $\text{Zn}^{2+}$  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  $\mu\text{m}$ ), 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 plasma – mass spectrometry (ICP-MS). Samples were also characterized for their morphology, surface, and

**Table 1**

Sample label, chemical composition, BET surface area, HRTEM revealed numbers of stacking layer per particle, as well as XRD determined crystallite size along *c* axis for the Zn-coprecipitated birnessite and  $\delta$ -MnO<sub>2</sub> samples.

Initial Zn/Mn molar ratio	Sample label	Chemical composition of the final solids					BET specific surface area (m <sup>2</sup> /g)	Number of stacking layers (by HRTEM)	Crystallite size along <i>c</i> axis (nm, by XRD)
		Mn (wt %)	Zn (wt %)	K (wt%)	Na (wt %)	Zn/Mn molar ratio			
Acid birnessite									
0	p-bir	45.2	0	10.5	–	0	27.4 ± 0.4	11 ± 3	6.4
1%	1Zn-bir	44.9	0.6	9.5	–	1.1%	30.2 ± 0.5	11 ± 3	6.7
5%	5Zn-bir	45.9	2.9	8.1	–	5.7%	32.5 ± 0.3	9 ± 4	5.6
10%	10Zn-bir	43.8	6.0	4.9	–	12.4%	29.2 ± 0.2	7 ± 2	5.1
20%	20Zn-bir	43.3	8.0	1.4	–	15.9%	19.3 ± 0.2	5 ± 1	4.5
$\delta$ -MnO <sub>2</sub>									
0	p-dMn	37.2	0	1.0	2.0	0	221.9 ± 1.3	5 ± 1	–
1%	1Zn-dMn	37.4	1.3	1.7	1.7	2.2%	159.2 ± 1.0	5 ± 1	–
5%	5Zn-dMn	38.3	2.4	2.1	1.8	4.2%	123.9 ± 0.7	5 ± 1	–
20%	20Zn-dMn	37.3	9.8	2.1	1.2	21.2%	131.6 ± 1.0	4 ± 1	–

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  $\delta$ -MnO<sub>2</sub> samples to investigate their structural characteristics. Suspensions containing MnO<sub>x</sub> were vacuum filtered through 0.2  $\mu$ m polycarbonate membranes and rinsed with DI water. The moist filter membranes loaded with MnO<sub>x</sub> 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 Lightsources (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 transmission and fluorescence mode using a Lytle detector (Beamlines 4-1 at SSRL and 12-BM-B at APS) or a vortex 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 MnO<sub>x</sub> under the X-ray beam.

XAS data analysis was performed using the programs SIXPACK (Webb, 2005), Ifeffit (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 MnSO<sub>4(aq)</sub>, MnPO<sub>4</sub>, ramsdellite, and K-birnessite, and the second set included MnSO<sub>4(s)</sub>, Mn<sub>2</sub>O<sub>3</sub>, and pyrolusite ( $\beta$ -MnO<sub>2</sub>).

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

Synchrotron high-energy X-ray total scattering data of the synthesized MnO<sub>x</sub> samples were collected at beamline 11-ID-B (~58.6 keV,  $\lambda = 0.2117$  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 PDFgetX2 (Qiu et al., 2004). The PDFs were calculated from the Fourier transforms of these data truncated at 26 Å<sup>-1</sup>.

## 3. Results

### 3.1. Chemical compositions

Composition analysis of the Zn-coprecipitated MnO<sub>x</sub> showed significant amount of Zn<sup>2+</sup> 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  $\delta$ -MnO<sub>2</sub>. This higher Zn<sup>2+</sup> uptake capacity of  $\delta$ -MnO<sub>2</sub> might be due to its intrinsic structural properties, as discussed later.

The presence of Zn<sup>2+</sup> significantly decreased the interlayer cation (K<sup>+</sup>) content for birnessite, but has little impact on the content of interlayer cations (K<sup>+</sup> and Na<sup>+</sup>) of  $\delta$ -MnO<sub>2</sub> (Table 1). Total Mn content was similar for birnessite or  $\delta$ -MnO<sub>2</sub> samples with different Zn<sup>2+</sup> loadings, except for a slight decrease at 20% Zn/Mn loading for acid birnessite. This suggests that Zn<sup>2+</sup> might have preferably replaced the interlayer cations in acid birnessite instead of substituting for Mn(III, IV) ions within the MnO<sub>6</sub> layers. This is consistent with previous studies where no Zn<sup>2+</sup> substitution into the layer structure was observed when Zn<sup>2+</sup> 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  $\delta$ -MnO<sub>2</sub> phases, as compared to their pure phases (Figs. 1 and S1). In general, birnessite samples contain larger particles with multiple layer stacking, while  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -

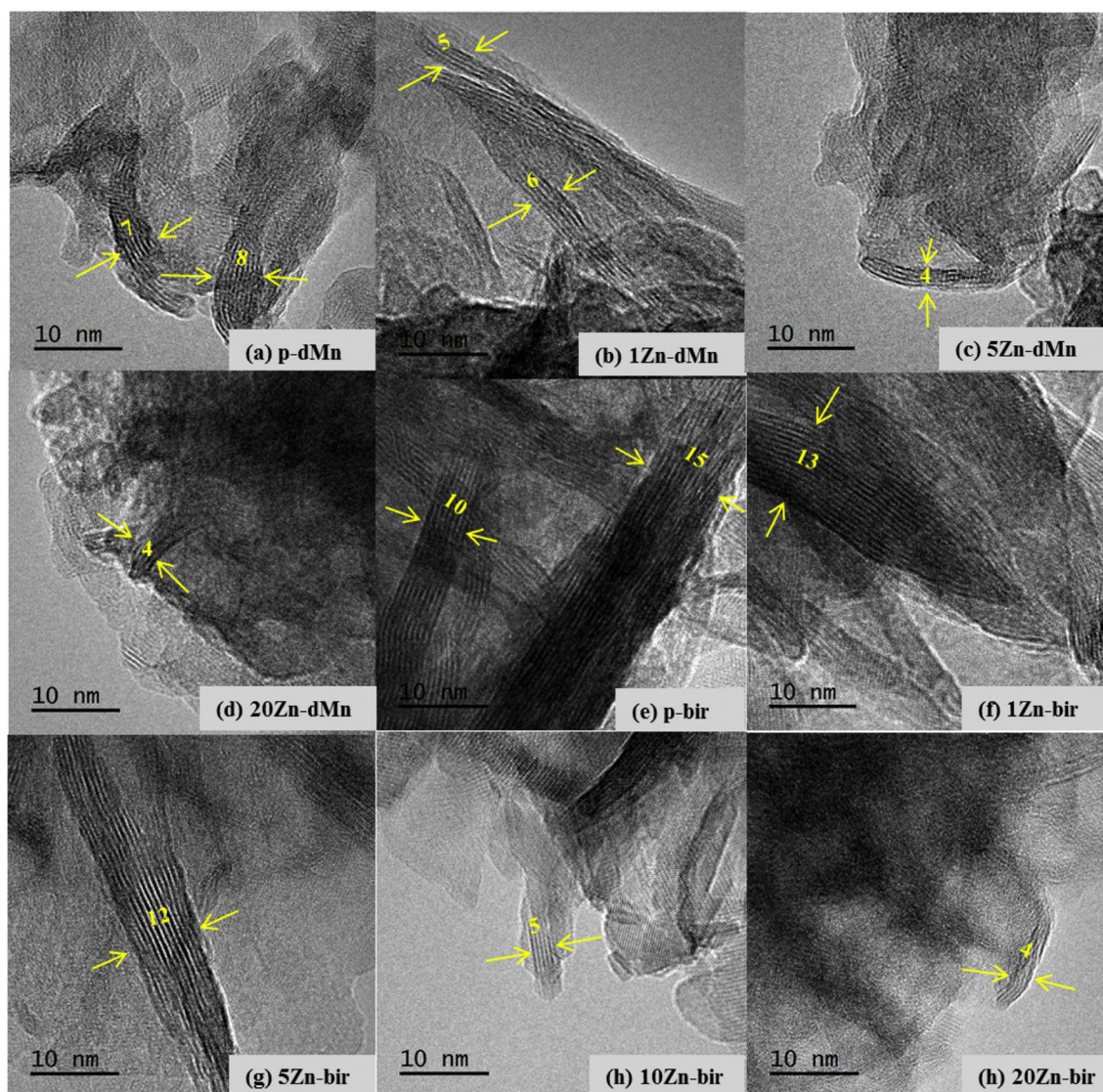


Fig. 1. HRTEM images of pure and Zn-coprecipitated  $\delta$ -MnO<sub>2</sub> and birnessite samples. (a) p-dMn (b) 1Zn-dMn, (c) 5Zn-dMn and (d) 20Zn-dMn for  $\delta$ -MnO<sub>2</sub>; (e) p-bir (f) 1Zn-bir, (g) 5Zn-bir, (h) 10Zn-bir and (i) 20Zn-bir for acid birnessite. Yellow numbers indicate the number of stacking layers between the yellow arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

MnO<sub>2</sub>. 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  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> were 27.4 and 221.9 m<sup>2</sup>/g, respectively (Table 1), consistent with previously reported values of 19–40.5 m<sup>2</sup>/g for acid birnessite and 114–274 m<sup>2</sup>/g for  $\delta$ -MnO<sub>2</sub> (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 m<sup>2</sup>/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  $\delta$ -MnO<sub>2</sub>, increasing Zn/Mn ratio caused a continuous decrease of the SSA from 221.9 (p-dMn) to 131.6 m<sup>2</sup>/g (20Zn-dMn), suggesting aggregation to be the dominant factor affecting SSA in the  $\delta$ -MnO<sub>2</sub> 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 Zn<sup>2+</sup> inner-sphere complexes on the oxide surfaces, because Zn<sup>2+</sup> has strong tendency to sorb on MnO<sub>x</sub> and low compatibility for structural incorporation into MnO<sub>x</sub>. Similar effects on surface charge were also previously observed during Zn<sup>2+</sup> adsorption onto birnessite (Power et al., 2005).

### 3.4. X-ray diffraction

XRD analysis was conducted to characterize the long-range order of

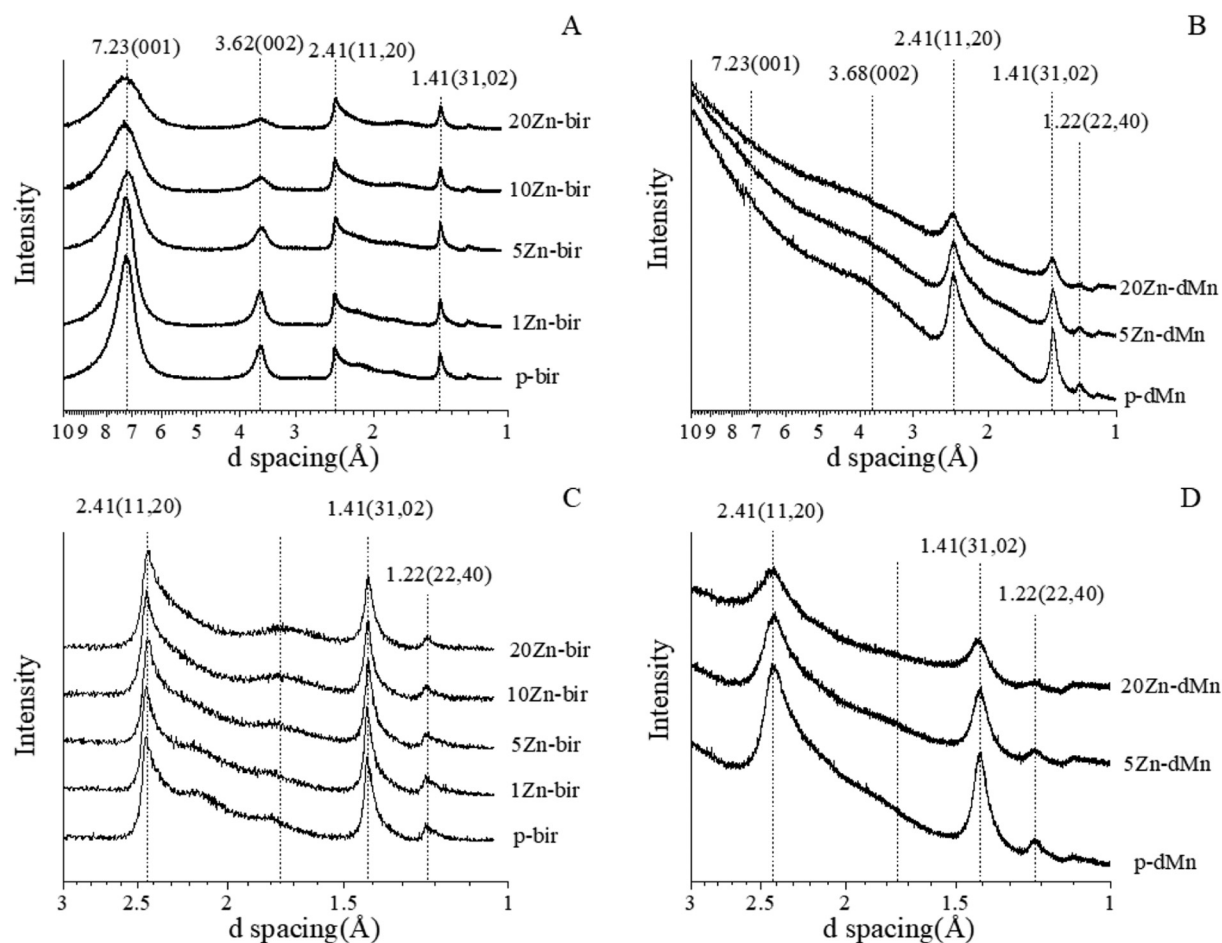


Fig. 2. XRD patterns of pure and Zn-coprecipitated birnessite (A) and  $\delta$ -MnO<sub>2</sub> (B), as well as their zoomed view at 1–3 Å (C and D, respectively).

all acid birnessite and  $\delta$ -MnO<sub>2</sub> samples (Fig. 2). The XRD patterns of pure acid birnessite and  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> phases showed no obvious peak at  $\sim$ 7.23 Å (001) and only a broad peak at  $\sim$ 3.68 Å (002), due to the weaker layer stacking of  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> phases are more affected in lateral layer size, as detailed below.

For birnessite phases, Zn-coprecipitation caused significant reduction in layer stacking. With increasing Zn<sup>2+</sup> content, XRD showed decreased peak height and increased peak width at 7.23 Å (001) and/or 3.62 Å (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 Zn<sup>2+</sup> contents (Table 1). Such effect on layer stacking was a result from the coprecipitation process, as Zn<sup>2+</sup> sorption (during mineral formation) on the vacancy sites disrupted layer formation. In contrast, when Zn<sup>2+</sup> was equilibrated with hexagonal birnessite (orderly stacked) and exchanged for H<sup>+</sup>, 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 Zn<sup>2+</sup> content, this hump became more significant due to vacancy site occupation by Zn<sup>2+</sup> (Drits et al., 2007; Grangeon et al., 2008).

For  $\delta$ -MnO<sub>2</sub> 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 Zn<sup>2+</sup> 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,  $\delta$ -MnO<sub>2</sub> 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

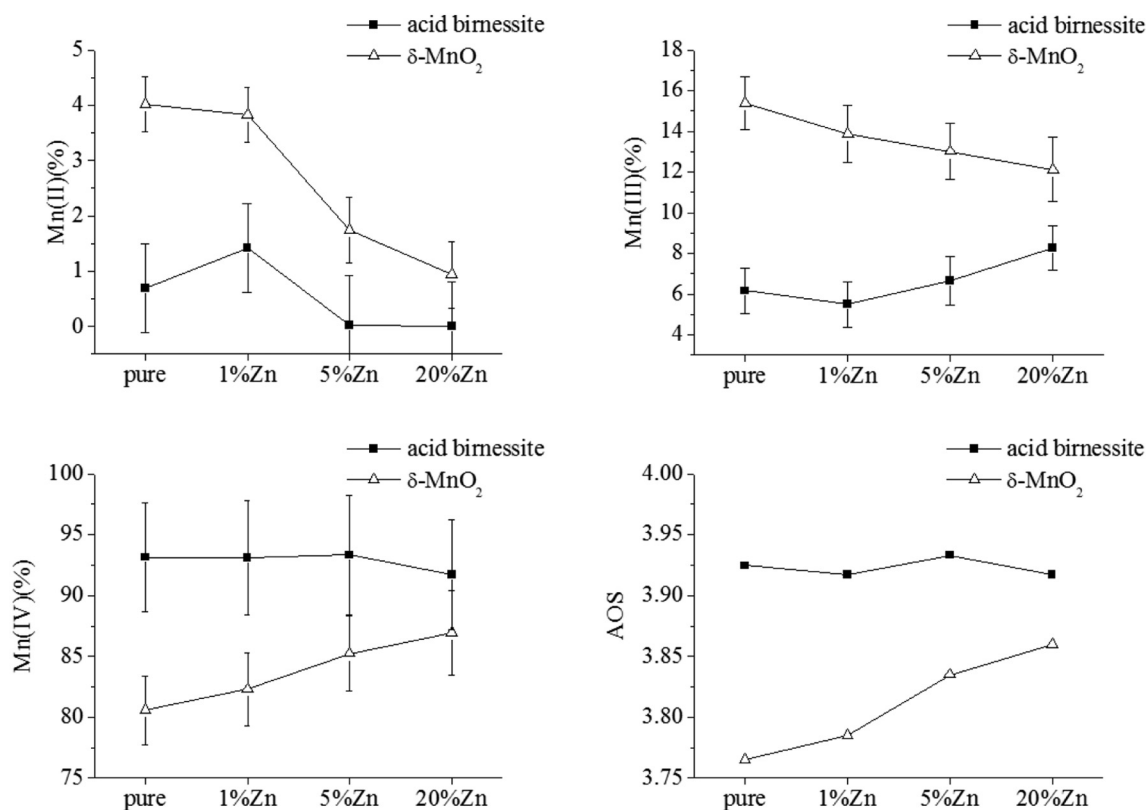


Fig. 3. Relative percentage of Mn(II), (III), and (IV), as well as average oxidation state (AOS) of pure and Zn-coprecipitated birnessite and  $\delta$ -MnO<sub>2</sub> phases, determined by linear combination fitting of Mn K-edge XANES using reference set 1.

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  $\delta$ -MnO<sub>2</sub> has an AOS of 3.77 and ~15% Mn(III), both similar to the values in Grangeon et al. (2012). Compared to  $\delta$ -MnO<sub>2</sub>, 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  $\delta$ -MnO<sub>2</sub>. For  $\delta$ -MnO<sub>2</sub> samples, increasing Zn<sup>2+</sup> 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 phyllosulfates (Grangeon et al., 2012; Lanson et al., 2002b). The AOS of acid birnessite showed no significant change with increasing Zn<sup>2+</sup>, likely due to the already low Mn(II, III) contents in pure acid birnessite thus the replacement effects were not significant.

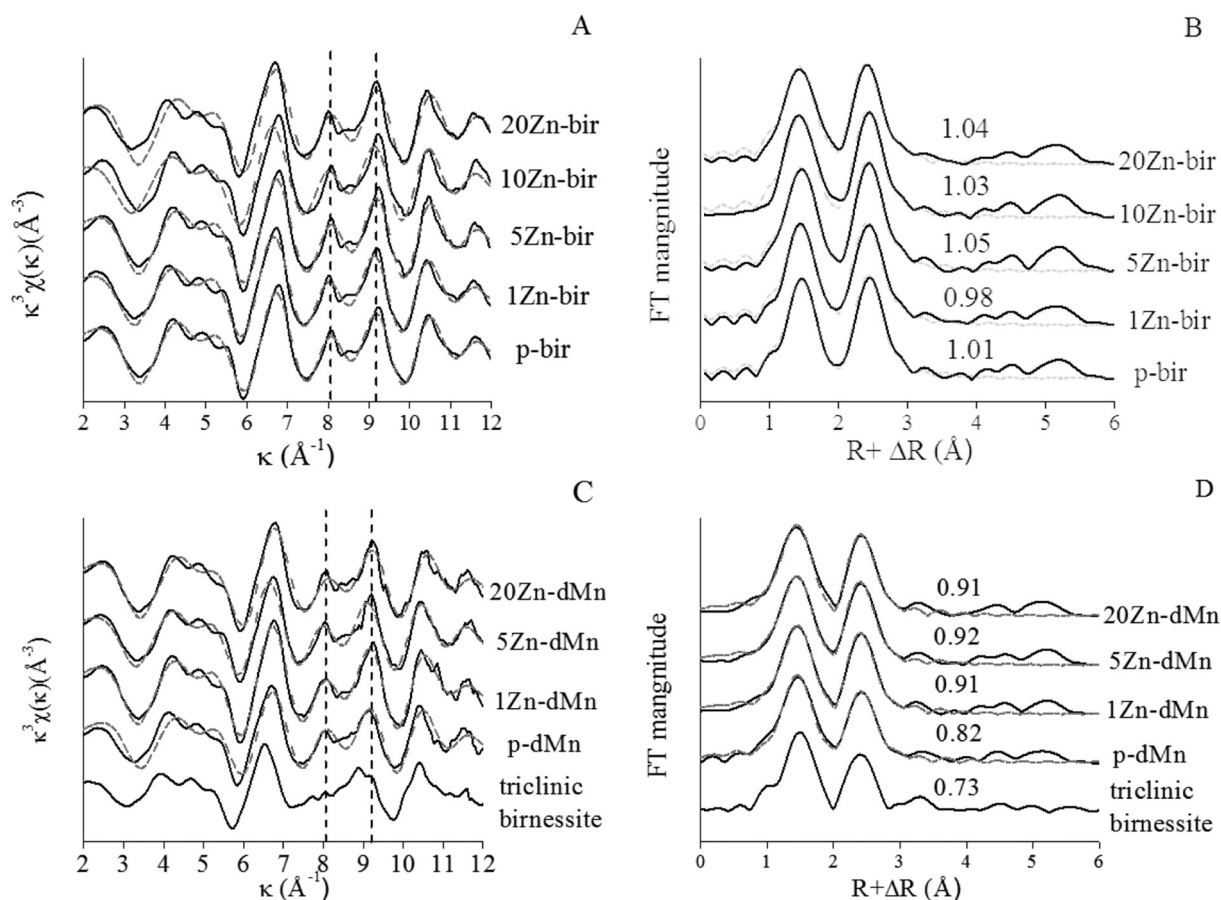
A second fitting of the Mn XANES data (Fitting 2) was conducted using reference set 2 (Fig. S5). The AOS of pure acid birnessite (3.79) and  $\delta$ -MnO<sub>2</sub> (3.71) from Fitting 2 are lower than Fitting 1, confirming that LCF fitting method to achieve Mn AOS largely depends on the reference compounds. Based on the results of Fitting 2, Mn AOS of acid birnessite had no significant change with increasing Zn content, as compared to an increase of AOS for  $\delta$ -MnO<sub>2</sub> 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. K<sup>3</sup>-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<sup>-1</sup> (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  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub>, 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 Zn<sup>2+</sup> content, the peak at 9.2 Å<sup>-1</sup> of  $\delta$ -MnO<sub>2</sub> 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-Mn<sub>edge</sub>) shells, respectively (Manceau and Combes, 1988). Previous studies suggested that the peak height ratio H<sub>Mn-Mn(edge)</sub>/H<sub>Mn-o</sub> corresponds to several factors, such as layer vacancy site occupation fraction (*f<sub>occ</sub>*) 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 (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, triclinic birnessite has large amount of layer Mn(III) occupying vacancy sites (Lanson et al., 2002a) and a low ratio of 0.73 (Fig. 4D). This ratio was 0.82 in pure  $\delta$ -MnO<sub>2</sub> and 1.01 in pure acid birnessite, both with less layer Mn(III) and more unoccupied



**Fig. 4.**  $k^3$ -weighted Mn K-edge EXAFS and Fourier transformed (FT) spectra (not corrected for phase shift) of pure and Zn-coprecipitated acid birnessite (A, B) and  $\delta$ - $\text{MnO}_2$  (C, D). Raw and fitted data are in solid and dotted lines, respectively. Triclinic birnessite was also plotted to compare with  $\delta$ - $\text{MnO}_2$  samples. Vertical dashed lines in (A) and (C) highlight the indicator region. The ratios of second shell (Mn-Mn edge sharing) and first shell (Mn-O) in FT spectra are shown in (B) and (D).

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  $H_{\text{Mn-Mn}}/H_{\text{Mn-O}}$  ratio. Zhu et al. found the inverse proportionality between  $f_{\text{occ}}$  and  $H_{\text{Mn-Mn}}/H_{\text{Mn-O}}$  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  $\delta$ - $\text{MnO}_2$ , decreased particle size could reduce the relative amplitude of Mn-Mn<sub>edge</sub> peak (Kawashima et al., 1986; Wang et al., 2016; Webb et al., 2005a) while less layer Mn(III) in Zn-coprecipitated  $\delta$ - $\text{MnO}_2$  samples could increase the amplitude (Sherman and Peacock, 2010; Webb et al., 2005a; Zhu et al., 2010). In this study,  $H_{\text{Mn-Mn(edge)}}/H_{\text{Mn-O}}$  increased slightly from 0.82 (pure  $\delta$ - $\text{MnO}_2$ ) 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  $\text{Zn}^{2+}$  content for acid birnessite samples, showing relatively unchanged layer Mn(III) contents. This is also consistent with the unchanged peak sharpness at  $\sim 8$ – $9.2 \text{ \AA}^{-1}$  region in  $k$  space and our EXAFS fitting results of acid birnessite below.

Mn EXAFS fitting of all the oxide samples used a single scattering model considering the Mn-O, Mn-Mn edge sharing (Mn-Mn<sub>edge</sub>), and Mn-Mn corner sharing (Mn-Mn<sub>corner</sub>) paths (results in Table 2 and Fig. 4). For pure and Zn-coprecipitated birnessite samples, best fits were obtained with  $\sim 6$  O atoms at  $\sim 1.91$ – $1.92 \text{ \AA}$  (consistent with Mn in

octahedral coordination),  $\sim 5$ – $6$  Mn atoms at  $2.87$ – $2.88 \text{ \AA}$ , and  $\sim 1$  Mn atom at  $3.47$ – $3.49 \text{ \AA}$ . The distances for the two Mn-Mn paths were consistent with previously reported values (Learman et al., 2011b; Manceau and Combes, 1988; Villalobos et al., 2006; Webb et al., 2005a). The Mn-Mn<sub>edge</sub> path is attributed to layer  $\text{MnO}_6$  octahedra, and the coordination number (CN) can be affected by both particle size and layer vacancy site density (i.e. a fully filled  $\text{MnO}_6$  layer has CN of 6; both decreasing particle size and increasing amount of vacancy sites will lead to smaller CN values). When Mn(III) incorporates in vacancy sites, increasing amount of layer Mn(III) would increase CN and result in a slightly longer Mn-Mn<sub>edge</sub> distance (Manceau et al., 2005; Villalobos et al., 2006; Zhu et al., 2010). The Mn-Mn<sub>corner</sub> path is attributed to adsorbed interlayer Mn(II,III) ions (Villalobos et al., 2006; Zhu et al., 2010). Increasing amount of interlayer Mn(II) would result in a longer Mn-Mn<sub>corner</sub> distance, whereas increasing amount of interlayer Mn(III) would result in an increase in the CN (Webb et al., 2005a). For Zn-coprecipitated birnessite samples, increasing  $\text{Zn}^{2+}$  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<sub>corner</sub> distance at 10 and 20%  $\text{Zn}^{2+}$  contents), suggesting little changes to the vacancy site density and layer/interlayer Mn(III) contents. This is consistent with no changes in the  $8$ – $9.2 \text{ \AA}^{-1}$  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  $\delta$ - $\text{MnO}_2$ , with increasing  $\text{Zn}^{2+}$  content, the Mn-Mn<sub>edge</sub> path showed a decrease in distance from  $2.884$  (pure  $\delta$ - $\text{MnO}_2$ ) to  $2.871$ – $2.872 \text{ \AA}$  (all the Zn-coprecipitated  $\delta$ - $\text{MnO}_2$  samples), suggesting less layer Mn(III) content. This was also observed in  $\text{Ni}^{2+}$  coprecipitated biogenic Mn oxides (Zhu et al., 2010). The CN for the Mn-Mn<sub>edge</sub> path also decreased from 6.2 (pure  $\delta$ - $\text{MnO}_2$ )

**Table 2**  
Mn EXAFS fitting results for pure and Zn-coprecipitated acid birnessite and  $\delta$ -MnO<sub>2</sub> samples.

Sample label	R	Shell	CN	Distance (Å)	$\sigma^2$
Acid birnessite					
p-bir	0.0049	Mn-O	6.0 (0.8)	1.919 (0.006)	0.007 (0.001)
		Mn-Mn <sub>edge</sub>	5.5 (0.8)	2.877 (0.007)	0.007 (0.001)
		Mn-Mn <sub>corner</sub>	0.9 (0.7)	3.487 (0.047)	0.007 (0.001)
1Zn-bir	0.0094	Mn-O	6.0 (1.1)	1.916 (0.009)	0.006 (0.002)
		Mn-Mn <sub>edge</sub>	5.8 (1.2)	2.877 (0.009)	0.007 (0.001)
		Mn-Mn <sub>corner</sub>	1.0 (1.0)	3.491 (0.058)	0.007 (0.001)
5Zn-bir	0.0032	Mn-O	6.3 (0.7)	1.914 (0.005)	0.007 (0.001)
		Mn-Mn <sub>edge</sub>	5.5 (0.7)	2.871 (0.005)	0.007 (0.001)
		Mn-Mn <sub>corner</sub>	0.9 (0.6)	3.490 (0.033)	0.007 (0.001)
10Zn-bir	0.0183	Mn-O	7.0 (1.5)	1.913 (0.013)	0.008 (0.002)
		Mn-Mn <sub>edge</sub>	5.2 (1.3)	2.869 (0.013)	0.006 (0.002)
		Mn-Mn <sub>corner</sub>	0.9 (1.1)	3.476 (0.083)	0.006 (0.002)
20Zn-bir	0.0081	Mn-O	6.7 (1.1)	1.914 (0.008)	0.007 (0.001)
		Mn-Mn <sub>edge</sub>	5.2 (1.0)	2.868 (0.009)	0.006 (0.001)
		Mn-Mn <sub>corner</sub>	1.0 (0.8)	3.469 (0.045)	0.006 (0.001)
$\delta$ -MnO <sub>2</sub>					
p-dMn	0.0077	Mn-O	5.6 (0.9)	1.921 (0.008)	0.005 (0.001)
		Mn-Mn <sub>edge</sub>	6.2 (0.9)	2.884 (0.008)	0.008 (0.001)
		Mn-Mn <sub>corner</sub>	1.0 (0.8)	3.515 (0.061)	0.008 (0.001)
1Zn-dMn	0.0049	Mn-O	6.0 (0.8)	1.914 (0.006)	0.005 (0.001)
		Mn-Mn <sub>edge</sub>	4.9 (1.0)	2.872 (0.007)	0.008 (0.001)
		Mn-Mn <sub>corner</sub>	0.8 (0.9)	3.453 (0.054)	0.008 (0.001)
5Zn-dMn	0.0034	Mn-O	6.8 (0.6)	1.913 (0.005)	0.006 (0.001)
		Mn-Mn <sub>edge</sub>	4.8 (0.6)	2.871 (0.005)	0.006 (0.001)
		Mn-Mn <sub>corner</sub>	0.6 (0.5)	3.471 (0.040)	0.006 (0.001)
20Zn-dMn	0.0075	Mn-O	6.9 (1.0)	1.910 (0.007)	0.006 (0.001)
		Mn-Mn <sub>edge</sub>	4.7 (1.1)	2.871 (0.009)	0.007 (0.001)
		Mn-Mn <sub>corner</sub>	0.5 (0.8)	3.451 (0.049)	0.007 (0.001)

to 4.6–4.8 (Zn-coprecipitated  $\delta$ -MnO<sub>2</sub>). The decreased CN can be caused by decrease in both layer Mn(III) and particle size. The Mn-Mn<sub>corner</sub> path showed decreased CN from 1.0 (pure  $\delta$ -MnO<sub>2</sub>) to 0.5 (20Zn-dMn), suggesting decreasing amount of adsorbed Mn(II,III) at interlayer region. A continuous decrease in distance was also observed for the Mn-Mn<sub>corner</sub> path, from 3.515 (pure  $\delta$ -MnO<sub>2</sub>) to 3.451 Å (20Zn-dMn), suggesting relatively less interlayer Mn(II) in the presence of Zn<sup>2+</sup> (Silvester et al., 1997).

### 3.6. Pair distribution function analysis

The PDF,  $G(r)$ , for all pure and Zn-coprecipitated birnessite and  $\delta$ -MnO<sub>2</sub> samples are shown in Fig. 5. Compared to  $\delta$ -MnO<sub>2</sub>, acid birnessite has sharper peaks extending to longer R range, indicating better crystallinity and consistent with TEM and XRD results. The attenuation of  $G(r)$  intensity can be used to estimate the size of coherent scattering domain (CSD) (Manceau et al., 2013; Nandy and Pradhan, 2015; Yin et al., 2015b; Zhu et al., 2012). Estimated CSD size is  $\sim$ 30 Å for  $\delta$ -MnO<sub>2</sub> and  $\sim$ 50 Å for acid birnessite. Zn coprecipitation did not change the CSD size for both birnessite and  $\delta$ -MnO<sub>2</sub> systems.

Fig. 5(B, D) show the  $G(r)$  at 7 Å range. PDF structure models for Mn oxides have been developed and discussed in previous studies (Manceau et al., 2013; Zhu et al., 2012) to describe the atomic pair contributions for the peaks in  $G(r)$ . Based on these models, the first peak at  $\sim$ 1.9 Å is attributed to Mn-O atomic pairs within the MnO<sub>6</sub> layer. Based on Zn EXAFS analysis (Fig. S3, Table S1), Zn exists as octahedrally coordinated inner-sphere surface complexes below/above vacancy sites for all Zn-coprecipitated birnessite and  $\delta$ -MnO<sub>2</sub> samples, with the first shell Zn-O distance of 2.02–2.06 Å. For both birnessite and  $\delta$ -MnO<sub>2</sub> samples, no obvious changes were observed for this peak (Fig. 5A & B), indicating little effects of Zn-O pairs on the peak at  $\sim$ 1.9 Å. The peak at  $\sim$ 2.85 Å corresponds to (Mn-Mn)<sub>layer</sub> and (O-O)<sub>layer</sub> pairs between two edge-sharing octahedra (Manceau et al., 2013; Zhu et al., 2012). With increasing Zn content, both birnessite and  $\delta$ -MnO<sub>2</sub> samples showed decreased peak intensities and the decrease was more significant for the

$\delta$ -MnO<sub>2</sub> samples (Fig. 5A and C). Increase of layer vacancy sites (i.e. less layer Mn) and/or reduced particle size can both cause such change. As discussed previously, the PDF CSD size for both the birnessite and  $\delta$ -MnO<sub>2</sub> samples are not affected by Zn coprecipitation. Furthermore, Zn-Mn distance (due to Zn sorption) is longer (above  $\sim$ 3.4 Å) for both the birnessite and  $\delta$ -MnO<sub>2</sub> samples, therefore does not affect this peak. Therefore the change to this peak is more likely due to the increase of layer vacancy sites, consistent with Mn EXAFS fitting results. The peak at  $\sim$ 3.5 Å can be attributed to several atomic pairs: (Mn-O)<sub>layer</sub>, Mn<sub>layer</sub>-Mn<sub>inter</sub>, Mn<sub>inter</sub>-O<sub>layer</sub> (Zhu et al., 2012), as well as Zn-Mn<sub>1</sub> due to Zn sorption. For Zn-coprecipitated birnessite, the intensity of this peak increased with increasing Zn content with no obvious changes in peak width and position. For Zn-coprecipitated  $\delta$ -MnO<sub>2</sub>, no obvious changes were observed for this peak. Due to the complexity of the contributing atomic pairs, these changes were not further analyzed.

## 4. Discussion

### 4.1. Layer stacking

Based on HRTEM observations, pure  $\delta$ -MnO<sub>2</sub> had  $5 \pm 1$  layers and pure acid birnessite had  $11 \pm 1$  layers. Both numbers are higher than previously reported values obtained by XRD (3–4 layers for  $\delta$ -MnO<sub>2</sub> and  $\sim$ 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 MnO<sub>6</sub> layers (and more significant with Zn coprecipitation); therefore, we used HRTEM to estimate the numbers of stacked layers.

Both birnessite and  $\delta$ -MnO<sub>2</sub> 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., 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<sup>+</sup>, K<sup>+</sup>) 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  $\delta$ -MnO<sub>2</sub> (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  $\delta$ -MnO<sub>2</sub>.

### 4.2. Interlayer structure

Zn EXAFS spectra (Fig. S3) and fitting results (Table S1) revealed that Zn<sup>2+</sup> formed inner-sphere sorption complexes (Zn<sup>IV</sup> or Zn<sup>VI</sup>) 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 Zn<sup>2+</sup> substitution at vacancy sites, likely due to the large size difference between octahedrally coordinated Zn<sup>2+</sup> (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 Zn<sup>2+</sup> to enter vacancy sites (Kwon et al., 2013). As discussed above, the interlayer alkali cation content was much higher for acid birnessite ( $\sim$ 2.7 mmol g<sup>-1</sup> in pure birnessite) than  $\delta$ -MnO<sub>2</sub> ( $\sim$ 1.1 mmol g<sup>-1</sup> in pure  $\delta$ -MnO<sub>2</sub>), and showed more obvious decrease with increasing Zn<sup>2+</sup> contents (Table 1), suggesting more Zn<sup>2+</sup> replacement. Compared to alkali cations, the release of Mn(II)/Mn(III) by surface adsorbed Zn<sup>2+</sup> was more significant in the  $\delta$ -MnO<sub>2</sub> system. This was confirmed



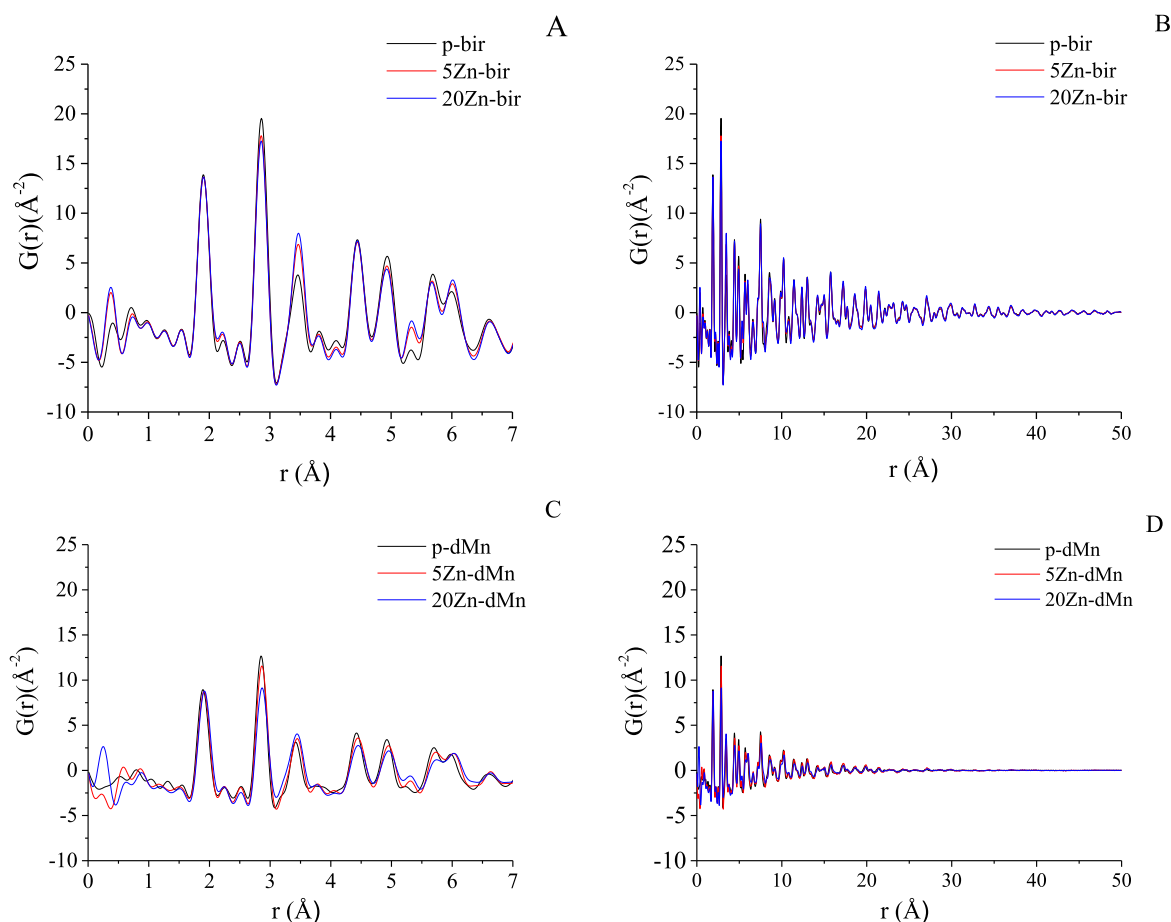


Fig. 5. PDF data of pure and Zn-coprecipitated Mn oxides plotted at 7 (left) and 50 Å scales (right). (A, B) acid birnessite, (C, D)  $\delta$ -MnO<sub>2</sub>.

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<sub>corner</sub> CN in Mn EXAFS fitting (Table 2). The slight decrease in the Mn-Mn<sub>corner</sub> path distance suggests that the ratio of Mn(II)/Mn(III) is lower in Zn-coprecipitated  $\delta$ -MnO<sub>2</sub> samples. This indicates that Mn(II) is less strongly bound to layers and the expelling effects of Mn(II) is more significant compared to Mn(III).

#### 4.3. Layer structure

Based on previous studies and the results above, Zn<sup>2+</sup> repelling of layer Mn(III) is more likely to happen in phyllosulfate phases with low AOS and high Mn(III). Grangeon et al. found that Zn<sup>2+</sup> expelled Mn(III) during its adsorption on  $\delta$ -MnO<sub>2</sub> with an AOS of 3.76 with ~13% layer Mn(III) (Grangeon et al., 2012). Similar effects were also observed in our Zn-coprecipitated  $\delta$ -MnO<sub>2</sub> systems with an AOS of 3.77 and ~15% Mn(III) contents. However, our EXAFS fitting results showed no change of the Mn-Mn<sub>edge</sub> CN and distance for the acid birnessite system, suggesting that Zn<sup>2+</sup> 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<sup>2+</sup> to be not as obvious as the  $\delta$ -MnO<sub>2</sub> system. Natural biogenic Mn oxides are typically nanocrystalline phases with lower AOS and more Mn(III) contents than synthetic phyllosulfate analogs (i.e., acid birnessite and  $\delta$ -MnO<sub>2</sub>) (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<sup>2+</sup> can cause significant modifications of biogenic MnO<sub>x</sub> layer structure. Boonfueng et al. studied Zn<sup>2+</sup> coprecipitation with biogenic MnO<sub>x</sub> and found modifications to the 8–9.2 Å<sup>-1</sup> 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<sup>2+</sup> coprecipitation. First, metal doping/coprecipitation during phyllosulfate synthesis is a common method for producing MnO<sub>x</sub> 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<sup>2+</sup> during mineral formation slightly decreased the pH in the synthesis suspensions (Fig. S7). Yu et al. also found that Zn<sup>2+</sup> addition decreased the pH of fungi growth media during the formation of biogenic MnO<sub>x</sub> (Yu et al., 2013). Grangeon et al. found that acidic condition caused the dissolution and smaller layer size when pre-formed  $\delta$ -MnO<sub>2</sub> 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 phyllosulfates (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

et al., 2011) and PDF (Hammersley et al., 1996; Yin et al., 2015b; Zhu et al., 2012) analyses have been conducted to estimate the size dimensions of Mn oxides. Size estimation of phyllosulfates using BET surface area analysis is difficult due to the complex morphology and strong aggregation, and can be simplified using a spherical model (Villalobos et al., 2014b). Smaller particle size in Zn-coprecipitated samples, as revealed by other techniques, was supposed to expose more external surfaces, yet lower surface area was observed by BET due to aggregation (Yin et al., 2011a). Therefore, cautions should be taken when using BET specific surface area to estimate the size of heavily aggregated particles.

Estimation of acid birnessite and  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> 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 MnO<sub>6</sub> 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 (Manceau 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  $\delta$ -MnO<sub>2</sub> (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  $\delta$ -MnO<sub>2</sub> 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  $\delta$ -MnO<sub>2</sub> samples) (Wang et al., 2016). Zn coprecipitation caused more incoherence in both phyllosulfates, 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 Zn<sup>2+</sup> during phyllosulfate (acid birnessite and  $\delta$ -MnO<sub>2</sub>) formation are much more significant than by Zn<sup>2+</sup> adsorption alone (Grangeon et al., 2012). Zn<sup>2+</sup> neutralized the negative surface charge of phyllosulfates and caused great particle aggregation. Zn-coprecipitation with acid birnessite expelled interlayer alkaline cations and water molecules and interrupted the layer stacking along *c* axis. The AOS of  $\delta$ -MnO<sub>2</sub> increased due to Mn(II)/Mn(III) expelling by Zn<sup>2+</sup>, 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. Zn<sup>2+</sup> existed as inner-sphere surface complexes (Zn<sup>IV</sup> or Zn<sup>VI</sup>) above/below vacancy sites as adsorbed species instead of substitution at vacancy sites. Zn<sup>2+</sup> decreased Mn(III) contents within MnO<sub>x</sub> 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  $\delta$ -MnO<sub>2</sub> 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 Zn<sup>2+</sup> and other similar incompatible cations on natural and synthetic phyllosulfates 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). Zn<sup>2+</sup> 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 MnO<sub>x</sub> 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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