X-ray absorption spectroscopy study of Mn reference compounds for Mn speciation in terrestrial surface environments

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ABSTRACT

X-ray absorption spectroscopy (XAS) offers great potential to identify and quantify Mn species in surface environments by means of linear combination fit (LCF), fingerprint, and shell-fit analyses of bulk Mn XAS spectra. However, these approaches are complicated by the lack of a comprehensive and accessible spectrum library. Additionally, molecular-level information on Mn coordination in some potentially important Mn species occurring in soils and sediments is missing. Therefore, we investigated a suite of 32 natural and synthetic Mn reference compounds, including Mn oxide, oxyhydroxide, carbonate, phosphate, and silicate minerals, as well as organic and adsorbed Mn species, by Mn K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The ability of XAS to infer the average oxidation state (AOS) of Mn was assessed by comparing XANES-derived AOS with the AOS obtained from redox titrations. All reference compounds were studied for their local (<5 Å) Mn coordination environment using EXAFS shell-fit analysis. Statistical analyses were employed to clarify how well and to what extent individual Mn species (groups) can be distinguished by XAS based on spectral uniqueness. Our results show that LCF analysis of normalized XANES spectra can reliably quantify the Mn AOS within ~0.1 v.u. in the range +2 to +4. These spectra are diagnostic for most Mn species investigated, but unsuitable to identify and quantify members of the manganate and Mn(III)-oxyhydroxide groups. First-derivative XANES fingerprinting allows the unique identification of pyrolusite, ramsdellite, and potentially lithiophorite within the manganate group. However, XANES spectra of individual Mn compounds can vary significantly depending on chemical composition and/or crystallinity, which limits the accuracy of XANES-based speciation analyses. In contrast, EXAFS spectra provide a much better discriminatory power to identify and quantify Mn species. Principal component and cluster analyses of \( k^2 \)-weighted EXAFS spectra of Mn reference compounds implied that EXAFS LCF analysis of environmental samples can identi-
fy and quantify at least the following primary Mn species groups: (1) Phyllo- and tectomanganates with large tunnel sizes (2×2 and larger; hollandite, romanèchite, todorokite), (2) tectomanganates with small tunnel sizes (2×2 and smaller; cryptomelane, pyrolusite, ramsdellite), (3) Mn(III)-dominated species (nesosilicates, oxyhydroxides, organic compounds, spinels), (4) Mn(II) species (carbonate, phosphate, and phyllosilicate minerals, adsorbed and organic species), and (5) manganosite. All Mn compounds, except for members of the manganate group (excluding pyrolusite) and adsorbed Mn(II) species, exhibit unique EXAFS spectra that would allow their identification and quantification in mixtures. Therefore, our results highlight the potential of Mn K-edge EXAFS spectroscopy to assess bulk Mn speciation in soils and sediments. A complete XAS-based speciation analysis of bulk Mn in environmental samples should preferably include the determination of Mn valences following the ‘Combo’ method of Manceau et al. (2012) (American Mineralogist 97, 816-827), EXAFS LCF analyses based on principal component and target transformation results, as well as EXAFS shell-fit analyses for the validation of LCF results. For this purpose, all 32 XAS reference spectra are provided in the Supplementary material for further use by the scientific community.

INTRODUCTION

Manganese (Mn) is a redox-sensitive element with a crustal abundance of about 0.1 wt.% (Yaroshevsky, 2006). It participates in numerous globally important environmental processes such as photosynthetic oxygen production and oxidative lignin degradation, and serves as an activator of more than 35 enzymes (Broadley et al., 2012; Burnell, 1988; Jensen et al., 1996; Keiluweit et al., 2015). The three naturally occurring Mn oxidation states +2, +3, and +4 account for the large variety of mono- and mixed-valent Mn species in environmental samples, including oxides and oxyhydroxides (collectively termed (oxyhydr)oxides), carbonates, phos-
phates, silicates, organic compounds or Mn species being adsorbed to (in)organic surfaces. Manganese concentrations in sediments and bedrocks may be as low as 20 mg/kg in quartz sands and >1,000 mg/kg in basic rocks like basalt and gabbro (Blume et al., 2016; Gilkes and McKenzie, 1988). Natural background levels of soil Mn range between 40 and 1,000 mg/kg (Blume et al., 2016), but neither total nor exchangeable Mn in soil is correlated with bedrock composition, indicative of a high Mn mobility in the Earth’s crust (Mortvedt, 2000).

The mobility of Mn in soils and sediments depends largely on biological processes controlling its redox state (Tebo et al., 2005). Since Mn$^{2+}$ is more soluble than Mn$^{4+}$, Mn bioavailability tends to increase with decreasing pH and redox potential (Blume et al., 2016). A particularly important role in the cycling of Mn in surface environments is attributed to Mn(III/IV) (oxyhydr)oxides, since their precipitation and dissolution primarily control the amount of soluble and thus bioavailable Mn$^{2+}$ (Martin, 2005; Tebo et al., 2004). These minerals exist either as layer or tunnel structures. Layer-type Mn(III/IV) (oxyhydr)oxides (‘phyllomanganates’) consist of stacked sheets of edge-sharing MnO$_6$ octahedra, whereas in Mn(III/IV) (oxyhydr)oxides with tunnel structure (‘tectomanganates’) MnO$_6$ octahedra form single, double or triple chains by sharing edges, which are linked together via MnO$_6$ corners to produce tunnels of varying size (McKenzie, 1989). Positive charge deficits created by Mn$^{4+}$-site vacancies or the substitution of structural Mn$^{3+/4+}$ by cations of lower valence are compensated by exchangeable cations (e.g., H$^+$, Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, etc.) occupying the tunnel or interlayer spaces (McKenzie, 1989).

Manganate minerals are thought to be primarily formed via fast enzymatic Mn$^{2+}$ oxidation by bacteria and fungi (Tebo et al., 2004). Resulting Mn(III/IV) (oxyhydr)oxides are poorly crystalline phyllomanganates structurally akin to H$^+$-birnessite (‘acid birnessite’) or δ-MnO$_2$, and may serve as precursors for more crystalline Mn oxides (e.g., todorokite) and
Mn(III) oxyhydroxides (e.g., feitknechtite, manganite) through ageing and/or redox reactions involving dissolved Mn(II) (Elzinga, 2011; Feng et al., 2010; Miyata et al., 2007). The role of Mn(III/IV) (oxyhydr)oxides as strong oxidants for inorganic and organic soil and sediment constituents is well documented (Bartlett, 1981; Ehlert et al., 2016; Feng et al., 2007; Remucal and Ginder-Vogel, 2014; Villinski et al., 2001). Owing to their low point of zero charge and high specific surface area, biogenic Mn(III/IV) (oxyhydr)oxides show a high affinity towards heavy metals like Co, Cu, Ni, and Zn, which frequently exceeds that of Fe(III) (oxyhydr)oxides (O'Reilly and Hochella Jr, 2003; Tebo et al., 2004). As a consequence, soil Mn contained in ferromanganese nodules and concretions is often associated with these trace metals (Latrille et al., 2001; Liu et al., 2002; Manceau et al., 2003).

Despite the ecological importance and omnipresence of Mn in terrestrial surface environments, studies targeting the identification and quantification of chemical forms (species) of Mn are surprisingly rare. Available Mn speciation studies can be grouped into three categories. Category 1 studies used sequential extraction methods (Habibah et al., 2014; Kalembkiewicz et al., 2008; Narwall and Singh, 2001; Qiang et al., 1994), which provide valuable information on operationally defined Mn fractions. However, poor selectivity of extractants, Mn redistribution during extractions, and the use of a large variety of non-standardized extraction procedures severely limit the explanatory power of this speciation approach (Hass and Fine, 2010; Hlavay et al., 2004; Sutherland and Tack, 2003). Category 2 studies employed X-ray or electron diffraction to identify and/or characterize Mn minerals in geomaterials. The use of these techniques is hampered by the fact that Mn minerals in soils and sediments are frequently nanocrystalline and amorphous to X-rays (Chukhrov and Gorshkov, 1981; Cornu et al., 2005; Latrille et al., 2001; Rhoton et al., 1993; Ross et al., 1976; Zhang and Karathanasis, 1997). Therefore, these studies almost exclusively focused on ferromanganese nodules and concretions in soils (Liu et al., 2002; Manceau et al., 2003;
Szymański et al., 2014; Taylor et al., 1964; Tokashiki et al., 1986; Uzochukwu and Dixon, 1986) or sediments (Lee and Xu, 2016; Taira et al., 1981). Category 3 studies utilized synchrotron-based Mn K-edge X-ray absorption spectroscopy (XAS) to speciate soil (Frommer et al., 2011; Hernandez-Soriano et al., 2012; Herndon et al., 2014; Keiluweit et al., 2015; Manceau et al., 2005) and sediment Mn (Carroll et al., 2002; Friedl et al., 1997; O'Day et al., 2000). Regardless of the type of Mn species present, high-brilliance synchrotron facilities provide the capability for non-destructive analysis of oxidation state and average local (<5 Å) coordination of Mn in environmental samples with Mn concentrations of several hundred milligrams per kilogram. Previous XAS studies mostly employed either Mn K-edge X-ray absorption near edge structure (XANES) or micro-focused extended X-ray absorption fine structure (EXAFS) spectroscopy. The XANES technique is useful to infer the average oxidation state (AOS) of Mn in soils and sediments based on the shift of the absorption edge towards higher energies with increasing Mn AOS (Manceau et al., 2012; McKeown and Post, 2001). Quantitative information on the fractional amounts of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ and the resulting Mn AOS in a sample can be obtained by the ‘Combo’ linear combination fit (LCF) analysis method of Manceau et al. (2012) using a XANES spectra database of well-characterized monovalent Mn references. The accuracy of this method was estimated to be 0.04 valence units (v.u.) in the Mn AOS range +3 to +4, which decreased when the proportion of divalent Mn was greater than 15% (Manceau et al., 2012). Although this state-of-the-art LCF approach has already been used to analyze the AOS of soil Mn (Herndon et al., 2014; Keiluweit et al., 2015), its generic applicability has not been validated by other methods available for Mn AOS quantification.

In addition to the determination of Mn oxidation states, Mn K-edge XANES spectra may in principle be useful for the identification and quantification of distinct Mn species in unknown samples using LCF analysis (Frommer et al., 2011; Leven et al., 2018; Morales-
Pérez et al., 2021). However, limited numbers of fit references, spectral similarity of different species, and non-unique LCF solutions can severely limit this approach (Gustafsson et al., 2020; Scheinost et al., 2002).

In contrast to XANES analyses, EXAFS spectroscopy has hitherto only rarely been used for the identification and quantification of Mn species in soils and sediments (Manceau et al., 2005; Mayanna et al., 2015). EXAFS evaluations of environmental samples typically include shell-fit and LCF analyses (Ahmad et al., 2019; Scheckel and Ryan, 2004), the latter often combined with principal component analysis (PCA) and target transformation (TT) testing (Langner et al., 2012; Manceau et al., 2002; Mikutta and Rothwell, 2016; Scheinost et al., 2002). Decisive for the success of Mn EXAFS LCF analysis is the existence of a comprehensive spectrum library including relevant Mn species potentially occurring in terrestrial environments. Several EXAFS studies provide fundamental information on the local Mn coordination in a range of Mn compounds (Ahmad et al., 2019; Battacharya and Elzinga, 2018; Manceau and Combes, 1988; Manceau et al., 2005; McKeown and Post, 2001; Silvester et al., 1997; Webb et al., 2005). However, the number of publicly available Mn EXAFS spectra is neither sufficient for validation of EXAFS parameters previously determined for specific Mn species, nor for Mn speciation analysis of soils and sediments. Additionally, systematic studies on spectral uniqueness of Mn compounds are largely missing. Complicating matters further, EXAFS data are lacking for various potentially important Mn species such as Mn-containing silicate and phosphate minerals, organic Mn(II/III) compounds, and adsorbed Mn(II) species.

The main objective of this study was to evaluate how well and to what extent different Mn species potentially occurring in terrestrial surface environments such as soils and sediments can be distinguished by Mn K-edge XANES and EXAFS spectroscopy. To this end, we collected XAS spectra of 32 well-characterized mineral and organic Mn compounds and ana-
analyzed these spectra for features and structural information that allow the discrimination of
distinct Mn species (groups). This information is indispensable for the correct analysis and
interpretation of Mn XAS spectra of environmental samples. In addition, we used redox titra-
tions to verify the accuracy of the ‘Combo’ XANES LCF method of Manceau et al. (2012) for
determining the AOS of Mn in geomaterials.

MATERIALS AND METHODS

Manganese reference compounds

The 32 Mn reference samples analyzed in this study, 15 natural and 17 synthetic, belong to
seven main groups: (1) Phyllomanganates, (2) tectomanganates, (3) oxide minerals without
tunnel or layer structure, (4) Mn(III) oxyhydroxides, (5) carbonate, phosphate, and silicate
minerals, (6) organic Mn(II/III) compounds, and (7) Mn(II) adsorbed to (in)organic materials.
Table 1 lists all reference compounds along with information on, for example, ideal and em-
pirical formulas, structure type where appropriate, Mn content, and XAS spectrum source.

Table 1

Natural mineral samples were carefully handpicked using a binocular microscope. The clean-
est looking crystals or parts with least alteration were chosen for further analysis. Synthetic
bixbyite, manganosite, and pyrolusite were purchased as mineral powders. Cryptomelane was
synthesized according to McKenzie (1971), δ-MnO₂, hexagonal acid and triclinic Na-
birnessites following Villalobos et al. (2003), manganite was synthesized using a slightly
modified protocol from Chiu and Hering (2000), and Ba-free romanèchite following Shen et
al. (2005).

Manganese(II) adsorption samples were prepared by batch experiments using a natural
85:15-90:10 illite-smectite mineral with R3 ordering from Füzérradvány, Hungary (<2-µm
fraction; Dohrmann et al., 2009) and peat from a raised peat bog (Federseemoor) near Bad
Characterization of Mn reference compounds

X-ray diffraction. All available solids were analyzed by powder X-ray diffraction in Bragg-Brentano geometry using a Bruker AXS D4 Endeavor diffractometer equipped with a secondary graphite monochromator (CuKα1,2 radiation) and a scintillation counter. X-ray diffraction patterns were collected at room temperature within a 2theta range of 5-110° using a measuring time of 4-10 s per 0.02° step (tube settings: 40 kV/40 mA). The identity of all minerals was confirmed (Figs. S1 and S2). Minor impurities in ramsdellite result from its transition to pyrolusite. Natural pyrolusite and groutite showed minor manganite impurities. An unknown reflection was found in the diffractograms of triclinic Na-birnessite and synthetic cryptomelane. Remaining additional diffraction peaks in different Mn compounds could be assigned to non-Mn phases such as calcite in groutite, annite in hendricksite, and quartz in braunite and in the peat sample. Literature references or powder diffraction file (pdf) numbers used for XRD evaluation are compiled in Table S1.

Chemical composition. Twelve natural minerals were prepared as polished and carbon-coated thin sections. Their chemical composition was determined by electron probe microanalysis (EPMA) using a CAMECA SX100 instrument equipped with five wavelength-dispersive spectrometers. A focused beam was used with an acceleration voltage of 15 kV and a beam current of 15 nA for major elements (Al, Cr, K, Mg, Mn, P, Si, Ti) and 100 nA for minor or trace elements (Ba, Ca, Cl, F, Fe, Na, Sr, Zn). Counting time on element peaks was 10 s for Al, Ba, Cr, K, Mn, Na, Si, 20 s for Ca, Cl, Fe, Mg, P, Sr, Ti, 30 s for Zn, and 50 s for F. Background counting times were half on-peak counting times. The following standards were used for calibrations (element, analyzer crystal): Fe2O3 (Fe, large lithium fluoride...
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(LLIF)), jadeite (Na, thallium acid phthalate (TAP)), kyanite (Al, TAP), Mn$_3$O$_4$ (Mn, LLIF), orthoclase (K, pentaerythritol (PET)), wollastonite (Si, Ca, TAP and PET, respectively), olivine (Mg, TAP), TiO$_2$ (Ti, large pentaerythritol (LPET)), Cr$_2$O$_3$ (Cr, LPET), apatite (P, PET), NaCl (Cl, LPET), ZnS (Zn, LLIF), SrF$_2$ (F, Sr, TAP and LPET, respectively), BaSO$_4$ (Ba, LPET). Results of these analyses are summarized in Table S2. Detection limits for each element measured are listed in Table S3.

The chemical composition of six synthetic mineral compounds (acid Na-birnessite, cryptomelane, δ-MnO$_2$, manganite, Na-birnessite (tricl), romanèchite) was determined by inductively coupled plasma–optical emission spectrometry (ICP-OES, Agilent 5900 SVDV) after acid digestion of the samples at 120-140 °C (Table S2). Acid reagents included 69% HNO$_3$ (Suprapur®, Roth), 37% HCl (p.a., Roth), and, if necessary, 40% HF (p.a., Merck) and 30% H$_2$O$_2$ (Suprapur®, Merck). Peat samples were previously combusted at 550 °C overnight in a ceramic crucible. The digestions are described in the Supplement material, and detection limits for each element measured can be found in Table S3. The elemental composition of remaining reference compounds is given as provided by the supplier (synthetic bixbyite, manganosite, pyrolusite, organic Mn(II/III) Mn compounds) or as stated in the respective publications (synthetic feitknechtite and todorokite) (Table 1). For references with adsorbed Mn(II), the Mn content was determined as described in the Supplementary material.

Based on chemical composition, empirical mineral formulas (Table 1) were calculated after normalization to oxygen. Fractional amounts of Mn valences per formula unit were determined by charge-balance calculations (Deer, 1992). Mineral formulas of synthetic Na-birnessites and δ-MnO$_2$ are those stated in their respective synthesis protocols. Details on empirical formula calculations are presented in the Supplementary material.

**Redox titrations.** Redox titrations for the determination of bulk Mn AOS were performed after Grangeon et al. (2012) using an automated titration system (TitroLine 7800, SI Analyt-
Briefly, (NH₄)₂Fe(SO₄)₂·6H₂O (‘Mohr’s salt’) was used to reduce Mn³⁺/⁴⁺ in Mn reference compounds to dissolved Mn²⁺. The excess reductant (Fe²⁺) was back-titrated with KMnO₄ solution and total Mn determined by the re-oxidation of Mn²⁺ to Mn³⁺, stabilized by pyrophosphate (P₂O₇⁴⁻). All measurements were carried out in duplicates or triplicates.

**Manganese K-edge XAS.** Bulk Mn K-edge XAS spectra of 26 Mn reference compounds were collected at beamline 7-3 of the Stanford Synchrotron Radiation Lightsource (SSRL, Menlo Park, USA), beamline 5-BM-D of the Advanced Photon Source (APS, Argonne, USA), and beamlines P64 and P65 of PETRA III at the Deutsches Elektronen-Synchrotron (DESY, Hamburg, Germany). The beamlines were equipped with Si(220) (7-3) and Si(111) double-crystal monochromators (5-BM-D, P64, P65), which were calibrated by setting the first-derivative maximum of the K-edge absorption spectrum of elemental Mn to 6,539 eV. Higher harmonics in the beam were reduced by detuning monochromators by 15-50% and by harmonic rejection mirrors (P65). In addition, 3-µm Cr filters were used to reduce undesired fluorescence radiation at beamlines 7-3 and P65. Measurements were performed in both fluorescence and transmission mode utilizing solid-state fluorescence detectors (7- or 30-element Ge detectors, Vortex SDDs) and ionic chambers, respectively. To avoid beam damage, all samples were measured at 5-20 K employing He-cryostats or at 77 K (5-BM-D) using a Lin-cam cell. Details of the sample preparation can be found in the Supplementary material.

Spectra were recorded with a maximum energy increment of 5 eV before the edge and 0.2-0.3 eV along the edge. The EXAFS was recorded with a k-space resolution of 0.05 Å⁻¹. Five to 20 scans were collected per sample. Spectra of a Mn metal foil were used to correct for slight energy shifts during sample measurements.

Spectral pre-processing, including merging of individual scans, rebinning, and energy calibration, was conducted in SIXPack (Webb, 2005) or Athena (Ravel and Newville, 2005). The spectra were further processed in Athena following standard routines. The pre-edge re-
gion was fit with a linear function and the post-edge region with a quadratic polynomial. The edge-step energy, $E_0$, was defined as the first maximum of the first XANES derivative. For background removal the Autobk algorithm was applied. The frequency cut-off parameter, $R_{\text{bkg}}$, was set to 0.9-1.1, and the $k$-weight for background removal to two or three. A Hanning window function with a sill width of 2 Å$^{-1}$ was used to Fourier transform the data.

In addition to the measured spectra, six XAS spectra were obtained from external sources (Table 1). Details on their origin and measurement can be found in the respective publications.

**Manganese XAS data analysis.** For the determination of Mn AOS and the fractional amount of each Mn oxidation state present in the reference compounds, we applied the ‘Combo’ LCF method of Manceau et al. (2012). For this, normalized XANES spectra were fit using 17 Mn K-edge XANES spectra of monovalent Mn references available as open source in Manceau et al. (2012) (deposit item AM-12-037), which were processed as described above. The fits were performed in Athena over an energy range of -20 to 30 eV ($E-E_0$) by applying a non-negativity constraint. A single $E_0$ shift was used for all standards. During the fits, negatively loaded references were progressively eliminated until only references with positive (or zero) loadings remained. Each previously deleted reference was then again randomly added and the fit run again to assure that the global minimum was found using the normalized sum of squared residuals ($R$-factor) as best-fit criterion (Manceau et al., 2012). Eventually, no negative loadings remained and the total fraction of each Mn oxidation state in the sample analyzed was calculated as the sum of the individual component fractions (Manceau et al., 2012).

Least-squares fits of $k^3$-weighted EXAFS spectra of Mn reference compounds were performed in Artemis (Ravel and Newville, 2005) on a shell-by-shell basis in $R$-space ($R+\Delta R \approx 1-4$ Å). $R$-space resolution as given by the Rayleigh criterion ($0.5 \pi/(k_{\text{max}}-k_{\text{min}})$) was 0.14-0.20 Å, such that atomic shells separated by lower values could not be resolved. Theoretical
phase-shift and amplitude functions were calculated with FEFF6 (Ankudinov et al., 1998) based on crystal-structure information. Partial occupancies due to chemical substitution as revealed by chemical analyses were accounted for by adding additional atoms into the respective feff.inp file. For structures containing two or more inequivalent Mn sites (e.g., bixbyite, hausmannite) aggregated FEFF calculations were used, that is, path lists of individual sites were automatically merged together and weighted by the fractional population of the site in the unit cell (Ravel, 2014). The passive amplitude reduction factor, $S_0^2$, was fixed to 0.8 during optimization. If individually fitted Debye-Waller parameters, $\sigma^2$, converged towards similar values, they were equated in the final fit to reduce the number of fit variables.

**Statistics.** The Pearson correlation coefficient was used as a similarity metric for normalized and first-derivative XANES ($E = 6,530-6,600$ eV) as well as $k^2$-weighted EXAFS spectra ($k = 2.0-11.5$ Å$^{-1}$, $E_0 = 6,563$ eV). Principal component analysis (PCA) was performed on the $k^2$-weighted Mn EXAFS spectra. Suitability of this data for PCA was confirmed by the Kaiser-Meyer-Olkin (KMO) test in SPSS Statistics (IBM Corp.). In addition, an unsupervised hierarchical cluster analysis of the EXAFS spectra was conducted using Ward's clustering algorithm (Ward, 1963) with squared Euclidean distances as distance measure. Correlation, PC, and cluster analyses were conducted in Statistica (TIBCO Software Inc.). For linear regression between XANES- and titration-based Mn AOS, normal distribution of data points, constant variance of the dependent variable, and independence of residuals were assured by Shapiro-Wilk and Spearman rank correlation tests as well as Durbin-Watson statistic, respectively, using SigmaPlot v.14 (Systat Software Inc.).

**RESULTS AND DISCUSSION**

**XANES spectra of Mn reference compounds**
Figure 1 illustrates absorbance shifts to higher energies with increasing Mn AOS of Mn reference compounds. Here, a zero-energy value was defined by setting the first maximum of the first XANES derivative in the pre-edge region (~6,539 eV) to 0 eV. The ordinate represents the relative energy at which the normalized absorbance XANES signal first reaches 50% of the edge absorption maximum. Manganese compounds belonging to different Mn AOS groups are clearly separated, confirming that XANES data allow a general classification of Mn species with respect to Mn oxidation state.

Figures 2 and 3 show normalized XANES and corresponding first-derivative spectra of Mn reference compounds, and Table 2 summarizes primary absorption peaks identified up to 6,570 eV. Phyllo- and tectomanganates with varying amounts of Mn$^{3+}$ and Mn$^{4+}$ generally show XANES spectra with broad pre-peaks at 6,541.5-6,543.4 eV, smoothly rising absorption edges, and maximal absorbances between 6,560.3 and 6,562.5 eV (Fig. 2, Table 2). The similarity of their XANES features suggests that a unique identification of single members in mixtures would not generally be possible. However, lithiophorite exhibits a unique edge feature, leading to two distinct peaks in the first-derivative XANES spectrum at 6,551.5 and 6,557.5 eV. This feature may aid the identification of lithiophorite in mixtures with other phyllosilicates. Among tectomanganates, cryptomelane (2×2 tunnels), hollandite sensu stricto (s.s.) (2×2 tunnels), romanèchite (2×3 tunnels), and todorokite (3×3 tunnels) possess similar XANES spectra. In contrast, the first-derivative XANES of pyrolusite (1×1 tunnels) and ramsdellite (1×2 tunnels) feature characteristic double peaks at ~6,552 and ~6,558 eV (Fig. 2, Table 2), potentially allowing the identification of tectomanganates with the smallest tunnel sizes in environmental samples. Differences in XANES spectra observed for natural and syn-
thetic tectomanganates (cryptomelanes, pyrolusites, todorokites) reflect the sensitivity of XANES spectroscopy to variations in mineral composition and/or crystallinity (Fig. 2).

Manganese oxides without layer or tunnel structure such as bixbyite (ferric Mn(III) oxide), hausmannite (Mn(II/III) spinel), and manganosite (Mn(II) oxide) show a greater variability in their XANES spectra, reflecting different Mn oxidation states and Mn coordination environments (Fig. 3). While natural and synthetic bixbyites show featureless absorption edges similar to phyllo- and tectomanganates (but distinct differences in their first-derivative spectra), hausmannite exhibits a prominent shoulder in the absorption edge at ~6,553 eV and a well-defined absorption maximum at 6,559.1 eV (Fig. 3, Table 2). Similarly, the XANES of manganosite possesses a modulated absorption edge, a well-defined absorption maximum at 6,555.0 eV, and a distinct post-edge oscillation at 6,568.6 eV (Fig. 3, Table 2). These results suggest that hausmannite and manganosite can be readily identified in soils and sediments based on XANES analysis.

The Mn$^{3+}$O(OH) polymorphs feitknechtite, groutite, and manganite exhibit similar XANES features, consisting of smoothly rising absorption edges with two inflection points at ~6,549 and ~6,556 eV, and absorption maxima located at ~6,560 eV (Fig. 3, Table 2). Variations among these minerals are subtle, and suggest that groutite and manganite are virtually indistinguishable by XANES spectroscopy.

Carbonate, phosphate, and silicate minerals have unique XANES spectra which also differ from those of Mn (oxyhydr)oxide minerals. Unsurprisingly, this group displays the greatest diversity of XANES characteristics. Triplite, a Mn$^{2+}$-containing phosphate, shows a steep rise in the absorption edge with a non-unique absorption maximum of 6,552.7 eV. In contrast, rhodochrosite has a pronounced absorption-edge maximum at 6,551.1 eV and a distinct post-edge absorption maximum at 6,562.4 eV, leading to diagnostic first-derivative XANES maxima at 6,548.9 and 6,559.9 eV (Fig. 3, Table 2). The two Mn$^{2+}$-bearing triocta-
hedral micas hendricksite and masutomilite show similar spectral features with double absorbance peaks at ~6,552 and ~6,557 eV, which are distinct from all other Mn compounds. The identification of 2:1 phyllosilicates with structural Mn$^{2+}$ may thus be possible in unknown sample materials. Braunite, a Mn(II/III) nesosilicate, shows a marked step in the absorption edge and two pronounced peaks in the first-derivative XANES at 6,548.1 and 6,552.9 eV (Fig. 3, Table 2), comparable to feitknechtite.

The XANES of organic Mn compounds differ from each other: While Mn(II) acetate tetrahydrate has a smoothly rising absorption edge and a broad absorbance maximum similar to triplite, Mn(II) oxalate dihydrate shows a marked shoulder in the rising part of the edge, a sharp absorption maximum at 6,553.3 eV, and a characteristic double peak in the first-derivative XANES at 6,547.0 and 6,551.5 eV (Fig. 3, Table 2). In contrast, Mn(III) acetate dihydrate exhibits a broad, undulating absorption maximum, which is distinct from all other Mn references (Fig. 3).

Samples with adsorbed Mn(II) (illite, peat) are characterized by smoothly rising absorption edges, well-defined absorption maxima at ~6,553 eV, and a comparatively featureless post-edge absorption (Fig. 3, Table 2). In comparison to the peat samples, Mn(II) adsorbed to illite has a less prominent white-line and two discernable main peaks in the first-derivative XANES (Fig. 3). The XANES spectra of the peat samples are different from all other references, and resemble those of Mn(II) citrate, Mn(II) malate, and Mn(II) succinate (Fernando et al., 2010). This result suggests that Mn(II) complexed by natural organic matter should be uniquely identifiable in environmental samples. Noteworthy, peat samples prepared at pH 5 and 7 possess identical XANES spectra, implying that pH had no effect on the coordination environment of organically bound Mn(II) (Fig. 3).

Our results illustrate that Mn compounds differ in absorption-edge energies as related to Mn AOS, and that several Mn compounds and mineral classes show characteristic inflec-
tion points in their XANES spectra. Manganese K-edge XANES features are more pronounced in the respective first-derivative spectra. Since small post-edge normalization errors do not affect the shape of the derivatives (Manceau et al., 2012), they might be better suited for fingerprinting and LCF analysis than the respective absorbance spectrum. However, XANES LCF analyses of natural samples may become biased because XANES spectra of individual Mn compounds can differ substantially due to variations in chemical composition and/or crystallinity, as evidenced for bixbyites, cryptomelanes, pyrolusites, and todorokites (Figs. 2 and 3).

Average oxidation state of Mn reference compounds

To obtain information on the Mn AOS and relative fractions of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ in the reference compounds, we used the XANES LCF ‘Combo’ method (Manceau et al., 2012). The results are tabulated in Table 3. Note, different from other LCF procedures, the ‘Combo’ method does not claim the samples to be mixtures of the standards (Manceau et al., 2012; Manceau and Nagy, 2012). Therefore, no uncertainties are assigned to individual fractions or the derived AOS. Manceau et al. (2012) estimated the accuracy of AOS determination by the ‘Combo’ method to be ~0.04 v.u. in phyllo- and tectomanganates (AOS range 3.0-4.0) with a negligible amount of Mn$^{3+}$ in layer structures and less than about 15% Mn$^{2+}$. Based on our fit results for the synthetic monovalent Mn references manganosite (AOS 2.0), bixbyte (AOS 3.0), and pyrolusite (AOS 4.0), the absolute accuracy of Mn AOS determination using the ‘Combo’ method was not better than 0.12 v.u. Regression of nominal vs. LCF-derived AOS for these references resulted in a standard error of the AOS estimate of 0.07 v.u. ($R^2 = 0.995$, $p <0.001$). This result is consistent with Manceau et al. (2012) showing that increasing proportions of Mn$^{2+}$ lead to a decreased accuracy of the LCF ‘Combo’ method.
Manganese reference compounds with a nominal Mn AOS of two \((N = 10)\) yielded XANES-derived AOS of 2.0-2.49 \((\bar{x} = 2.13)\). In this group, higher AOS determined for hendericksite (2.21), masutomilite (2.49), and Mn(II) adsorbed to illite (2.35) suggest the presence of up to 50\% Mn\(^{3+}\). For the mica minerals, this result can be explained by partial oxidation of Mn\(^{2+}\) in their octahedral layers. For the illite sample, the result may indicate the formation of a Mn(III/IV) phase upon partial re-oxidation of adsorbed Mn(II), but this could not be confirmed by EXAFS shell-fit results (see below). LCF results of reference compounds with a nominal AOS of three \((N = 6)\) and four \((N = 4)\), were largely in agreement with their nominal AOS \((\bar{x} = 3.07\) and 3.96, respectively; Table 3).  

Table 3  

In order to validate XANES-based Mn AOS, we performed redox titrations for selected reference compounds with Mn concentrations >1.5 wt.% \((N = 25)\). These experiments showed that the AOS of hausmannite was significantly overestimated by the ‘Combo’ method, most likely because its pronounced Jahn-Teller distortion of Mn\(^{3+}\)O\(_6\) octahedra (Jarosch, 1987) was not adequately reflected by the standard spectra used (Manceau et al., 2012). An unreasonable titration-based Mn AOS was also observed for triplite (Table 3), which can be attributed to incomplete reductive dissolution of the sample during the experiment. With the exception of these two references, the Mn AOS derived from redox titrations were in excellent agreement with the XANES-based AOS \((R^2 = 0.988)\) (Fig. 4). The regression slope was 0.997±0.024 \((p <0.0001)\) and the standard error of estimate 0.08. This result implies that the ‘Combo’ LCF method, when applied to environmental samples, provides accurate Mn AOS data within approximately 0.1 v.u. for the entire Mn valence range +2 to +4.  

Figure 4  

**EXAFS spectra of Mn references compounds**
Figure 5 shows $k^3$-weighted Mn K-edge EXAFS spectra and Fourier-transform (FT) magnitudes and real parts of one representative of each Mn species group along with the corresponding model fit. The figure exemplifies the diversity of local Mn bonding environments, which can be expected in natural samples. Corresponding data of the remaining references are shown in Figures S3 and S4. EXAFS shell-fit parameters of all compounds are summarized in Table 4. In the following, we detail EXAFS results for each species group, and clarify (dis)similarities of EXAFS parameters among species (groups).

Phyllo- and tectomanganates. Figure 6 illustrates $k^3$-weighted Mn K-edge EXAFS spectra of phyllo- and tectomanganates. Phylloganates with hexagonal layer symmetry (acid Na-birnessite, δ-MnO$_2$, lithiophorite) show very similar EXAFS spectra featuring comparatively symmetrical oscillations centered at approximately 4.2, 6.7, 9.2, and 10.4 Å$^{-1}$. In contrast, the spectrum of triclinic birnessite exhibits a split of the small oscillation between 7.9 and 8.2 Å$^{-1}$. This antinode splitting is attributed to the ordering of structural Mn$^{3+}$ in triclinic birnessite (Ling et al., 2018; Webb et al., 2005) and allows the distinction of phylloganates with hexagonal and triclinic layer symmetry. The peak near 8.0 Å$^{-1}$ was previously used as a diagnostic fingerprint to differentiate between phyllo- and tectomanganates (McKeown and Post, 2001). In this study, however, also 2×3 and 3×3 tectomanganates exhibit a similar spectral feature in this region (Fig. 6).

Tectomanganates can be generally discerned from phylloganates by a gradually emerging left-side shoulder of the 6.7-Å$^{-1}$ oscillation. This shoulder becomes more intense with increasing content of corner-sharing octahedra (i.e., smaller tunnel size) and eventually results in a split oscillation at 6.4 and 6.7 Å$^{-1}$. The relative intensities of this double-feature are reversed for pyrolusite (1×1 tunnel) as compared to other tectomanganates (Manceau and
Combes, 1988) (Fig. 6). Tectomanganates with $2 \times 2$ (hollandite s.s., cryptomelane), $1 \times 2$
(ramsdellite), and $1 \times 1$ (pyrolusite) tunnel structure also possess a pronounced and diagnostic
oscillation at $\sim 7.4$ Å$^{-1}$, which increases and shifts to lower wavenumbers with decreasing tun-
nel size (Fig. 6). Pyrolusites show two distinct troughs at 7.8 and 8.1 Å$^{-1}$, which are also visi-
ble in attenuated form for ramsdellite, and thus can serve as another diagnostic fingerprint for
tectomanganates with small tunnel sizes. In combination with the pronounced peak near 7.4
Å$^{-1}$ and the unique oscillation at 9.5 Å$^{-1}$, these results suggest that pyrolusite should be unam-
biguously identifiable in mixtures of phyllo- and tectomanganates.

All manganates are additionally characterized by an oscillation at 10.2-10.5 Å$^{-1}$ (Fig.
6). Because this oscillation is not accompanied by a pronounced right-side shoulder in case of
phyllomanganates with hexagonal layer structure (Fig. 6), it can aid the identification of tec-
tomanganates, especially those with $1 \times 1$, $1 \times 2$, and $2 \times 2$ tunnel structures, in mixtures with
hexagonal phyllomanganates.

First O neighbors of Mn in phyllomanganates could be modelled with a single shell at
1.90-1.92 Å (Figs. 5 and S3a). Mn-Mn distances of edge-sharing octahedra (Mn-Mn1) were
fit at 2.87-2.92 Å, which accord with values published for hexagonal and pseudo-orthogonal
phyllomanganate structures (Webb et al., 2005). For hexagonal birnessite and $\delta$-MnO$_2$, we
obtained Mn-Mn2 distances of 3.44-3.49 Å (Table 4). These distances are typically assigned
to triple corner-sharing Mn$^{3+}$ octahedra at interlayer sites above or below cation vacancies
(Ling et al., 2018; Silvester et al., 1997; Villalobos et al., 2003). Similar to triclinic birnessite,
no Mn-Mn2 contribution was observed for lithiophorite, in agreement with the presence of
exclusively edge-sharing octahedra (Lanson et al., 2000; McKeown and Post, 2001; Silvester
et al., 1997; Villalobos et al., 2003). Two additional O shells were fit at 3.56(3) and 4.14(12)
Å, which accord with the lithiophorite structure published by Wadsley (1952) (Table 4).
Tectomanganates (Figs. 5 and S3b) show similar variations in their Mn-O, Mn-Mn1, and Mn-Mn2 distances as compared to phylloganganates (Table 4). Within this group, first-shell O neighbors are located at 1.88-1.92 Å, and second- and third-shell Mn neighbors at 2.87-2.90 and 3.43-3.48 Å, respectively. Shell-fit models also included additional O shells at 3.7-3.8 Å (todorokites) and 3.9-4.0 Å (pyrolusites) as well as higher Mn shells at 3.7-3.8 Å (hollandite s.s.) and 4.4 Å (pyrolusites) (Bolzan et al., 1993; Miura, 1986; Post et al., 2003) (Table 4). It generally follows that Mn coordination environments in phyllo- and tectomanganates are largely similar, such that interatomic distances up to the third coordination shell preclude any meaningful discrimination of these minerals in environmental samples using EXAFS shell-fit analysis.

Oxide minerals without layer or tunnel structure. Bixbyite possesses two inequivalent Mn sites with an occupancy of 25 and 75% in its unit cell (Geshnizgani, 2014). As a result, two O subshells at ~1.91 and ~2.24 Å were needed to account for the generally low first-shell amplitudes of natural and synthetic bixbyite (Fig. S3c). The cubic structure of bixbyite is further characterized by edge- and corner-sharing Mn\(^{3+}\) octahedra, for which we obtained Mn-Mn distances of 3.09-3.11 and 3.54-3.57 Å, respectively (Table 4). These distances are consistent with those published by Longo et al. (2010).

The unit cell of hausmannite also contains two inequivalent Mn sites (Jarosch, 1987). Here, tetrahedral sites are occupied by Mn\(^{2+}\) and octahedral sites by Mn\(^{3+}\) cations. For octahedrally coordinated Mn\(^{3+}\), Mn-O distances were fit with 4.1(3) equatorial O atoms at 1.95(1) Å and 1.9(3) axial O atoms at 2.27(1) Å, which account for the octahedral Jahn-Teller distortion approximately parallel to [001] (Jarosch, 1987). A third O shell (~2.01 Å) for tetrahedrally coordinated Mn\(^{2+}\) (Longo et al., 2010) was too close to the Mn-O\(_{eq}\) distance to be included in
the model and did not improve the fit ($F$-test; Hamilton, 1965). First-shell oxygens are followed by two Mn subshells at 2.88(1) and 3.10(0) Å, corresponding to edge-sharing Mn$^{3+}$ octahedra (Longo et al., 2010). The third FT peak of hausmannite (Figs. 5 and S3c) was reproduced with Mn shells at 3.44(1) and 3.73(1) Å (Table 4). These values are consistent with tetrahedra-octahedra corner linkages (Longo et al., 2010) and Mn-Mn distances of Mn$^{2+}$ tetrahedra, respectively (Jarosch, 1987).

In contrast to the former two minerals, the first FT peak of cubic manganosite could be modeled with a single O shell at 2.22(0) Å (Fig. S3c). Analogous to Ressler et al. (1999), higher coordination shells were fit with Mn neighbors at 3.13(0) Å, indicative of edge-sharing Mn$^{2+}$ octahedra, and third-shell O atoms at 3.84(0) Å (Fig. S3c, Table 4).

**Manganese(III) oxyhydroxides.** Minerals of this group are characterized by reduced first-shell amplitudes typically caused by the broad distribution of Mn-O bond lengths and associated scattering cancellation effects (Silvester et al., 1997; Webb et al., 2005) (Figs. 5 and S4a). Consequently, first-shell oxygens in Mn(III) oxyhydroxides were fit with two or three O subshells. For feitknechtite, we obtained Mn-O distances of 1.91(0) and 2.22(1) Å, for groutite 1.93(1), 2.15(4), and 2.34(2) Å, and for manganite 1.93(0) and 2.28(1) Å (Table 4). Second-shell Mn in feitknechtite was fit at 2.83(1) and 2.99(0) Å, respectively, and third-shell Mn at 3.33(1) Å (Table 4). The latter distance is considerably shorter than the 3.43 Å reported by Mackle et al. (1993), but more consistent with the presumed sole presence of edge-sharing Mn$^{3+}$ octahedra in feitknechtite. The coordination numbers ($CN$s) of the two Mn1 subshells in feitknechtite were previously either set to four and two, respectively (Ressler et al., 1999), or to unity (Mackle et al., 1993). We obtained $CN$s of 1.9(3) and 3.8(11) (Table 4), which are in good agreement with the values used by Ressler et al. (1999).

In contrast to the other two polymorphs, first Mn neighbors in groutite could be fit with a single shell at 2.88(1) Å (Table 4). Higher Mn coordination shells corresponding to
edge- and corner-sharing $\text{Mn}^{3+}$ octahedra occur at 3.38(3) and 3.61(1) Å, respectively (Table 4). These distances are within the error range of values published by Scheinost et al. (2001). For manganite, we obtained Mn-Mn1 distances of 2.77(1) and 2.98(2) Å, a Mn-Mn2 distance of 3.69(1), and a Mn-Mn3 distance of 3.83(2) Å (Table 4). The former can be assigned to Mn atoms in chains of edge-sharing $\text{Mn}^{3+}$ octahedra and the latter two to corner-sharing octahedra (Mackle et al., 1993). Even though our Mn-Mn1/2 distances are up to ~0.07 Å longer than those reported for manganite by Mackle et al. (1993), they fit well with crystallographic data (Dachs, 1963). Contrary to Mackle et al. (1993), who postulated a similar local Mn coordination environment in manganite and feitknechtite, our data imply a substantially different Mn coordination within these minerals.

**Carbonate, phosphate, and silicate minerals.** In minerals of this group, atoms other than O and Mn/Fe contribute to their EXAFS: Al/Si in masutomilite, C in rhodochrosite, P in triplite, and Zn in hendricksite. To the best of our knowledge, most of these minerals have not previously been studied by Mn EXAFS spectroscopy. Their spectra and model fits are depicted in Figs. 5 and S4b. Generally, first-shell O/F neighbors within this mineral group are found at distances of 1.94-2.55 Å, and were accounted for by one (hendricksite, masutomilite, rhodochrosite), two (triplite) or three subshells (braunite) (Table 4). Braunite shows a very broad first FT peak with low amplitude (Fig. S4b), which was fit with 2.6(2), 2.1(3), and 0.9(3) O neighbors at 1.94(1), 2.25(1), and 2.55(3) Å, respectively. Higher shells included 1.9(5) Mn atoms at 3.17(1) Å, typical of edge-sharing Mn octahedra, and 5.3(18) O atoms at 3.77(2) Å (Table 4). All parameters agree well with crystallographic data (Ohmann et al., 1998).

The first coordination shell of hendricksite was fit with 4.9(9) O atoms at 2.16(1) Å, implying fairly distorted $\text{Mn}^{2+}$ octahedra in this mica mineral. Second-shell signals arise from Mn/Fe and Zn neighbors at 3.14(1) Å, sharing the same atomic position in the unit cell (Robert, 1985). The CNs of second-shell Mn/Fe and Zn atoms were set to 2.0 and 2.5, respectively,
Similar to hendraidsite, the first coordination shell in masutomilite was reproduced by 4.9(9) O/F atoms at a distance of 2.15(1) Å. The CNs of second-shell Al and Mn, both located at 3.02(5) Å, were set to 2.5 and 0.4, respectively, based on chemical analysis (1.23 apfu Al and 0.18 apfu Mn in octahedral coordination). Octahedral-layer Li was not included in the model due to its low scattering amplitude. Higher shells of masutomilite include four Al/Si atoms at 3.24(3) Å and four O atoms at 3.47(3) Å (Table 4).

For rhodochrosite, the only important Mn carbonate occurring in soils and sediments (Barreto et al., 2016; Ying et al., 2011), first O neighbors belonging to the CO$_3^{2-}$ group were fit at 2.19(1) Å. These were followed by a C shell at 3.08(2) Å, Mn shells at 3.79(1) and 4.75(1) Å, and O shells at 3.28(1), 4.10(3), and 4.58(1) Å (Table 4). All distances are in agreement with Friedl et al. (1997), except for the longest Mn-O distance, which is ~0.03 Å shorter than previously reported.

The FT of triplite is dominated by first-shell F/O atoms, followed by two smaller peaks hosting Fe/Mn and P neighbors (Fig. S4b). First-shell F and O atoms were fit at 2.05(3) and 2.15(1) Å, respectively, atoms of edge-sharing Fe/Mn octahedra at 2.93(2) Å, and P atoms at 3.55(1) Å (Table 4). Chemical analysis suggested 1.6 F and 4.4 O neighbors (0.79 apfu F and 2.21 apfu O) in the first coordination shell, which is close to theoretical F and O CNs of two and four, respectively (Waldrop, 1969).

**Organic Mn(II/III) compounds.** The local Mn coordination in Mn(II) acetate tetrahydrate, Mn(II) oxalate dihydrate, and Mn(III) acetate dihydrate has, to our knowledge, not previously been studied by EXAFS spectroscopy. Their spectra are displayed in Figures 5 and S4c. The first coordination shell of both Mn(II) compounds was fit with approximately six O atoms at
2.18(1) Å. In contrast, two O subshells housing 5.2(5) and 1.5(5) O atoms at 1.93(0) and 2.20(1) Å, respectively, were needed to model the first FT peak of Mn(III) acetate dihydrate (Table 4). For Mn(II) acetate tetrahydrate, distances of C and Mn shells were fit at 3.19(4) and 3.40(2) Å, respectively (Table 4). Remarkably, the best fit was obtained with C and Mn CNs fixed to nominal values of monoclinic Mn(II) acetate dihydrate (P2_1/c) (Cheng and Wang, 1991). The determined Mn-Mn distance is 0.2 Å shorter than expected for single corner-sharing Mn octahedra present in monoclinic Mn(II) acetate tetrahydrate (P2_1/c) (Bertaut et al., 1974; Tranqui et al., 1977), but is consistent with long edge-sharing octahedral linkages as in Mn(II) acetate dihydrate (Cheng and Wang, 1991).

In Mn(II) oxalate dihydrate, four proximal C atoms are located at 2.95(2) Å, followed by distant O atoms at 3.93(2) Å. In addition, three multiple-scattering (MS) paths were included in the model (Table 4), which significantly improved the fit (F-test). Our fit results comply with XRD data for monoclinic Mn(II) oxalate dihydrate (C2/c), and demonstrate the absence of octahedral linkages in Mn(II) oxalate dihydrate (Puzan et al., 2018).

In Mn(III) acetate dihydrate, the first coordination shell is followed by four proximal C atoms at 2.98(2) Å, a substantially shorter distance compared to Mn(II) acetate tetrahydrate (Table 4). Best fits of higher coordination shells were obtained with two Mn atoms at 3.40(0) Å and two O atoms at 4.37(5) Å (Table 4). Both, distances and CNs comply with XRD data for monoclinic Mn(III) triacetate dihydrate (P2_1/m), in which Mn octahedra are linked to chains via single corners (Le Bail, 2016; personal communication to the crystallography open database (COD), COD ID 3500063).

**Adsorbed Mn(II) species.** To the best of our knowledge, molecular-scale information on Mn(II) adsorbed to clay minerals (illite) and particulate natural organic matter (peat) is currently not available. Spectra of Mn(II) adsorbed to illite and peat are illustrated in Figures 5 and S4d. The EXAFS of Mn(II) adsorbed to illite is dominated by first-shell signals, housing
two O atoms at 1.92(1) Å and four O atoms at 2.16(1) Å (Table 4). Implementation of Al or Si backscatterers into the model proved unsuccessful, suggesting that hydrated Mn$^{2+}$ ions are primarily adsorbed as outersphere complexes on siloxane surfaces. We found no evidence of a Mn(III/IV) phase, which could explain the XANES- and titration-derived AOS values >2 obtained for the illite sample (Table 3). This may suggest a similar adsorption mechanism for Mn$^{3+}$ ions or a systematic error in both AOS determination methods, which we consider less likely.

Nearly identical shell-fit results were obtained for Mn(II) adsorbed to peat at pH 5 and 7, showing that pH had a negligible effect on the coordination of organically bound Mn(II). Both EXAFS were well reproduced with one proximal C atom at 3.20(7) Å (pH 5) and 3.21(8) Å (pH 7), implying monodentate Mn$^{2+}$ complexation by carboxyl groups. Owing to their low scattering amplitudes, distal C atoms were not included in the model; instead, an obtuse triangle Mn-C-O MS path was used to reproduce the low FT peaks at ~4.5 Å (Fig. 5, Table 4). Interestingly, Mn$^{2+}$ complexation by particulate organic matter did not lead to Mn$^{2+}$ oxidation under oxic conditions (Table 3).

**Comparison of interatomic distances.** When XAS is applied to soils or sediments, overabsorption can frequently affect the EXAFS amplitude, leading to a bias of fitted CNs. Additionally, CNs can be influenced by poor crystallinity (i.e., high static disorder) and/or small particle size relative to crystalline reference compounds (O’Day et al., 2004). As these issues do not affect the EXAFS frequency, atomic distances are more robust parameters when comparing average Mn coordination environments of natural samples.

Figure 7 compiles all absorber-single scatter distances determined in this study. The figure also includes data from various literature sources for comparison (Table S4). Note that the designation of individual coordination shells is somewhat arbitrary, and for simplicity, atoms in subshells were considered part of a ‘shell’. As evidenced by Friedl et al. (1997), Mn-
O bond distances depend on the oxidation state of Mn. In agreement with this, the shortest Mn-O distances were observed for tectomanganates, and the longest Mn-O distances for (in)organic Mn(II) species (Fig. 7). In general, average first-shell distances of all reference compounds can be classified according to their XANES-derived Mn AOS: 2.14±0.04 Å ($\bar{x} \pm \sigma$) for AOS 2.0-2.5 members ($N = 10$), 2.02±0.06 Å for AOS 3.0-3.5 members ($N = 9$), and 1.90±0.01 Å for AOS 3.7-4.0 members ($N = 13$). Differences in average Mn-O/F bond lengths of AOS groups are significant at the $p <0.05$ level (Kruskal-Wallis rank-based ANOVA, Dunn’s method), except for the AOS 3.0-3.5 and 3.7-4.0 groups. Figure 7 also illustrates that split shells of first O neighbors are absent in the phyllo- and tectomanganate groups. In contrast, Mn-O1 subshells or longer Mn-O distances are typical features of all other Mn species groups. Likewise, Mn-Mn1 distances of edge-sharing Mn octahedra in phyllo- and tectomanganates (2.87-2.92 Å) are substantially shorter than corresponding (average) Mn-Mn distances in (1) oxides without layer or tunnel structure (3.03-3.13 Å; bixbyite, hausmannite, manganosite), (2) members of the phosphate and silicate group (2.93-3.17 Å; braunite, hendricksite, masutomilite, triplite), and (3) organic Mn(II) compounds (3.40 Å; Mn(II) acetate tetrahydrate). Although Mn-Mn1 distances of phyllo- and tectomanganates are similar to (average) Mn-Mn1 distances in Mn(III) oxyhydroxides, the need to fit two Mn-Mn1 subshells to an EXAFS spectrum of an environmental sample, may indicate the presence of feitknechtite and manganite (or hausmannite) (Fig. 7).

Organic Mn(II/III) compounds may possess edge- or corner-sharing MnO₆ linkages, whose Mn-Mn distances can overlap with those of manganate and oxyhydroxide minerals, notably groutite (Fig. 7). In contrast, organically complexed Mn(II) species lack Mn or other heavy atoms in higher coordination shells. Their Mn-C distances are either significantly shorter or longer than the Mn-C distance of rhodochrosite (3.08(2) Å), thus facilitating the
distinction between rhodochrosite and organic Mn(II) species in environmental samples (Fig. 7).

Figure 7

Statistical XAS spectrum comparisons

Key to species detection and quantification by means of Mn XAS LCF is spectral dissimilarity. Therefore, Pearson correlations were used to compare the (dis)similarity of XAS spectra of all reference compounds. Normalized XANES spectra (6,530-6,600 eV) were highly positively correlated due to similar overall shape (Fig. S5), complicating a meaningful species identification and quantification based on LCF analysis of this data without auxiliary information. Significantly lower spectral correlations for first-derivative XANES spectra (Fig. S6) indicate much better discriminative power of these data. Here, low and moderate correlations ($r \leq 0.7$) exist between adsorbed Mn(II) species and most other species-group members. The same holds for carbonate, silicate, and phosphate minerals as well organic Mn(II) compounds (Fig. S6). This suggests that members of these groups can likely be identified based on their first-derivative XANES, provided data quality is sufficient. However, high correlations ($r > 0.8$) were still observed between manganates, oxide minerals without layer or tunnel structure, and Mn(III) oxyhydroxides, making it difficult to identify and quantify individual members of these species groups in mixtures using first-derivative XANES spectra (Fig. S6). A much better discriminative power can be achieved on the basis of Mn EXAFS spectra. Figure 8 shows the Pearson correlation matrix of $k^2$-weighted EXAFS spectra ($k = 2.0-11.5$ Å$^{-1}$, $E_0 = 6,563$ eV) of all reference compounds. A $k^2$-weighting was chosen because environmental studies usually deal with low-Mn concentration samples that would not allow a higher $k$-weighting in
LCF analyses without risking excessive spectral noise amplification. However, caution must be exercised in interpreting these correlation coefficients because strong correlations were observed for species whose EXAFS spectra differ substantially, for example, pyrolusite and Ba-free romanèchite ($r = 0.82$) (cf. Fig. 6). It follows that correlation coefficients of less than approximately 0.8 can be taken as indication of spectral dissimilarity. Using this criterion, Figure 8 shows that EXAFS spectra of most reference compounds are unique, only exceptions being spectra of several members of manganates, organic Mn(II/III) compounds, adsorbed Mn(II) species, and triplite. This result confirms the supreme potential of EXAFS LCF analysis to identify and quantify individual Mn species in environmental samples.

Next, we performed a PCA to reduce the dimensionality of the $k^2$-weighted Mn K-edge EXAFS dataset and clarify spectral group membership. Output parameters for the first ten principal components (PCs) are summarized in Table S5. The number of statistical meaningful PCs based on eigenvalues >1 (Kaiser-Guttman criterion; Guttman, 1954) was five (Table S5). These PCs explained 88.6% of the total variance of all Mn EXAFS spectra, suggesting five superordinate variables defining spectral group membership. A loading plot of PC1 vs. PC2, explaining 56.08% and 13.33% of spectral variance, respectively, is illustrated in Figure 9. Here, PC1 mainly reflects the oxidation state of Mn reference compounds, as members of manganates load highly negatively, Mn(II) species positively, and species with predominantly Mn(III) intermediately and negatively on PC1. Combined, PCA implies that at least five Mn species (groups) can be distinguished in the entire EXAFS data set, and Figure 9 suggests that the Mn oxidation state plays a major role.

To validate the PCA results, an unsupervised tree-clustering analysis was performed using Ward’s method (Ward, 1963). Figure 10 shows the output of the cluster analysis. The length of the horizontal lines (linkage distances) is proportional to spectral dissimilarity. Like PCA, hierarchical cluster analysis generally separated Mn(III/IV) phases from Mn(III)- and
Mn(II)-containing compounds at a linkage distance of 25-40 (Fig. 10). A division into five meaningful clusters, as suggested by PCA, is given at a linkage distance of about 18. Here, cluster one consists of all phyllomanganates and tectomanganates with large tunnel sizes (2×2 and larger) including hollandite s.s. (2×2 tectomanganate). Cluster two comprises tectomanganates with small tunnel sizes (2×2 and smaller). Minerals dominated by Mn(III) are grouped into cluster three. Cluster four unites all Mn(II) species, and cluster five is exclusively formed by manganosite. A closer inspection of inner-cluster variability revealed that bixby-ite, hausmannite, hendricksite, masutomilite, pyrolusite, and rhodochrosite are clearly distinct within their respective clusters. While EXAFS spectra with a linkage distance >6 show discriminable spectral features, they become virtually indistinguishable at a linkage distance <5 based on direct comparisons. This implies that six of the 32 Mn reference compounds (hausmannite, hendricksite, manganosite, masutomilite, Mn(III) acetate dihydrate, rhodochrosite) are clearly recognizable and quantifiable as individual species when present in mixtures. All other Mn compounds can at least be reliably assigned to a particular species group.

Figures 8-10

IMPLICATIONS

Research on Mn oxidation states in soils and sediments is prerequisite to better understand redox cycling of Mn and its participation in environmental processes. Since accurate Mn AOS determination in soils and sediments by wet-chemical methods is impossible due to the excess of other electron donors/acceptors, especially Fe and organic matter, XANES spectroscopy is currently the only available tool for process-oriented research relying on this key parameter. By comparing XANES LCF- and redox titration-based AOS results for mono- and multivalent Mn compounds, we found that the XANES LCF ‘Combo’ method of Manceau et al.
Zahoransky et al. (2012) provides accurate Mn AOS data within approximately 0.1 v.u. over the entire natural Mn valence range.

Linear combination fitting of XAS spectra is a widely used method for the identification and quantification of element species in environmental samples (Hutchison et al., 2001; Langner et al., 2012; Leven et al., 2018; Mikutta and Rothwell, 2016; Scheckel and Ryan, 2004). This approach requires comprehensive databases with suitable reference spectra (Gustafsson et al., 2020; Scheinost et al., 2002). While these exist for several key elements such as Fe (O’Day et al., 2004; Wilke et al., 2001), they are not available for Mn. Therefore, we provide (energy-calibrated) XAS spectra of 32 Mn compounds, potentially occurring in soils and sediments, in the Supplementary material. This spectrum library can be used by the scientific community for Mn species identification and quantification in terrestrial surface environments.

Prerequisite to the application of XAS LCF for species recognition and quantification is spectral uniqueness (Gustafsson et al., 2020; Scheinost et al., 2002). Our results show that, compared to EXAFS spectra, normalized and first-derivative Mn K-edge XANES spectra provide far less discriminative power to distinguish and thus identify individual Mn species in environmental samples. Owing to high spectral correlations, the use of normalized Mn XANES spectra for species identification and quantification in LCF analysis of environmental samples is not recommended without proper justification based on auxiliary species information. First-derivative XANES spectra of most analyzed Mn compounds are unique, suggesting that identification and quantification of most Mn species would be possible. However, members of the manganate and Mn(III)-oxyhydroxide groups are probably indistinguishable in mixtures using (first-derivative) XANES spectra. Prominent exceptions are pyrolusite, ramsdellite, and perhaps lithiophorite, which possess unique first-derivative XANES fingerprints. Nonetheless, the employment of XANES LCF for Mn species identification and quan-
tification in natural samples is limited. First, because XANES features are not solely depend-
ent on the Mn oxidation state or structural and electronic factors, but also on energy calibra-
tion and monochromator resolution (Manceau et al., 2012; Manceau et al., 2002). Second,
because XANES spectra are influenced by subtle changes in chemical composition and/or
crystallinity of Mn compounds. Comparisons of XANES and EXAFS spectra of natural and
synthetic Mn compounds (bixbyites, cryptomelanes, pyrolusites, todorokites) document the
robustness of EXAFS spectroscopy to variations in chemistry and/or crystallinity, demonstrat-
ing its superior value for bulk Mn species identification and quantification in natural samples.
Based on PCA and cluster analyses, EXAFS LCF analysis of environmental samples is at
least capable of discriminating the following species groups: (1) phyllomanganates and tect-
omanganates with large tunnel sizes (2×2 and larger; hollandite s.s., romanèchite, 
todorokite), (2) tectomanganates with small tunnel sizes (2×2 and smaller; cryptomelane, py-
rolusite, ramsdellite), (3) Mn(III)-dominated species (nesosilicates, organic compounds, oxy-
hydroxides, spinels), (4) Mn(II) species (carbonate, phosphate, and phyllosilicate minerals,
adsorbed and organic species), and (5) manganosite. Within these conservatively established
species groups, most Mn compounds exhibit unique EXAFS features, which would assist
their identification and quantification in mixtures using EXAFS LCF analysis. Sole excep-
tions are manganate minerals (except for pyrolusite) and adsorbed Mn(II) species whose EX-
AFS are dominated by first-shell O signals. These results highlight the potential of Mn K-
edge EXAFS spectroscopy to quantitatively assess bulk Mn speciation in soils and sediments,
which so far has not been exploited. For speciation analysis of natural samples using Mn K-
edge EXAFS spectroscopy, we recommend stepwise application of PCA-TT and LCF analy-
ysis and subsequent validation of LCF results by spectral fingerprinting as well as EXAFS
shell-fitting in order to justify the presence of individual Mn species.
In summary, the results of this study provide a comprehensive framework for the analysis and interpretation of Mn XAS spectra of natural samples and for the evaluation of the role of Mn in environmental processes. Our spectrum library thus lays the foundation for further process-oriented environmental Mn research.

ACKNOWLEDGEMENTS

We are especially grateful to Evert Elzinga, Flora Brocza, Caroline Peacock, and David McKeown for providing additional XAS spectra and Reiner Dohrmann for the illite reference. Special thanks go to Julian Feige for the preparation of thin sections and Philip Weigel for EPMA assistance. Tobias Fußwinkel is thanked for sharing his knowledge on mineral formula calculation. Furthermore, we are indebted to Jens Gröger-Trampe and Bodo Mieke (LBEG) for their support during redox titrations. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515s. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357. We also thank PETRA III at DESY for providing us with beamtime. Assistance at synchrotron facilities by Ritimukta Sarangi (SSRL), Qing Ma (APS), and Edmund Welter, Wolfgang Caliebe, Akhil Tayal, and Vadim Murzin (all DESY) is gratefully acknowledged. This work was financially supported by the DFG (project no. 326242261).
REFERENCES


Zahoransky et al.  

Running head: Mn K-edge XAS of Mn reference compounds


**Figure Captions**

**Figure 1.** Classification plot of Mn reference compounds. Different XANES-derived Mn AOS based on absorption-edge position are shown relative to the first maximum in the first XANES derivative at ~6,540 eV (after Marcus et al., 2008). Note that masutomilite and hendricksite as well as hausmannite and braunite are separated from other members of the low- and medium-AOS range. Synthetic pyrolusite shows the highest Mn AOS of 4.0 of all reference compounds.

**Figure 2.** Stacked normalized Mn K-edge XANES (left) and corresponding first-derivative spectra (right) of phyllo- and tectomanganates. The spectrum numbers match the numbers in Table 1: 1 - acid Na-birnessite (hex, syn), 2 - δ-MnO$_2$ (syn), 3 - lithiophorite, 4 - Na-birnessite (tricl, syn), 5 - cryptomelane, 6 - cryptomelane (syn), 7 - hollandite s.s., 8 - pyrolusite, 9 - pyrolusite (syn), 10 - ramsdellite, 11 - romanèchite, 12 - romanèchite (Ba-free, syn), 13 - todorokite, 14 - todorokite (syn).

**Figure 3.** Stacked normalized Mn K-edge XANES (left) and corresponding first-derivative spectra (right) of Mn oxide minerals without layer or tunnel structure as well as Mn(III) hydroxides, carbonate, phosphate, and silicate minerals, organic Mn(II/III) compounds, and adsorbed Mn(II) species. The spectrum numbers match the numbers in Table 1: 15 - bixbyite, 16 - bixbyite (syn), 17 - hausmannite, 18 - manganosite, 19 - feitknechtite (syn), 20 - groutite, 21 - manganite (syn), 22 - braunite, 23 - hendricksite, 24 - masutomilite, 25 - rhodochrosite, 26 - triplite, 27 - Mn(II) acetate tetrahydrate (syn), 28 - Mn(II) oxalate dihydrate (syn), 29 - Mn(III) acetate dihydrate (syn), 30 - Mn(II) ads. illite pH7, 31 - Mn(II) ads. peat pH5, 32 - Mn(II) ads. peat pH7.

**Figure 4.** Linear regression (solid line) between average oxidation state (AOS) of Mn obtained from redox titrations against Mn AOS determined by XANES LCF. Confidence and prediction bands (95%) are indicated by dark and light blue color, respectively. Data for hausmannite and triplite (out of range) were excluded from analysis.

**Figure 5.** Stacked $k^3$-weighted Mn K-edge EXAFS spectra (left) as well as corresponding Fourier-transform magnitudes and real parts (right) of selected Mn reference compounds: 1 - δ-MnO$_2$ (syn), 2 - hollandite s.s., 3 - hausmannite, 4 - feitknechtite, 5 - rhodochrosite, 6 - Mn(II) oxalate dihydrate, 7 - Mn(II) ads. peat pH5. Solid lines represent experimental data and dotted lines model fits. EXAFS parameters are summarized in Table 4. The fits of other Mn compounds are displayed in Figures S3 and S4.

**Figure 6.** Stacked $k^3$-weighted Mn K-edge EXAFS spectra of phyllo- and tectomanganates. 1 - acid Na-birnessite (hex, syn), 2 - δ-MnO$_2$ (syn), 3 - Na-birnessite (tricl, syn), 4 - lithiophorite, 5 - todorokite, 6 - todorokite (syn), 7 - romanèchite (nat), 8 - romanèchite (Ba-free, syn), 9 - hollandite s.s., 10 - cryptomelane (nat), 11 - cryptomelane (syn), 12 - ramsdellite, 13 - pyrolusite (nat), 14 - pyrolusite (syn). Vertical lines and black arrows indicate important spectral features (see text for details).
Figure 7. Interatomic distances between Mn and near-neighbor atoms in Mn reference compounds obtained from this study (colored symbols) and the literature (gray symbols). Literature references are listed in Table S4. In masutomilite, first-shell O could also be F and third-shell Al could be Si. In triplite and hendricksite, second-shell Mn may also be Fe. Horizontal lines separate the seven different Mn species groups (see text for further details).

Figure 8. Pearson correlation matrix for $k^2$-weighted Mn K-edge EXAFS spectra ($k = 2.0$-$11.5$ Å$^{-1}$, $E_0 = 6,563$ eV) of Mn reference compounds. Only significant correlations ($p < 0.05$) are reported.

Figure 9. Loading plot of the first two PCs obtained from PCA of $k^2$-weighted Mn K-edge EXAFS spectra ($k = 2.0$-$11.5$ Å$^{-1}$, $E_0 = 6,563$ eV) of Mn reference compounds. Species are colored according to their XANES-derived Mn AOS.

Figure 10. Unsupervised tree clustering of $k^2$-weighted Mn K-edge EXAFS spectra ($k = 2.0$-$11.5$ Å$^{-1}$, $E_0 = 6,563$ eV) of Mn reference compounds using Ward’s method. Five clusters are indicated at a linkage distance of 18.
<table>
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<th>No.</th>
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<th>Mineral formula (nominal / empirical)</th>
<th>Remarks</th>
<th>Mn (wt.%)b</th>
<th>Spectrum source</th>
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<td>Lithiophorite</td>
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<td>39</td>
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<td>3+3 tunnel</td>
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*Nominal mineral formulas after Anthony et al. (2003). Empirical formulas of birnessites and ß-MnO$_2$ are taken from Villalobos et al. (2003, 2006), those of hollandite, lithiophorite, and romanéchite from McKeown and Post (2001), and the formula of todorokite (syn) from Feng (1995). All other empirical mineral formulas are based on chemical analysis of this study.*

*Calculated from mineral formula (empirical if two formulas are stated). No chemical analysis performed in this study.*

*Determined by chemical analysis of this study unless stated otherwise. n.d. = not determined.*

### Table 2. Primary XANES absorption and first-derivative peaks of Mn reference compounds

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<th>Absorption 2</th>
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<td>6540.5</td>
<td>6553.5</td>
<td>6558.0</td>
<td>6560.0</td>
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<td>Acid Na-birnessite (hex, syn)</td>
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<td>2</td>
<td>δ-MnO₂ (syn)</td>
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<td>6539.8</td>
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<td>Na-birnessite (tricl, syn)</td>
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Table 3. Nominal, titration-, and XANES-derived bulk Mn AOS of Mn reference compounds, as well as fractional amounts of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ (normalized to unity) determined from XANES analysis

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<th>AOS$^{a}$ (titration)</th>
<th>AOS (XANES)</th>
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<th>Mn$^{3+}$</th>
<th>Mn$^{4+}$</th>
<th>Fit sum</th>
<th>R-factor$^{c}$ (&lt; 10$^{5}$)</th>
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-a Based on nominal mineral formulas (cf. Table 1).
-b Errors are given as standard deviation of triplicate measurements for the last significant figure. n.d. = not determined. Figures without error assignment are based on single measurements due to limited sample availability.
-c $R$-factor = Σ(data−fit)$^2$/Σdata$^2$. 

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Table 4. EXAFS parameter determined by shell-fitting of $k^3$-weighted Mn K-edge EXAFS spectra of Mn reference compounds

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<th>$N_{\text{eq}}$ R-range</th>
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<th>CN$^\text{e}$</th>
<th>R(Å)$^c$</th>
<th>CN$^\text{e}$</th>
<th>R(Å)$^c$</th>
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*a* Data from Ref. [12].

*b* Data from Ref. [13].

*c* Data from Ref. [14].

*d* Data from Ref. [15].

*e* Data from Ref. [16].

*f* Data from Ref. [17].

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Always consult and cite the published, final version. See http://www.minsocam.org or GeoscienceWorld
Table 4. (continued)

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<td>5</td>
<td>3.4(10)</td>
<td>0.0051</td>
<td>2.18(1)</td>
<td>C: 1.0</td>
<td>0.0051</td>
<td>3.21(8)</td>
<td>C-O: 8.0</td>
</tr>
</tbody>
</table>

$^a$The amplitude reduction factor, $S_0^2$, was set to 0.8 for all fits. Parameter uncertainties are given in parenthesis for the last significant figure.

$^b$R-factor = $\sum$(data−fit)$^2$/Σdata and reduced $\chi^2 = (N_{idp}/N_{pts})\sum_i((data−fit)/\varepsilon_i)^2/(N_{idp}−N_{var})$, where $N_{idp}$ is the number of independent data points in the model fit, $N_{pts}$ the total number of data points, $N_{var}$ the number of fit variables (with all $CN$s set in the final fit), and $\varepsilon_i$ is the uncertainty of the $i$th data point.

$^c$Number of independent points and fit variables in final fit, respectively.

$^d$Energy-shift parameter.

$^e$Debye-Waller parameter. If no uncertainties are indicated, parameters were constrained.

$^f$Mean half path length.

$^g$A volumetric lattice expansion parameter was used to calculate atomic distances in bixbyites and manganosite (cubic crystal system).

$^h$Multiple-scattering (MS) path. For Mn(II) oxalate dihydrate, the Debye-Waller parameter of the Mn-O-C obtuse triangle MS path was defined as $\sigma^2$(Mn-O1)+0.5$\sigma^2$(Mn-C); MS2 (Mn-C-O-C) and MS3 (Mn-C-O) are forward triangle MS paths. Their Debye-Waller parameters were defined as $\sigma^2$(Mn-C)+$\sigma^2$(Mn-O1) and $\sigma^2$(Mn-C)+0.5$\sigma^2$(Mn-O1), respectively. For Mn(II) adsorbed to peat, the Debye-Waller parameter of the obtuse triangle MS path was defined as 1.5$\sigma^2$(Mn-O).
Figure 1

This figure illustrates the relationship between the relative position of the normalized absorption maximum (eV) and the relative position of 1/2 jump point (eV). The data points are color-coded to indicate different AOS ranges:
- AOS 2.0 - 2.5
- AOS 3.0 - 3.5
- AOS 3.7 - 4.0

The diagram includes the following mineral species:
- Rhodochrosite
- Triplite
- hollandite, Lithiophorite
- Braunite
- Hausmannite
- Masutomilite
- Hendricksite

Pyrolusite (syn) is also indicated on the diagram.
Figure 2

Normalized absorbance

1st derivative absorbance

Energy (eV)

Phyllophanates

Tectomanganates

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Figure 3

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Figure 5

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Figure 7

Shell: first
second
third and higher

Acid Na-birnessite (hex, syn)
α-MnO₂ (syn)
Lithiophorite
Na-birnessite (tric, syn)
Cryptomelane (Nat)
Cryptomelane (syn)
Hollandite
Pyrolusite
Pyrolusite (syn)
Ramsdellite
Romanéchite
Romanéchite (Ba-free, syn)
Todorokite
Todorokite (syn)
Bixbyte (Nat)
Bixbyte (syn)
Hausmannite
Manganosite (syn)
Feitknechtite
Groultite
Manganite (syn)
Braunite
Hendricksite
Masutomiite
Rhodochrosite
Triplite
Mn(II) acetate tetrahydrate
Mn(II) oxalate dihydrate
Mn(III) acetate dihydrate
Mn(II) ads. little pH7
Mn(II) ads. peat pH5
Mn(II) ads. peat pH7

Oxygen
Fluorine
Manganese
Aluminum
Zinc
Phosphorus
Carbon

R (Å)
Figure 8

Acid Na Bismellite (hex, syn) Lithiophorite
Na Bismellite (tric, syn) Cryptomelane
Cremnolite (syn) Hollandite
Pyrolusite (syn) Pyrocerite (syn)
Rammelkampite
Romanèche (Ba-free, syn) Romanèchite
Todorokite Todorokite (syn)
Biowbyte
Bixbyte (syn)
Hausmannite
Manganosite (syn) Fedkinite (syn)
Crustace (syn)
Braunite
Hendricksonite
Masutomiite
Rhodochrosite
Tritlite
Mn(ll) oxide dihydrate
Mn(ll) oxide hydrate
Mn(ll) oxide hydrate
Mn(ll) oxide dihydrate
Mn(ll) oxide dihydrate
Mn(ll) oxide dihydrate
Mn(ll) oxide dihydrate
Mn(ll) oxide dihydrate
Mn(ll) oxide dihydrate
Mn(ll) oxide dihydrate

1 >0.9 >0.8 >0.7 >0.6 ±0.6

*PM = Phyllomanganates

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Figure 9

The figure shows a principal component analysis (PCA) plot for various manganese oxide minerals. The plot is divided into quadrants based on the first two principal components (PC1 and PC2). The PC1 (56.08%) and PC2 (13.33%) axes are labeled, and the data points represent different manganese oxide species:

- **Bixbyites**
- **Braunite**
- **Feitknechtite**
- **Manganite**
- **Mn(III) acetate dihydrate**
- **Hausmannite**
- **Groutite**
- **Mn(III) acetate tetrahydrate**
- **Mn(II) oxalate dihydrate**
- **Mn(II) ads. illite pH7**
- **Mn(II) ads. peat pH5 and pH7**
- **Masutomilite, Rhodochrosite Triplite**

The plot also includes color-coded areas for different AOS (Aerobic Oxidation State) ranges:
- **AOS 2.0 - 2.5**
- **AOS 3.0 - 3.5**
- **AOS 3.7 - 4.0**

The described species and their positions on the PCA plot provide insights into the mineral's behavior and distribution based on their AOS ranges.
Figure 10

- Acid Na-birnessite (hex, syn)
- δ-MnO₂ (syn)
- Na-birnessite (tricl, syn)
- Romanèchite (Ba-free, syn)
- Todorokite
- Todorokite (syn)
- Hollandite
- Romanèchite
- Lithiophorite
- Cryptomelane
- Cryptomelane (syn)
- Ramsdellite
- Pyrolusite
- Pyrolusite (syn)
- Bixbyite
- Bixbyite (syn)
- Braunite
- Feitknechttite (syn)
- Mn(III) acetate dihydrate
- Groutite
- Manganite (syn)
- Hausmannite
- Hendricksite
- Masutomilite
- Mn(II) ads. illite
- Triplite
- Mn(II) ads. peat pH5
- Mn(II) ads. peat pH7
- Mn(II) acetate tetrahydrate
- Mn(II) oxalate dihydrate
- Rhodochrosite
- Manganeseite (syn)

Linkage Distance