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3   X-ray absorption spectroscopy study of Mn reference compounds

4   for Mn speciation in terrestrial surface environments

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26   **ABSTRACT**

27   X-ray absorption spectroscopy (XAS) offers great potential to identify and quantify Mn spe-

28   cies in surface environments by means of linear combination fit (LCF), fingerprint, and shell-

29   fit analyses of bulk Mn XAS spectra. However, these approaches are complicated by the lack

30   of a comprehensive and accessible spectrum library. Additionally, molecular-level infor-

31   mation on Mn coordination in some potentially important Mn species occurring in soils and

32   sediments is missing. Therefore, we investigated a suite of 32 natural and synthetic Mn refer-

33   ence compounds, including Mn oxide, oxyhydroxide, carbonate, phosphate, and silicate min-

34   erals, as well as organic and adsorbed Mn species, by Mn K-edge X-ray absorption near edge

35   structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The

36   ability of XAS to infer the average oxidation state (AOS) of Mn was assessed by comparing

37   XANES-derived AOS with the AOS obtained from redox titrations. All reference compounds

38   were studied for their local (<5 Å) Mn coordination environment using EXAFS shell-fit anal-

39   ysis. Statistical analyses were employed to clarify how well and to what extent individual Mn

40   species (groups) can be distinguished by XAS based on spectral uniqueness. Our results show

41   that LCF analysis of normalized XANES spectra can reliably quantify the Mn AOS within

42   ~0.1 v.u. in the range +2 to +4. These spectra are diagnostic for most Mn species investigated,

43   but unsuitable to identify and quantify members of the manganate and Mn(III)-oxyhydroxide

44   groups. First-derivative XANES fingerprinting allows the unique identification of pyrolusite,

45   ramsdellite, and potentially lithiophorite within the manganate group. However, XANES

46   spectra of individual Mn compounds can vary significantly depending on chemical composi-

47   tion and/or crystallinity, which limits the accuracy of XANES-based speciation analyses. In

48   contrast, EXAFS spectra provide a much better discriminatory power to identify and quantify

49   Mn species. Principal component and cluster analyses of k^2-weighted EXAFS spectra of Mn

50   reference compounds implied that EXAFS LCF analysis of environmental samples can identi-

51   fy and quantify at least the following primary Mn species groups: (1) Phyllo- and tectoman-

52   ganates with large tunnel sizes (2×2 and larger; hollandite, romanèchite, todorokite), (2) tec-

53   tomanganates with small tunnel sizes (2×2 and smaller; cryptomelane, pyrolusite,

54   ramsdellite), (3) Mn(III)-dominated species (nesosilicates, oxyhydroxides, organic com-

55   pounds, spinels), (4) Mn(II) species (carbonate, phosphate, and phyllosilicate minerals, ad-

56   sorbed and organic species), and (5) manganosite. All Mn compounds, except for members of

57   the manganate group (excluding pyrolusite) and adsorbed Mn(II) species, exhibit unique EX-

58   AFS spectra that would allow their identification and quantification in mixtures. Therefore,

59   our results highlight the potential of Mn K-edge EXAFS spectroscopy to assess bulk Mn spe-

60   ciation in soils and sediments. A complete XAS-based speciation analysis of bulk Mn in envi-

61   ronmental samples should preferably include the determination of Mn valences following the

62   'Combo' method of Manceau et al. (2012) (American Mineralogist 97, 816-827), EXAFS

63   LCF analyses based on principal component and target transformation results, as well as EX-

64   AFS shell-fit analyses for the validation of LCF results. For this purpose, all 32 XAS refer-

65   ence spectra are provided in the Supplementary material for further use by the scientific

66   community.

INTRODUCTION

68   Manganese (Mn) is a redox-sensitive element with a crustal abundance of about 0.1 wt.%

69   (Yaroshevsky, 2006). It participates in numerous globally important environmental processes

70   such as photosynthetic oxygen production and oxidative lignin degradation, and serves as an

71   activator of more than 35 enzymes (Broadley et al., 2012; Burnell, 1988; Jensen et al., 1996;

72   Keiluweit et al., 2015). The three naturally occurring Mn oxidation states +2, +3, and +4 ac-

73   count for the large variety of mono- and mixed-valent Mn species in environmental samples,

74   including oxides and oxyhydroxides (collectively termed (oxyhydr)oxides), carbonates, phos-

75   phates, silicates, organic compounds or Mn species being adsorbed to (in)organic surfaces.

76   Manganese concentrations in sediments and bedrocks may be as low as 20 mg/kg in quartz

77   sands and >1,000 mg/kg in basic rocks like basalt and gabbro (Blume et al., 2016; Gilkes and

78   McKenzie, 1988). Natural background levels of soil Mn range between 40 and 1,000 mg/kg

79   (Blume et al., 2016), but neither total nor exchangeable Mn in soil is correlated with bedrock

80   composition, indicative of a high Mn mobility in the Earth's crust (Mortvedt, 2000).

81   The mobility of Mn in soils and sediments depends largely on biological processes

82   controlling its redox state (Tebo et al., 2005). Since Mn^{2+} is more soluble than Mn^{4+}, Mn bio-

83   availability tends to increase with decreasing pH and redox potential (Blume et al., 2016). A

84   particularly important role in the cycling of Mn in surface environments is attributed to

85   Mn(III/IV) (oxyhydr)oxides, since their precipitation and dissolution primarily control the

86   amount of soluble and thus bioavailable Mn^{2+} (Martin, 2005; Tebo et al., 2004). These miner-

87   als exist either as layer or tunnel structures. Layer-type Mn(III/IV) (oxyhydr)oxides ('phyl-

88   lomanganates') consist of stacked sheets of edge-sharing MnO_6 octahedra, whereas in

89   Mn(III/IV) (oxyhydr)oxides with tunnel structure ('tectomanganates') MnO_6 octahedra form

90   single, double or triple chains by sharing edges, which are linked together via MnO_6 corners

91   to produce tunnels of varying size (McKenzie, 1989). Positive charge deficits created by Mn^{4+}

92   site vacancies or the substitution of structural $Mn^{3+/4+}$ by cations of lower valence are compen-

93   sated by exchangeable cations (e.g., H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, etc.) occupying the tunnel or

94   interlayer spaces (McKenzie, 1989).

95   Manganate minerals are thought to be primarily formed via fast enzymatic Mn^{2+} oxi-

96   dation by bacteria and fungi (Tebo et al., 2004). Resulting Mn(III/IV) (oxyhydr)oxides are

97   poorly crystalline phyllomanganates structurally akin to H^+-birnessite ('acid birnessite') or δ-

98   MnO_2, and may serve as precursors for more crystalline Mn oxides (e.g., todorokite) and

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99   Mn(III) oxyhydroxides (e.g., feitknechtite, manganite) through ageing and/or redox reactions

100   involving dissolved Mn(II) (Elzinga, 2011; Feng et al., 2010; Miyata et al., 2007).

101   The role of Mn(III/IV) (oxyhydr)oxides as strong oxidants for inorganic and organic

102   soil and sediment constituents is well documented (Bartlett, 1981; Ehlert et al., 2016; Feng et

103   al., 2007; Remucal and Ginder-Vogel, 2014; Villinski et al., 2001). Owing to their low point

104   of zero charge and high specific surface area, biogenic Mn(III/IV) (oxyhydr)oxides show a

105   high affinity towards heavy metals like Co, Cu, Ni, and Zn, which frequently exceeds that of

106   Fe(III) (oxyhydr)oxides (O'Reilly and Hochella Jr, 2003; Tebo et al., 2004). As a conse-

107   quence, soil Mn contained in ferromanganese nodules and concretions is often associated with

108   these trace metals (Latrille et al., 2001; Liu et al., 2002; Manceau et al., 2003).

109   Despite the ecological importance and omnipresence of Mn in terrestrial surface envi-

110   ronments, studies targeting the identification and quantification of chemical forms (species) of

111   Mn are surprisingly rare. Available Mn speciation studies can be grouped into three catego-

112   ries. Category 1 studies used sequential extraction methods (Habibah et al., 2014;

113   Kalembkiewicz et al., 2008; Narwall and Singh, 2001; Qiang et al., 1994), which provide val-

114   uable information on operationally defined Mn fractions. However, poor selectivity of ex-

115   tractants, Mn redistribution during extractions, and the use of a large variety of non-

116   standardized extraction procedures severely limit the explanatory power of this speciation

117   approach (Hass and Fine, 2010; Hlavay et al., 2004; Sutherland and Tack, 2003). Category 2

118   studies employed X-ray or electron diffraction to identify and/or characterize Mn minerals in

119   geomaterials. The use of these techniques is hampered by the fact that Mn minerals in soils

120   and sediments are frequently nanocrystalline and amorphous to X-rays (Chukhrov and

121   Gorshkov, 1981; Cornu et al., 2005; Latrille et al., 2001; Rhoton et al., 1993; Ross et al.,

122   1976; Zhang and Karathanasis, 1997). Therefore, these studies almost exclusively focused on

123   ferromanganese nodules and concretions in soils (Liu et al., 2002; Manceau et al., 2003;

124 Szymański et al., 2014; Taylor et al., 1964; Tokashiki et al., 1986; Uzochukwu and Dixon,

125 1986) or sediments (Lee and Xu, 2016; Taira et al., 1981). Category 3 studies utilized syn-

126 chrotron-based Mn K-edge X-ray absorption spectroscopy (XAS) to speciate soil (Frommer et

127 al., 2011; Hernandez-Soriano et al., 2012; Herndon et al., 2014; Keiluweit et al., 2015;

128 Manceau et al., 2005) and sediment Mn (Carroll et al., 2002; Friedl et al., 1997; O'Day et al.,

129 2000). Regardless of the type of Mn species present, high-brilliance synchrotron facilities

130 provide the capability for non-destructive analysis of oxidation state and average local (<5 Å)

131 coordination of Mn in environmental samples with Mn concentrations of several hundred mil-

132 ligrams per kilogram. Previous XAS studies mostly employed either Mn K-edge X-ray ab-

133 sorption near edge structure (XANES) or micro-focused extended X-ray absorption fine struc-

134 ture (EXAFS) spectroscopy. The XANES technique is useful to infer the average oxidation

135 state (AOS) of Mn in soils and sediments based on the shift of the absorption edge towards

136 higher energies with increasing Mn AOS (Manceau et al., 2012; McKeown and Post, 2001).

137 Quantitative information on the fractional amounts of Mn^{2+}, Mn^{3+}, and Mn^{4+} and the resulting

138 Mn AOS in a sample can be obtained by the 'Combo' linear combination fit (LCF) analysis

139 method of Manceau et al. (2012) using a XANES spectra database of well-characterized

140 monovalent Mn references. The accuracy of this method was estimated to be 0.04 valence

141 units (v.u.) in the Mn AOS range +3 to +4, which decreased when the proportion of divalent

142 Mn was greater than 15% (Manceau et al., 2012). Although this state-of-the-art LCF approach

143 has already been used to analyze the AOS of soil Mn (Herndon et al., 2014; Keiluweit et al.,

144 2015), its generic applicability has not been validated by other methods available for Mn AOS

145 quantification.

146   In addition to the determination of Mn oxidation states, Mn K-edge XANES spectra

147 may in principle be useful for the identification and quantification of distinct Mn species in

148 unknown samples using LCF analysis (Frommer et al., 2011; Leven et al., 2018; Morales-

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149   Pérez et al., 2021). However, limited numbers of fit references, spectral similarity of different

150   species, and non-unique LCF solutions can severely limit this approach (Gustafsson et al.,

151   2020; Scheinost et al., 2002).

152   In contrast to XANES analyses, EXAFS spectroscopy has hitherto only rarely been

153   used for the identification and quantification of Mn species in soils and sediments (Manceau

154   et al., 2005; Mayanna et al., 2015). EXAFS evaluations of environmental samples typically

155   include shell-fit and LCF analyses (Ahmad et al., 2019; Scheckel and Ryan, 2004), the latter

156   often combined with principal component analysis (PCA) and target transformation (TT) test-

157   ing (Langner et al., 2012; Manceau et al., 2002; Mikutta and Rothwell, 2016; Scheinost et al.,

158   2002). Decisive for the success of Mn EXAFS LCF analysis is the existence of a comprehen-

159   sive spectrum library including relevant Mn species potentially occurring in terrestrial envi-

160   ronments. Several EXAFS studies provide fundamental information on the local Mn coordi-

161   nation in a range of Mn compounds (Ahmad et al., 2019; Bhattacharya and Elzinga, 2018;

162   Manceau and Combes, 1988; Manceau et al., 2005; McKeown and Post, 2001; Silvester et al.,

163   1997; Webb et al., 2005). However, the number of publicly available Mn EXAFS spectra is

164   neither sufficient for validation of EXAFS parameters previously determined for specific Mn

165   species, nor for Mn speciation analysis of soils and sediments. Additionally, systematic stud-

166   ies on spectral uniqueness of Mn compounds are largely missing. Complicating matters fur-

167   ther, EXAFS data are lacking for various potentially important Mn species such as Mn-

168   containing silicate and phosphate minerals, organic Mn(II/III) compounds, and adsorbed

169   Mn(II) species.

170   The main objective of this study was to evaluate how well and to what extent different

171   Mn species potentially occurring in terrestrial surface environments such as soils and sedi-

172   ments can be distinguished by Mn K-edge XANES and EXAFS spectroscopy. To this end, we

173   collected XAS spectra of 32 well-characterized mineral and organic Mn compounds and ana-

174   lyzed these spectra for features and structural information that allow the discrimination of

175   distinct Mn species (groups). This information is indispensable for the correct analysis and

176   interpretation of Mn XAS spectra of environmental samples. In addition, we used redox titra-

177   tions to verify the accuracy of the 'Combo' XANES LCF method of Manceau et al. (2012) for

178   determining the AOS of Mn in geomaterials.

<div align="center">

MATERIALS AND METHODS

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180   **Manganese reference compounds**

181   The 32 Mn reference samples analyzed in this study, 15 natural and 17 synthetic, belong to

182   seven main groups: (1) Phyllomanganates, (2) tectomanganates, (3) oxide minerals without

183   tunnel or layer structure, (4) Mn(III) oxyhydroxides, (5) carbonate, phosphate, and silicate

184   minerals, (6) organic Mn(II/III) compounds, and (7) Mn(II) adsorbed to (in)organic materials.

185   Table 1 lists all reference compounds along with information on, for example, ideal and em-

186   pirical formulas, structure type where appropriate, Mn content, and XAS spectrum source.

187   Table 1

188   Natural mineral samples were carefully handpicked using a binocular microscope. The clean-

189   est looking crystals or parts with least alteration were chosen for further analysis. Synthetic

190   bixbyite, manganosite, and pyrolusite were purchased as mineral powders. Cryptomelane was

191   synthesized according to McKenzie (1971), δ-MnO$_2$, hexagonal acid and triclinic Na-

192   birnessites following Villalobos et al. (2003), manganite was synthesized using a slightly

193   modified protocol from Chiu and Hering (2000), and Ba-free romanèchite following Shen et

194   al. (2005).

195   Manganese(II) adsorption samples were prepared by batch experiments using a natural

196   85:15-90:10 illite-smectite mineral with R3 ordering from Füzérradvány, Hungary (<2-µm

197   fraction; Dohrmann et al., 2009) and peat from a raised peat bog (Federseemoor) near Bad

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198   Buchau, Germany (40-250-µm fraction; Hoffmann et al., 2012) as adsorbents. Experimental

199   conditions are detailed in the Supplementary material.

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201   **Characterization of Mn reference compounds**

202   **X-ray diffraction.** All available solids were analyzed by powder X-ray diffraction in Bragg-

203   Brentano geometry using a Bruker AXS D4 Endeavor diffractometer equipped with a second-

204   ary graphite monochromator ($CuK\alpha_{1,2}$ radiation) and a scintillation counter. X-ray diffraction

205   patterns were collected at room temperature within a 2theta range of 5-110° using a measur-

206   ing time of 4-10 s per 0.02° step (tube settings: 40 kV/40 mA). The identity of all minerals

207   was confirmed (Figs. S1 and S2). Minor impurities in ramsdellite result from its transition to

208   pyrolusite. Natural pyrolusite and groutite showed minor manganite impurities. An unknown

209   reflection was found in the diffractograms of triclinic Na-birnessite and synthetic cryptome-

210   lane. Remaining additional diffraction peaks in different Mn compounds could be assigned to

211   non-Mn phases such as calcite in groutite, annite in hendricksite, and quartz in braunite and in

212   the peat sample. Literature references or powder diffraction file (pdf) numbers used for XRD

213   evaluation are compiled in Table S1.

214   **Chemical composition.** Twelve natural minerals were prepared as polished and carbon-

215   coated thin sections. Their chemical composition was determined by electron probe microa-

216   nalysis (EPMA) using a CAMECA SX100 instrument equipped with five wavelength-

217   dispersive spectrometers. A focused beam was used with an acceleration voltage of 15 kV and

218   a beam current of 15 nA for major elements (Al, Cr, K, Mg, Mn, P, Si, Ti) and 100 nA for

219   minor or trace elements (Ba, Ca, Cl, F, Fe, Na, Sr, Zn). Counting time on element peaks was

220   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

221   F. Background counting times were half on-peak counting times. The following standards

222   were used for calibrations (element, analyzer crystal): Fe_2O_3 (Fe, large lithium fluoride

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223   (LLIF)), jadeite (Na, thallium acid phthalate (TAP)), kyanite (Al, TAP), Mn_3O_4 (Mn, LLIF),

224   orthoclase (K, pentaerythritol (PET)), wollastonite (Si, Ca, TAP and PET, respectively), oli-

225   vine (Mg, TAP), TiO_2 (Ti, large pentaerythritol (LPET)), Cr_2O_3 (Cr, LPET), apatite (P, PET),

226   NaCl (Cl, LPET), ZnS (Zn, LLIF), SrF_2 (F, Sr, TAP and LPET, respectively), $BaSO_4$ (Ba,

227   LPET). Results of these analyses are summarized in Table S2. Detection limits for each ele-

228   ment measured are listed in Table S3.

229   The chemical composition of six synthetic mineral compounds (acid Na-birnessite,

230   cryptomelane, δ-MnO_2, manganite, Na-birnessite (tricl), romanèchite) was determined by

231   inductively coupled plasma–optical emission spectrometry (ICP-OES, Agilent 5900 SVDV)

232   after acid digestion of the samples at 120-140 °C (Table S2). Acid reagents included 69%

233   HNO_3 (Suprapur[®], Roth), 37% HCl (p.a., Roth), and, if necessary, 40% HF (p.a., Merck) and

234   30% H_2O_2 (Suprapur[®], Merck). Peat samples were previously combusted at 550 °C overnight

235   in a ceramic crucible. The digestions are described in the Supplement material, and detection

236   limits for each element measured can be found in Table S3. The elemental composition of

237   remaining reference compounds is given as provided by the supplier (synthetic bixbyite,

238   manganosite, pyrolusite, organic Mn(II/III) Mn compounds) or as stated in the respective pub-

239   lications (synthetic feitknechtite and todorokite) (Table 1). For references with adsorbed

240   Mn(II), the Mn content was determined as described in the Supplementary material.

241   Based on chemical composition, empirical mineral formulas (Table 1) were calculated

242   after normalization to oxygen. Fractional amounts of Mn valences per formula unit were de-

243   termined by charge-balance calculations (Deer, 1992). Mineral formulas of synthetic Na-

244   birnessites and δ-MnO_2 are those stated in their respective synthesis protocols. Details on em-

245   pirical formula calculations are presented in the Supplementary material.

246   **Redox titrations.** Redox titrations for the determination of bulk Mn AOS were performed

247   after Grangeon et al. (2012) using an automated titration system (TitroLine 7800, SI Analyt-

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248   ics). Briefly, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ ('Mohr's salt') was used to reduce $Mn^{3+/4+}$ in Mn refer-

249   ence compounds to dissolved Mn^{2+}. The excess reductant (Fe^{2+}) was back-titrated with

250   $KMnO_4$ solution and total Mn determined by the re-oxidation of Mn^{2+} to Mn^{3+}, stabilized by

251   pyrophosphate ($P_2O_7^{4-}$). All measurements were carried out in duplicates or triplicates.

252   **Manganese K-edge XAS.** Bulk Mn K-edge XAS spectra of 26 Mn reference compounds

253   were collected at beamline 7-3 of the Stanford Synchrotron Radiation Lightsource (SSRL,

254   Menlo Park, USA), beamline 5-BM-D of the Advanced Photon Source (APS, Argonne,

255   USA), and beamlines P64 and P65 of PETRA III at the Deutsches Elektronen-Synchrotron

256   (DESY, Hamburg, Germany). The beamlines were equipped with Si(220) (7-3) and Si(111)

257   double-crystal monochromators (5-BM-D, P64, P65), which were calibrated by setting the

258   first-derivative maximum of the K-edge absorption spectrum of elemental Mn to 6,539 eV.

259   Higher harmonics in the beam were reduced by detuning monochromators by 15-50% and by

260   harmonic rejection mirrors (P65). In addition, 3-µm Cr filters were used to reduce undesired

261   fluorescence radiation at beamlines 7-3 and P65. Measurements were performed in both fluo-

262   rescence and transmission mode utilizing solid-state fluorescence detectors (7- or 30-element

263   Ge detectors, Vortex SDDs) and ionic chambers, respectively. To avoid beam damage, all

264   samples were measured at 5-20 K employing He-cryostats or at 77 K (5-BM-D) using a Lin-

265   cam cell. Details of the sample preparation can be found in the Supplementary material.

266   Spectra were recorded with a maximum energy increment of 5 eV before the edge and

267   0.2-0.3 eV along the edge. The EXAFS was recorded with a *k*-space resolution of 0.05 $Å^{-1}$.

268   Five to 20 scans were collected per sample. Spectra of a Mn metal foil were used to correct

269   for slight energy shifts during sample measurements.

270   Spectral pre-processing, including merging of individual scans, rebinning, and energy

271   calibration, was conducted in SIXPack (Webb, 2005) or Athena (Ravel and Newville, 2005).

272   The spectra were further processed in Athena following standard routines. The pre-edge re-

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273   gion was fit with a linear function and the post-edge region with a quadratic polynomial. The

274   edge-step energy, E_0, was defined as the first maximum of the first XANES derivative. For

275   background removal the Autobk algorithm was applied. The frequency cut-off parameter,

276   R_{bkg}, was set to 0.9-1.1, and the k-weight for background removal to two or three. A Hanning

277   window function with a sill width of 2 Å^{-1} was used to Fourier transform the data.

278   In addition to the measured spectra, six XAS spectra were obtained from external

279   sources (Table 1). Details on their origin and measurement can be found in the respective

280   publications.

281   **Manganese XAS data analysis.** For the determination of Mn AOS and the fractional amount

282   of each Mn oxidation state present in the reference compounds, we applied the 'Combo' LCF

283   method of Manceau et al. (2012). For this, normalized XANES spectra were fit using 17 Mn

284   K-edge XANES spectra of monovalent Mn references available as open source in Manceau et

285   al. (2012) (deposit item AM-12-037), which were processed as described above. The fits were

286   performed in Athena over an energy range of -20 to 30 eV (E–E_0) by applying a non-

287   negativity constraint. A single E_0 shift was used for all standards. During the fits, negatively

288   loaded references were progressively eliminated until only references with positive (or zero)

289   loadings remained. Each previously deleted reference was then again randomly added and the

290   fit run again to assure that the global minimum was found using the normalized sum of

291   squared residuals (R-factor) as best-fit criterion (Manceau et al., 2012). Eventually, no nega-

292   tive loadings remained and the total fraction of each Mn oxidation state in the sample ana-

293   lyzed was calculated as the sum of the individual component fractions (Manceau et al., 2012).

294   Least-squares fits of k^3-weighted EXAFS spectra of Mn reference compounds were

295   performed in Artemis (Ravel and Newville, 2005) on a shell-by-shell basis in R-space (R+ΔR

296   ~1-4 Å). R-space resolution as given by the Rayleigh criterion ($0.5\pi/(k_{max}–k_{min})$) was 0.14-

297   0.20 Å, such that atomic shells separated by lower values could not be resolved. Theoretical

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298   phase-shift and amplitude functions were calculated with FEFF6 (Ankudinov et al., 1998)

299   based on crystal-structure information. Partial occupancies due to chemical substitution as

300   revealed by chemical analyses were accounted for by adding additional atoms into the respec-

301   tive feff.inp file. For structures containing two or more inequivalent Mn sites (e.g., bixbyite,

302   hausmannite) aggregated FEFF calculations were used, that is, path lists of individual sites

303   were automatically merged together and weighted by the fractional population of the site in

304   the unit cell (Ravel, 2014). The passive amplitude reduction factor, S_0^2, was fixed to 0.8 dur-

305   ing optimization. If individually fitted Debye-Waller parameters, σ^2, converged towards simi-

306   lar values, they were equated in the final fit to reduce the number of fit variables.

307   **Statistics.** The Pearson correlation coefficient was used as a similarity metric for normalized

308   and first-derivative XANES (E = 6,530-6,600 eV) as well as k^2-weighted EXAFS spectra (k =

309   2.0-11.5 Å^{-1}, E_0 = 6,563 eV). Principal component analysis (PCA) was performed on the k^2-

310   weighted Mn EXAFS spectra. Suitability of this data for PCA was confirmed by the Kaiser-

311   Meyer-Olkin (KMO) test in SPSS Statistics (IBM Corp.). In addition, an unsupervised hierar-

312   chical cluster analysis of the EXAFS spectra was conducted using Ward's clustering algorithm

313   (Ward, 1963) with squared Euclidean distances as distance measure. Correlation, PC, and

314   cluster analyses were conducted in Statistica (TIBCO Software Inc.). For linear regression

315   between XANES- and titration-based Mn AOS, normal distribution of data points, constant

316   variance of the dependent variable, and independence of residuals were assured by Shapiro-

317   Wilk and Spearman rank correlation tests as well as Durbin-Watson statistic, respectively,

318   using SigmaPlot v.14 (Systat Software Inc.).

319   **RESULTS AND DISCUSSION**

320   **XANES spectra of Mn references compounds**

321 Figure 1 illustrates absorbance shifts to higher energies with increasing Mn AOS of Mn refer-

322 ence compounds. Here, a zero-energy value was defined by setting the first maximum of the

323 first XANES derivative in the pre-edge region (~6,539 eV) to 0 eV. The ordinate represents

324 the relative energy at which the normalized absorbance XANES signal first reaches 50% of

325 the edge absorption maximum. Manganese compounds belonging to different Mn AOS

326 groups are clearly separated, confirming that XANES data allow a general classification of

327 Mn species with respect to Mn oxidation state.

328   Figure 1

329 Figures 2 and 3 show normalized XANES and corresponding first-derivative spectra of Mn

330 reference compounds, and Table 2 summarizes primary absorption peaks identified up to

331 6,570 eV. Phyllo- and tectomanganates with varying amounts of Mn^{3+} and Mn^{4+} generally

332 show XANES spectra with broad pre-peaks at 6,541.5-6,543.4 eV, smoothly rising absorption

333 edges, and maximal absorbances between 6,560.3 and 6,562.5 eV (Fig. 2, Table 2). The simi-

334 larity of their XANES features suggests that a unique identification of single members in mix-

335 tures would not generally be possible. However, lithiophorite exhibits a unique edge feature,

336 leading to two distinct peaks in the first-derivative XANES spectrum at 6,551.5 and 6,557.5

337 eV. This feature may aid the identification of lithiophorite in mixtures with other phyl-

338 lomanganates. Among tectomanganates, cryptomelane (2×2 tunnels), hollandite sensu stricto

339 (s.s.) (2×2 tunnels), romanèchite (2×3 tunnels), and todorokite (3×3 tunnels) possess similar

340 XANES spectra. In contrast, the first-derivative XANES of pyrolusite (1×1 tunnels) and

341 ramsdellite (1×2 tunnels) feature characteristic double peaks at ~6,552 and ~6,558 eV (Fig. 2,

342 Table 2), potentially allowing the identification of tectomanganates with the smallest tunnel

343 sizes in environmental samples. Differences in XANES spectra observed for natural and syn-

14

344   thetic tectomanganates (cryptomelanes, pyrolusites, todorokites) reflect the sensitivity of

345   XANES spectroscopy to variations in mineral composition and/or crystallinity (Fig. 2).

346   Manganese oxides without layer or tunnel structure such as bixbyite (ferric Mn(III)

347   oxide), hausmannite (Mn(II/III) spinel), and manganosite (Mn(II) oxide) show a greater vari-

348   ability in their XANES spectra, reflecting different Mn oxidation states and Mn coordination

349   environments (Fig. 3). While natural and synthetic bixbyites show featureless absorption edg-

350   es similar to phyllo- and tectomanganates (but distinct differences in their first-derivative

351   spectra), hausmannite exhibits a prominent shoulder in the absorption edge at ~6,553 eV and

352   a well-defined absorption maximum at 6,559.1 eV (Fig. 3, Table 2). Similarly, the XANES of

353   manganosite possesses a modulated absorption edge, a well-defined absorption maximum at

354   6,555.0 eV, and a distinct post-edge oscillation at 6,568.6 eV (Fig. 3, Table 2). These results

355   suggest that hausmannite and manganosite can be readily identified in soils and sediments

356   based on XANES analysis.

357   The $Mn^{3+}O(OH)$ polymorphs feitknechtite, groutite, and manganite exhibit similar

358   XANES features, consisting of smoothly rising absorption edges with two inflection points at

359   ~6,549 and ~6,556 eV, and absorption maxima located at ~6,560 eV (Fig. 3, Table 2). Varia-

360   tions among these minerals are subtle, and suggest that groutite and manganite are virtually

361   indistinguishable by XANES spectroscopy.

362   Carbonate, phosphate, and silicate minerals have unique XANES spectra which also

363   differ from those of Mn (oxyhydr)oxide minerals. Unsurprisingly, this group displays the

364   greatest diversity of XANES characteristics. Triplite, a Mn^{2+}-containing phosphate, shows a

365   steep rise in the absorption edge with a non-unique absorption maximum of 6,552.7 eV. In

366   contrast, rhodochrosite has a pronounced absorption-edge maximum at 6,551.1 eV and a dis-

367   tinct post-edge absorption maximum at 6,562.4 eV, leading to diagnostic first-derivative

368   XANES maxima at 6,548.9 and 6,559.9 eV (Fig. 3, Table 2). The two Mn^{2+}-bearing triocta-

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369   hedral micas hendricksite and masutomilite show similar spectral features with double ab-

370   sorbance peaks at ~6,552 and ~6,557 eV, which are distinct from all other Mn compounds.

371   The identification of 2:1 phyllosilicates with structural Mn^{2+} may thus be possible in unknown

372   sample materials. Braunite, a Mn(II/III) nesosilicate, shows a marked step in the absorption

373   edge and two pronounced peaks in the first-derivative XANES at 6,548.1 and 6,552.9 eV

374   (Fig. 3, Table 2), comparable to feitknechtite.

375   The XANES of organic Mn compounds differ from each other: While Mn(II) acetate

376   tetrahydrate has a smoothly rising absorption edge and a broad absorbance maximum similar

377   to triplite, Mn(II) oxalate dihydrate shows a marked shoulder in the rising part of the edge, a

378   sharp absorption maximum at 6,553.3 eV, and a characteristic double peak in the first-

379   derivative XANES at 6,547.0 and 6,551.5 eV (Fig. 3, Table 2). In contrast, Mn(III) acetate

380   dihydrate exhibits a broad, undulating absorption maximum, which is distinct from all other

381   Mn references (Fig. 3).

382   Samples with adsorbed Mn(II) (illite, peat) are characterized by smoothly rising ab-

383   sorption edges, well-defined absorption maxima at ~6,553 eV, and a comparatively feature-

384   less post-edge absorption (Fig. 3, Table 2). In comparison to the peat samples, Mn(II) ad-

385   sorbed to illite has a less prominent white-line and two discernable main peaks in the first-

386   derivative XANES (Fig. 3). The XANES spectra of the peat samples are different from all

387   other references, and resemble those of Mn(II) citrate, Mn(II) malate, and Mn(II) succinate

388   (Fernando et al., 2010). This result suggests that Mn(II) complexed by natural organic matter

389   should be uniquely identifiable in environmental samples. Noteworthy, peat samples prepared

390   at pH 5 and 7 possess identical XANES spectra, implying that pH had no effect on the coor-

391   dination environment of organically bound Mn(II) (Fig. 3).

392   Our results illustrate that Mn compounds differ in absorption-edge energies as related

393   to Mn AOS, and that several Mn compounds and mineral classes show characteristic inflec-

394   tion points in their XANES spectra. Manganese K-edge XANES features are more pro-

395   nounced in the respective first-derivative spectra. Since small post-edge normalization errors

396   do not affect the shape of the derivatives (Manceau et al., 2012), they might be better suited

397   for fingerprinting and LCF analysis than the respective absorbance spectrum. However,

398   XANES LCF analyses of natural samples may become biased because XANES spectra of

399   individual Mn compounds can differ substantially due to variations in chemical composition

400   and/or crystallinity, as evidenced for bixbyites, cryptomelanes, pyrolusites, and todorokites

401   (Figs. 2 and 3).

402   Figures 2 and 3, Table 2

403   **Average oxidation state of Mn reference compounds**

404   To obtain information on the Mn AOS and relative fractions of Mn^{2+}, Mn^{3+}, and Mn^{4+} in the

405   reference compounds, we used the XANES LCF 'Combo' method (Manceau et al., 2012).

406   The results are tabulated in Table 3. Note, different from other LCF procedures, the 'Combo'

407   method does not claim the samples to be mixtures of the standards (Manceau et al., 2012;

408   Manceau and Nagy, 2012). Therefore, no uncertainties are assigned to individual fractions or

409   the derived AOS. Manceau et al. (2012) estimated the accuracy of AOS determination by the

410   'Combo' method to be ~0.04 v.u. in phyllo- and tectomanganates (AOS range 3.0-4.0) with a

411   negligible amount of Mn^{3+} in layer structures and less than about 15% Mn^{2+}. Based on our fit

412   results for the synthetic monovalent Mn references manganosite (AOS 2.0), bixbyite (AOS

413   3.0), and pyrolusite (AOS 4.0), the absolute accuracy of Mn AOS determination using the

414   'Combo' method was not better than 0.12 v.u. Regression of nominal vs. LCF-derived AOS

415   for these references resulted in a standard error of the AOS estimate of 0.07 v.u. ($R^2 = 0.995$,

416    $p < 0.001$). This result is consistent with Manceau et al. (2012) showing that increasing pro-

417   portions of Mn^{2+} lead to a decreased accuracy of the LCF 'Combo' method.

418   Manganese reference compounds with a nominal Mn AOS of two ($N = 10$) yielded

419   XANES-derived AOS of 2.0-2.49 ($\bar{x} = 2.13$). In this group, higher AOS determined for hen-

420   drickside (2.21), masutomilite (2.49), and Mn(II) adsorbed to illite (2.35) suggest the presence

421   of up to 50% Mn^{3+}. For the mica minerals, this result can be explained by partial oxidation of

422   Mn^{2+} in their octahedral layers. For the illite sample, the result may indicate the formation of

423   a Mn(III/IV) phase upon partial re-oxidation of adsorbed Mn(II), but this could not be con-

424   firmed by EXAFS shell-fit results (see below). LCF results of reference compounds with a

425   nominal AOS of three ($N = 6$) and four ($N = 4$), were largely in agreement with their nominal

426   AOS ($\bar{x} = 3.07$ and 3.96, respectively; Table 3).

427   Table 3

428   In order to validate XANES-based Mn AOS, we performed redox titrations for selected refer-

429   ence compounds with Mn concentrations >1.5 wt.% ($N = 25$). These experiments showed that

430   the AOS of hausmannite was significantly overestimated by the 'Combo' method, most likely

431   because its pronounced Jahn-Teller distortion of $Mn^{3+}O_6$ octahedra (Jarosch, 1987) was not

432   adequately reflected by the standard spectra used (Manceau et al., 2012). An unreasonable

433   titration-based Mn AOS was also observed for triplite (Table 3), which can be attributed to

434   incomplete reductive dissolution of the sample during the experiment. With the exception of

435   these two references, the Mn AOS derived from redox titrations were in excellent agreement

436   with the XANES-based AOS ($R^2 = 0.988$) (Fig. 4). The regression slope was 0.997±0.024 (*p*

437   <0.0001) and the standard error of estimate 0.08. This result implies that the 'Combo' LCF

438   method, when applied to environmental samples, provides accurate Mn AOS data within ap-

439   proximately 0.1 v.u. for the entire Mn valence range +2 to +4.

440   Figure 4

441   **EXAFS spectra of Mn references compounds**

18

442   Figure 5 shows k^3-weighted Mn K-edge EXAFS spectra and Fourier-transform (FT) magni-

443   tudes and real parts of one representative of each Mn species group along with the corre-

444   sponding model fit. The figure exemplifies the diversity of local Mn bonding environments,

445   which can be expected in natural samples. Corresponding data of the remaining references are

446   shown in Figures S3 and S4. EXAFS shell-fit parameters of all compounds are summarized in

447   Table 4. In the following, we detail EXAFS results for each species group, and clarify

448   (dis)similarities of EXAFS parameters among species (groups).

449   Figure 5, Table 4

450   **Phyllo- and tectomanganates.** Figure 6 illustrates k^3-weighted Mn K-edge EXAFS spectra of

451   phyllo- and tectomanganates. Phyllomanganates with hexagonal layer symmetry (acid Na-

452   birnessite, δ-MnO$_2$, lithiophorite) show very similar EXAFS spectra featuring comparatively

453   symmetrical oscillations centered at approximately 4.2, 6.7, 9.2, and 10.4 Å^{-1}. In contrast, the

454   spectrum of triclinic birnessite exhibits a split of the small oscillation between 7.9 and 8.2 Å^{-1}.

455   This antinode splitting is attributed to the ordering of structural Mn^{3+} in triclinic birnessite

456   (Ling et al., 2018; Webb et al., 2005) and allows the distinction of phyllomanganates with

457   hexagonal and triclinic layer symmetry. The peak near 8.0 Å^{-1} was previously used as a diag-

458   nostic fingerprint to differentiate between phyllo- and tectomanganates (McKeown and Post,

459   2001). In this study, however, also 2×3 and 3×3 tectomanganates exhibit a similar spectral

460   feature in this region (Fig. 6).

461   Tectomanganates can be generally discerned from phyllomanganates by a gradually

462   emerging left-side shoulder of the 6.7-Å^{-1} oscillation. This shoulder becomes more intense

463   with increasing content of corner-sharing octahedra (i.e., smaller tunnel size) and eventually

464   results in a split oscillation at 6.4 and 6.7 Å^{-1}. The relative intensities of this double-feature

465   are reversed for pyrolusite (1×1 tunnel) as compared to other tectomanganates (Manceau and

19

466   Combes, 1988) (Fig. 6). Tectomanganates with 2×2 (hollandite s.s., cryptomelane), 1×2

467   (ramsdellite), and 1×1 (pyrolusite) tunnel structure also possess a pronounced and diagnostic

468   oscillation at ~7.4 Å^{-1}, which increases and shifts to lower wavenumbers with decreasing tun-

469   nel size (Fig. 6). Pyrolusites show two distinct troughs at 7.8 and 8.1 Å^{-1}, which are also visi-

470   ble in attenuated form for ramsdellite, and thus can serve as another diagnostic fingerprint for

471   tectomanganates with small tunnel sizes. In combination with the pronounced peak near 7.4

472   Å^{-1} and the unique oscillation at 9.5 Å^{-1}, these results suggest that pyrolusite should be unam-

473   biguously identifiable in mixtures of phyllo- and tectomanganates.

474   All manganates are additionally characterized by an oscillation at 10.2-10.5 Å^{-1} (Fig.

475   6). Because this oscillation is not accompanied by a pronounced right-side shoulder in case of

476   phyllomanganates with hexagonal layer structure (Fig. 6), it can aid the identification of tec-

477   tomanganates, especially those with 1×1, 1×2, and 2×2 tunnel structures, in mixtures with

478   hexagonal phyllomanganates.

479   First O neighbors of Mn in phyllomanganates could be modelled with a single shell at

480   1.90-1.92 Å (Figs. 5 and S3a). Mn-Mn distances of edge-sharing octahedra (Mn-Mn1) were

481   fit at 2.87-2.92 Å, which accord with values published for hexagonal and pseudo-orthogonal

482   phyllomanganate structures (Webb et al., 2005). For hexagonal birnessite and δ-MnO_2, we

483   obtained Mn-Mn2 distances of 3.44-3.49 Å (Table 4). These distances are typically assigned

484   to triple corner-sharing Mn^{3+} octahedra at interlayer sites above or below cation vacancies

485   (Ling et al., 2018; Silvester et al., 1997; Villalobos et al., 2003). Similar to triclinic birnessite,

486   no Mn-Mn2 contribution was observed for lithiophorite, in agreement with the presence of

487   exclusively edge-sharing octahedra (Lanson et al., 2000; McKeown and Post, 2001; Silvester

488   et al., 1997; Villalobos et al., 2003). Two additional O shells were fit at 3.56(3) and 4.14(12)

489   Å, which accord with the lithiophorite structure published by Wadsley (1952) (Table 4).

490   Tectomanganates (Figs. 5 and S3b) show similar variations in their Mn-O, Mn-Mn1,

491   and Mn-Mn2 distances as compared to phyllomanganates (Table 4). Within this group, first-

492   shell O neighbors are located at 1.88-1.92 Å, and second- and third-shell Mn neighbors at

493   2.87-2.90 and 3.43-3.48 Å, respectively. Shell-fit models also included additional O shells at

494   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

495   (hollandite s.s.) and 4.4 Å (pyrolusites) (Bolzan et al., 1993; Miura, 1986; Post et al., 2003)

496   (Table 4). It generally follows that Mn coordination environments in phyllo- and tectomanga-

497   nates are largely similar, such that interatomic distances up to the third coordination shell pre-

498   clude any meaningful discrimination of these minerals in environmental samples using EX-

499   AFS shell-fit analysis.

500   Figure 6

501   **Oxide minerals without layer or tunnel structure.** Bixbyite possesses two inequivalent Mn

502   sites with an occupancy of 25 and 75% in its unit cell (Geshnizgani, 2014). As a result, two O

503   subshells at ~1.91 and ~2.24 Å were needed to account for the generally low first-shell ampli-

504   tudes of natural and synthetic bixbyite (Fig. S3c). The cubic structure of bixbyite is further

505   characterized by edge- and corner-sharing Mn^{3+} octahedra, for which we obtained Mn-Mn

506   distances of 3.09-3.11 and 3.54-3.57 Å, respectively (Table 4). These distances are consistent

507   with those published by Longo et al. (2010).

508   The unit cell of hausmannite also contains two inequivalent Mn sites (Jarosch, 1987).

509   Here, tetrahedral sites are occupied by Mn^{2+} and octahedral sites by Mn^{3+} cations. For octahe-

510   drally coordinated Mn^{3+}, Mn-O distances were fit with 4.1(3) equatorial O atoms at 1.95(1) Å

511   and 1.9(3) axial O atoms at 2.27(1) Å, which account for the octahedral Jahn-Teller distortion

512   approximately parallel to [001] (Jarosch, 1987). A third O shell (~2.01 Å) for tetrahedrally

513   coordinated Mn^{2+} (Longo et al., 2010) was too close to the $Mn-O_{eq}$ distance to be included in

514   the model and did not improve the fit (*F*-test; Hamilton, 1965). First-shell oxygens are fol-

515   lowed by two Mn subshells at 2.88(1) and 3.10(0) Å, corresponding to edge-sharing Mn^{3+}

516   octahedra (Longo et al., 2010). The third FT peak of hausmannite (Figs. 5 and S3c) was re-

517   produced with Mn shells at 3.44(1) and 3.73(1) Å (Table 4). These values are consistent with

518   tetrahedra-octahedra corner linkages (Longo et al., 2010) and Mn-Mn distances of Mn^{2+} tetra-

519   hedra, respectively (Jarosch, 1987).

520   In contrast to the former two minerals, the first FT peak of cubic manganosite could be

521   modeled with a single O shell at 2.22(0) Å (Fig. S3c). Analogous to Ressler et al. (1999),

522   higher coordination shells were fit with Mn neighbors at 3.13(0) Å, indicative of edge-sharing

523   Mn^{2+} octahedra, and third-shell O atoms at 3.84(0) Å (Fig. S3c, Table 4).

524   **Manganese(III) oxyhydroxides.** Minerals of this group are characterized by reduced first-

525   shell amplitudes typically caused by the broad distribution of Mn-O bond lengths and associ-

526   ated scattering cancellation effects (Silvester et al., 1997; Webb et al., 2005) (Figs. 5 and

527   S4a). Consequently, first-shell oxygens in Mn(III) oxyhydroxides were fit with two or three O

528   subshells. For feitknechtite, we obtained Mn-O distances of 1.91(0) and 2.22(1) Å, for grout-

529   ite 1.93(1), 2.15(4), and 2.34(2) Å, and for manganite 1.93(0) and 2.28(1) Å (Table 4). Sec-

530   ond-shell Mn in feitknechtite was fit at 2.83(1) and 2.99(0) Å, respectively, and third-shell

531   Mn at 3.33(1) Å (Table 4). The latter distance is considerably shorter than the 3.43 Å reported

532   by Mackle et al. (1993), but more consistent with the presumed sole presence of edge-sharing

533   Mn^{3+} octahedra in feitknechtite. The coordination numbers (*CN*s) of the two Mn1 subshells in

534   feitknechtite were previously either set to four and two, respectively (Ressler et al., 1999), or

535   to unity (Mackle et al., 1993). We obtained *CN*s of 1.9(3) and 3.8(11) (Table 4), which are in

536   good agreement with the values used by Ressler et al. (1999).

537   In contrast to the other two polymorphs, first Mn neighbors in groutite could be fit

538   with a single shell at 2.88(1) Å (Table 4). Higher Mn coordination shells corresponding to

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539   edge- and corner-sharing Mn^{3+} octahedra occur at 3.38(3) and 3.61(1) Å, respectively (Table

540   4). These distances are within the error range of values published by Scheinost et al. (2001).

541   For manganite, we obtained Mn-Mn1 distances of 2.77(1) and 2.98(2) Å, a Mn-Mn2 distance

542   of 3.69(1), and a Mn-Mn3 distance of 3.83(2) Å (Table 4). The former can be assigned to Mn

543   atoms in chains of edge-sharing Mn^{3+} octahedra and the latter two to corner-sharing octahedra

544   (Mackle et al., 1993). Even though our Mn-Mn1/2 distances are up to ~0.07 Å longer than

545   those reported for manganite by Mackle et al. (1993), they fit well with crystallographic data

546   (Dachs, 1963). Contrary to Mackle et al. (1993), who postulated a similar local Mn coordina-

547   tion environment in manganite and feitknechtite, our data imply a substantially different Mn

548   coordination within these minerals.

549   **Carbonate, phosphate, and silicate minerals.** In minerals of this group, atoms other than O

550   and Mn/Fe contribute to their EXAFS: Al/Si in masutomilite, C in rhodochrosite, P in triplite,

551   and Zn in hendricksite. To the best of our knowledge, most of these minerals have not previ-

552   ously been studied by Mn EXAFS spectroscopy. Their spectra and model fits are depicted in

553   Figs. 5 and S4b. Generally, first-shell O/F neighbors within this mineral group are found at

554   distances of 1.94-2.55 Å, and were accounted for by one (hendricksite, masutomilite, rhodo-

555   chrosite), two (triplite) or three subshells (braunite) (Table 4). Braunite shows a very broad

556   first FT peak with low amplitude (Fig. S4b), which was fit with 2.6(2), 2.1(3), and 0.9(3) O

557   neighbors at 1.94(1), 2.25(1), and 2.55(3) Å, respectively. Higher shells included 1.9(5) Mn

558   atoms at 3.17(1) Å, typical of edge-sharing Mn octahedra, and 5.3(18) O atoms at 3.77(2) Å

559   (Table 4). All parameters agree well with crystallographic data (Ohmann et al., 1998).

560   The first coordination shell of hendricksite was fit with 4.9(9) O atoms at 2.16(1) Å,

561   implying fairly distorted Mn^{2+} octahedra in this mica mineral. Second-shell signals arise from

562   Mn/Fe and Zn neighbors at 3.14(1) Å, sharing the same atomic position in the unit cell (Rob-

563   ert, 1985). The *CN*s of second-shell Mn/Fe and Zn atoms were set to 2.0 and 2.5, respectively,

23

564   based on chemical analysis (1.04 apfu Mn+Fe and 1.28 apfu Zn in octahedral coordination).

565   Magnesium was neglected due to its low scattering amplitude, and Ba and Ti atoms due to

566   their low concentrations (Table 1).

567   Similar to hendrickside, the first coordination shell in masutomilite was reproduced by

568   4.9(9) O/F atoms at a distance of 2.15(1) Å. The *CN*s of second-shell Al and Mn, both located

569   at 3.02(5) Å, were set to 2.5 and 0.4, respectively, based on chemical analysis (1.23 apfu Al

570   and 0.18 apfu Mn in octahedral coordination). Octahedral-layer Li was not included in the

571   model due to its low scattering amplitude. Higher shells of masutomilite include four Al/Si

572   atoms at 3.24(3) Å and four O atoms at 3.47(3) Å (Table 4).

573   For rhodochrosite, the only important Mn carbonate occurring in soils and sediments

574   (Barreto et al., 2016; Ying et al., 2011), first O neighbors belonging to the CO_3^{2-} group were

575   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

576   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

577   agreement with Friedl et al. (1997), except for the longest Mn-O distance, which is ~0.03 Å

578   shorter than previously reported.

579   The FT of triplite is dominated by first-shell F/O atoms, followed by two smaller

580   peaks hosting Fe/Mn and P neighbors (Fig. S4b). First-shell F and O atoms were fit at 2.05(3)

581   and 2.15(1) Å, respectively, atoms of edge-sharing Fe/Mn octahedra at 2.93(2) Å, and P at-

582   oms at 3.55(1) Å (Table 4). Chemical analysis suggested 1.6 F and 4.4 O neighbors (0.79 apfu

583   F and 2.21 apfu O) in the first coordination shell, which is close to theoretical F and O *CN*s of

584   two and four, respectively (Waldrop, 1969).

585   **Organic Mn(II/III) compounds.** The local Mn coordination in Mn(II) acetate tetrahydrate,

586   Mn(II) oxalate dihydrate, and Mn(III) acetate dihydrate has, to our knowledge, not previously

587   been studied by EXAFS spectroscopy. Their spectra are displayed in Figures 5 and S4c. The

588   first coordination shell of both Mn(II) compounds was fit with approximately six O atoms at

24

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589   2.18(1) Å. In contrast, two O subshells housing 5.2(5) and 1.5(5) O atoms at 1.93(0) and

590   2.20(1) Å, respectively, were needed to model the first FT peak of Mn(III) acetate dihydrate

591   (Table 4). For Mn(II) acetate tetrahydrate, distances of C and Mn shells were fit at 3.19(4)

592   and 3.40(2) Å, respectively (Table 4). Remarkably, the best fit was obtained with C and Mn

593   CNs fixed to nominal values of monoclinic Mn(II) acetate dihydrate ($P2_1/c$) (Cheng and

594   Wang, 1991). The determined Mn-Mn distance is 0.2 Å shorter than expected for single cor-

595   ner-sharing Mn octahedra present in monoclinic Mn(II) acetate tetrahydrate ($P2_1/c$) (Bertaut

596   et al., 1974; Tranqui et al., 1977), but is consistent with long edge-sharing octahedral linkages

597   as in Mn(II) acetate dihydrate (Cheng and Wang, 1991).

598   In Mn(II) oxalate dihydrate, four proximal C atoms are located at 2.95(2) Å, followed

599   by distant O atoms at 3.93(2) Å. In addition, three multiple-scattering (MS) paths were in-

600   cluded in the model (Table 4), which significantly improved the fit (F-test). Our fit results

601   comply with XRD data for monoclinic Mn(II) oxalate dihydrate ($C2/c$), and demonstrate the

602   absence of octahedral linkages in Mn(II) oxalate dihydrate (Puzan et al., 2018).

603   In Mn(III) acetate dihydrate, the first coordination shell is followed by four proximal

604   C atoms at 2.98(2) Å, a substantially shorter distance compared to Mn(II) acetate tetrahydrate

605   (Table 4). Best fits of higher coordination shells were obtained with two Mn atoms at

606   3.40(0) Å and two O atoms at 4.37(5) Å (Table 4). Both, distances and CNs comply with

607   XRD data for monoclinic Mn(III) triacetate dihydrate ($P2_1/m$), in which Mn octahedra are

608   linked to chains via single corners (Le Bail, 2016; personal communication to the crystallog-

609   raphy open database (COD), COD ID 3500063).

610   **Adsorbed Mn(II) species**. To the best of our knowledge, molecular-scale information on

611   Mn(II) adsorbed to clay minerals (illite) and particulate natural organic matter (peat) is cur-

612   rently not available. Spectra of Mn(II) adsorbed to illite and peat are illustrated in Figures 5

613   and S4d. The EXAFS of Mn(II) adsorbed to illite is dominated by first-shell signals, housing

25

614   two O atoms at 1.92(1) Å and four O atoms at 2.16(1) Å (Table 4). Implementation of Al or

615   Si backscatterers into the model proved unsuccessful, suggesting that hydrated Mn^{2+} ions are

616   primarily adsorbed as outersphere complexes on siloxane surfaces. We found no evidence of a

617   Mn(III/IV) phase, which could explain the XANES- and titration-derived AOS values >2 ob-

618   tained for the illite sample (Table 3). This may suggest a similar adsorption mechanism for

619   Mn^{3+} ions or a systematic error in both AOS determination methods, which we consider less

620   likely.

621   Nearly identical shell-fit results were obtained for Mn(II) adsorbed to peat at pH 5 and

622   7, showing that pH had a negligible effect on the coordination of organically bound Mn(II).

623   Both EXAFS were well reproduced with one proximal C atom at 3.20(7) (pH 5) and

624   3.21(8) Å (pH 7), implying monodentate Mn^{2+} complexation by carboxyl groups. Owing to

625   their low scattering amplitudes, distal C atoms were not included in the model; instead, an

626   obtuse triangle Mn-C-O MS path was used to reproduce the low FT peaks at ~4.5 Å (Fig. 5,

627   Table 4). Interestingly, Mn^{2+} complexation by particulate organic matter did not lead to Mn^{2+}

628   oxidation under oxic conditions (Table 3).

629   **Comparison of interatomic distances.** When XAS is applied to soils or sediments, over-

630   absorption can frequently affect the EXAFS amplitude, leading to a bias of fitted *CN*s. Addi-

631   tionally, *CN*s can be influenced by poor crystallinity (i.e., high static disorder) and/or small

632   particle size relative to crystalline reference compounds (O'Day et al., 2004). As these issues

633   do not affect the EXAFS frequency, atomic distances are more robust parameters when com-

634   paring average Mn coordination environments of natural samples.

635   Figure 7 compiles all absorber-single scatter distances determined in this study. The

636   figure also includes data from various literature sources for comparison (Table S4). Note that

637   the designation of individual coordination shells is somewhat arbitrary, and for simplicity,

638   atoms in subshells were considered part of a 'shell'. As evidenced by Friedl et al. (1997), Mn-

26

639   O bond distances depend on the oxidation state of Mn. In agreement with this, the shortest

640   Mn-O distances were observed for tectomanganates, and the longest Mn-O distances for

641   (in)organic Mn(II) species (Fig. 7). In general, average first-shell distances of all reference

642   compounds can be classified according to their XANES-derived Mn AOS: 2.14±0.04 Å ($\bar{x}\pm\sigma$)

643   for AOS 2.0-2.5 members ($N = 10$), 2.02±0.06 Å for AOS 3.0-3.5 members ($N = 9$), and

644   1.90±0.01 Å for AOS 3.7-4.0 members ($N = 13$). Differences in average Mn-O/F bond

645   lengths of AOS groups are significant at the p <0.05 level (Kruskal-Wallis rank-based ANO-

646   VA, Dunn´s method), except for the AOS 3.0-3.5 and 3.7-4.0 groups. Figure 7 also illustrates

647   that split shells of first O neighbors are absent in the phyllo- and tectomanganate groups. In

648   contrast, Mn-O1 subshells or longer Mn-O distances are typical features of all other Mn spe-

649   cies groups. Likewise, Mn-Mn1 distances of edge-sharing Mn octahedra in phyllo- and tec-

650   tomanganates (2.87-2.92 Å) are substantially shorter than corresponding (average) Mn-Mn

651   distances in (1) oxides without layer or tunnel structure (3.03-3.13 Å; bixbyite, hausmannite,

652   manganosite), (2) members of the phosphate and silicate group (2.93-3.17 Å; braunite, hen-

653   dricksite, masutomilite, triplite), and (3) organic Mn(II) compounds (3.40 Å; Mn(II) acetate

654   tetrahydrate). Although Mn-Mn1 distances of phyllo- and tectomanganates are similar to (av-

655   erage) Mn-Mn1 distances in Mn(III) oxyhydroxides, the need to fit two Mn-Mn1 subshells to

656   an EXAFS spectrum of an environmental sample, may indicate the presence of feitknechtite

657   and manganite (or hausmannite) (Fig. 7).

658   Organic Mn(II/III) compounds may possess edge- or corner-sharing MnO_6 linkages,

659   whose Mn-Mn distances can overlap with those of manganate and oxyhydroxide minerals,

660   notably groutite (Fig. 7). In contrast, organically complexed Mn(II) species lack Mn or other

661   heavy atoms in higher coordination shells. Their Mn-C distances are either significantly

662   shorter or longer than the Mn-C distance of rhodochrosite (3.08(2) Å), thus facilitating the

663　distinction between rhodochrosite and organic Mn(II) species in environmental samples

664　(Fig. 7).

665　　　　　　　　　　　　　　　　Figure 7

666

667

Statistical XAS spectrum comparisons

669　Key to species detection and quantification by means of Mn XAS LCF is spectral dissimilari-

670　ty. Therefore, Pearson correlations were used to compare the (dis)similarity of XAS spectra of

671　all reference compounds. Normalized XANES spectra (6,530-6,600 eV) were highly positive-

672　ly correlated due to similar overall shape (Fig. S5), complicating a meaningful species identi-

673　fication and quantification based on LCF analysis of this data without auxiliary information.

674　Significantly lower spectral correlations for first-derivative XANES spectra (Fig. S6) indicate

675　much better discriminative power of these data. Here, low and moderate correlations ($r \leq 0.7$)

676　exist between adsorbed Mn(II) species and most other species-group members. The same

677　holds for carbonate, silicate, and phosphate minerals as well organic Mn(II) compounds (Fig.

678　S6). This suggests that members of these groups can likely be identified based on their first-

679　derivative XANES, provided data quality is sufficient. However, high correlations ($r > 0.8$)

680　were still observed between manganates, oxide minerals without layer or tunnel structure, and

681　Mn(III) oxyhydroxides, making it difficult to identify and quantify individual members of

682　these species groups in mixtures using first-derivative XANES spectra (Fig. S6). A much bet-

683　ter discriminative power can be achieved on the basis of Mn EXAFS spectra. Figure 8 shows

684　the Pearson correlation matrix of k^2-weighted EXAFS spectra ($k = 2.0\text{-}11.5$ Å^{-1}, $E_0 = 6,563$

685　eV) of all reference compounds. A k^2-weighting was chosen because environmental studies

686　usually deal with low-Mn concentration samples that would not allow a higher k-weighting in

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687   LCF analyses without risking excessive spectral noise amplification. However, caution must

688   be exercised in interpreting these correlation coefficients because strong correlations were

689   observed for species whose EXAFS spectra differ substantially, for example, pyrolusite and

690   Ba-free romanèchite ($r = 0.82$) (cf. Fig. 6). It follows that correlation coefficients of less than

691   approximately 0.8 can be taken as indication of spectral dissimilarity. Using this criterion,

692   Figure 8 shows that EXAFS spectra of most reference compounds are unique, only exceptions

693   being spectra of several members of manganates, organic Mn(II/III) compounds, adsorbed

694   Mn(II) species, and triplite. This result confirms the supreme potential of EXAFS LCF analy-

695   sis to identify and quantify individual Mn species in environmental samples.

696   Next, we performed a PCA to reduce the dimensionality of the k^2-weighted Mn K-

697   edge EXAFS dataset and clarify spectral group membership. Output parameters for the first

698   ten principal components (PCs) are summarized in Table S5. The number of statistical mean-

699   ingful PCs based on eigenvalues >1 (Kaiser-Guttman criterion; Guttman, 1954) was five (Ta-

700   ble S5). These PCs explained 88.6% of the total variance of all Mn EXAFS spectra, suggest-

701   ing five superordinate variables defining spectral group membership. A loading plot of PC1

702   vs. PC2, explaining 56.08% and 13.33% of spectral variance, respectively, is illustrated in

703   Figure 9. Here, PC1 mainly reflects the oxidation state of Mn reference compounds, as mem-

704   bers of manganates load highly negatively, Mn(II) species positively, and species with pre-

705   dominantly Mn(III) intermediately and negatively on PC1. Combined, PCA implies that at

706   least five Mn species (groups) can be distinguished in the entire EXAFS data set, and Figure 9

707   suggests that the Mn oxidation state plays a major role.

708   To validate the PCA results, an unsupervised tree-clustering analysis was performed

709   using Ward´s method (Ward, 1963). Figure 10 shows the output of the cluster analysis. The

710   length of the horizontal lines (linkage distances) is proportional to spectral dissimilarity. Like

711   PCA, hierarchical cluster analysis generally separated Mn(III/IV) phases from Mn(III)- and

712   Mn(II)-containing compounds at a linkage distance of 25-40 (Fig. 10). A division into five

713   meaningful clusters, as suggested by PCA, is given at a linkage distance of about 18. Here,

714   cluster one consists of all phyllomanganates and tectomanganates with large tunnel sizes (2×2

715   and larger) including hollandite s.s. (2×2 tectomanganate). Cluster two comprises tectoman-

716   ganates with small tunnel sizes (2×2 and smaller). Minerals dominated by Mn(III) are

717   grouped into cluster three. Cluster four unites all Mn(II) species, and cluster five is exclusive-

718   ly formed by manganosite. A closer inspection of inner-cluster variability revealed that bixby-

719   ite, hausmannite, hendricksite, masutomilite, pyrolusite, and rhodochrosite are clearly distinct

720   within their respective clusters. While EXAFS spectra with a linkage distance >6 show dis-

721   criminable spectral features, they become virtually indistinguishable at a linkage distance <5

722   based on direct comparisons. This implies that six of the 32 Mn reference compounds (haus-

723   mannite, hendricksite, manganosite, masutomilite, Mn(III) acetate dihydrate, rhodochrosite)

724   are clearly recognizable and quantifiable as individual species when present in mixtures. All

725   other Mn compounds can at least be reliably assigned to a particular species group.

726   Figures 8-10

727   **IMPLICATIONS**

728   Research on Mn oxidation states in soils and sediments is prerequisite to better understand

729   redox cycling of Mn and its participation in environmental processes. Since accurate Mn AOS

730   determination in soils and sediments by wet-chemical methods is impossible due to the excess

731   of other electron donors/acceptors, especially Fe and organic matter, XANES spectroscopy is

732   currently the only available tool for process-oriented research relying on this key parameter.

733   By comparing XANES LCF- and redox titration-based AOS results for mono- and multiva-

734   lent Mn compounds, we found that the XANES LCF 'Combo' method of Manceau et al.

30

735 (2012) provides accurate Mn AOS data within approximately 0.1 v.u. over the entire natural

736 Mn valence range.

737   Linear combination fitting of XAS spectra is a widely used method for the identifica-

738 tion and quantification of element species in environmental samples (Hutchison et al., 2001;

739 Langner et al., 2012; Leven et al., 2018; Mikutta and Rothwell, 2016; Scheckel and Ryan,

740 2004). This approach requires comprehensive databases with suitable reference spectra

741 (Gustafsson et al., 2020; Scheinost et al., 2002). While these exist for several key elements

742 such as Fe (O'Day et al., 2004; Wilke et al., 2001), they are not available for Mn. Therefore,

743 we provide (energy-calibrated) XAS spectra of 32 Mn compounds, potentially occurring in

744 soils and sediments, in the Supplementary material. This spectrum library can be used by the

745 scientific community for Mn species identification and quantification in terrestrial surface

746 environments.

747   Prerequisite to the application of XAS LCF for species recognition and quantification

748 is spectral uniqueness (Gustafsson et al., 2020; Scheinost et al., 2002). Our results show that,

749 compared to EXAFS spectra, normalized and first-derivative Mn K-edge XANES spectra

750 provide far less discriminative power to distinguish and thus identify individual Mn species in

751 environmental samples. Owing to high spectral correlations, the use of normalized Mn

752 XANES spectra for species identification and quantification in LCF analysis of environmental

753 samples is not recommended without proper justification based on auxiliary species infor-

754 mation. First-derivative XANES spectra of most analyzed Mn compounds are unique, sug-

755 gesting that identification and quantification of most Mn species would be possible. However,

756 members of the manganate and Mn(III)-oxyhydroxide groups are probably indistinguishable

757 in mixtures using (first-derivative) XANES spectra. Prominent exceptions are pyrolusite,

758 ramsdellite, and perhaps lithiophorite, which possess unique first-derivative XANES finger-

759 prints. Nonetheless, the employment of XANES LCF for Mn species identification and quan-

31

760   tification in natural samples is limited. First, because XANES features are not solely depend-

761   ent on the Mn oxidation state or structural and electronic factors, but also on energy calibra-

762   tion and monochromator resolution (Manceau et al., 2012; Manceau et al., 2002). Second,

763   because XANES spectra are influenced by subtle changes in chemical composition and/or

764   crystallinity of Mn compounds. Comparisons of XANES and EXAFS spectra of natural and

765   synthetic Mn compounds (bixbyites, cryptomelanes, pyrolusites, todorokites) document the

766   robustness of EXAFS spectroscopy to variations in chemistry and/or crystallinity, demonstrat-

767   ing its superior value for bulk Mn species identification and quantification in natural samples.

768   Based on PCA and cluster analyses, EXAFS LCF analysis of environmental samples is at

769   least capable of discriminating the following species groups: (1) phyllomanganates and tec-

770   tomanganates with large tunnel sizes (2×2 and larger; hollandite s.s., romanèchite,

771   todorokite), (2) tectomanganates with small tunnel sizes (2×2 and smaller; cryptomelane, py-

772   rolusite, ramsdellite), (3) Mn(III)-dominated species (nesosilicates, organic compounds, oxy-

773   hydroxides, spinels), (4) Mn(II) species (carbonate, phosphate, and phyllosilicate minerals,

774   adsorbed and organic species), and (5) manganosite. Within these conservatively established

775   species groups, most Mn compounds exhibit unique EXAFS features, which would assist

776   their identification and quantification in mixtures using EXAFS LCF analysis. Sole excep-

777   tions are manganate minerals (except for pyrolusite) and adsorbed Mn(II) species whose EX-

778   AFS are dominated by first-shell O signals. These results highlight the potential of Mn K-

779   edge EXAFS spectroscopy to quantitatively assess bulk Mn speciation in soils and sediments,

780   which so far has not been exploited. For speciation analysis of natural samples using Mn K-

781   edge EXAFS spectroscopy, we recommend stepwise application of PCA-TT and LCF analy-

782   sis and subsequent validation of LCF results by spectral fingerprinting as well as EXAFS

783   shell-fitting in order to justify the presence of individual Mn species.

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784   In summary, the results of this study provide a comprehensive framework for the anal-

785   ysis and interpretation of Mn XAS spectra of natural samples and for the evaluation of the

786   role of Mn in environmental processes. Our spectrum library thus lays the foundation for fur-

787   ther process-oriented environmental Mn research.

788   **ACKNOWLEDGEMENTS**

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1115

1116

1117   **FIGURE CAPTIONS**

1118   **Figure 1.** Classification plot of Mn reference compounds. Different XANES-derived Mn
1119   AOS based on absorption-edge position are shown relative to the first maximum in the first
1120   XANES derivative at ~6,540 eV (after Marcus et al., 2008). Note that masutomilite and hen-
1121   dricksite as well as hausmannite and braunite are separated from other members of the low-
1122   and medium-AOS range. Synthetic pyrolusite shows the highest Mn AOS of 4.0 of all refer-
1123   ence compounds.
1124
1125   **Figure 2.** Stacked normalized Mn K-edge XANES (left) and corresponding first-derivative
1126   spectra (right) of phyllo- and tectomanganates. The spectrum numbers match the numbers in
1127   Table 1: 1 - acid Na-birnessite (hex, syn), 2 - δ-MnO_2 (syn), 3 - lithiophorite, 4 - Na-birnessite
1128   (tricl, syn), 5 - cryptomelane, 6 - cryptomelane (syn), 7 - hollandite s.s., 8 - pyrolusite, 9 -
1129   pyrolusite (syn), 10 - ramsdellite, 11 - romanèchite, 12 - romanèchite (Ba-free, syn), 13 -
1130   todorokite, 14 - todorokite (syn).
1131
1132   **Figure 3.** Stacked normalized Mn K-edge XANES (left) and corresponding first-derivative
1133   spectra (right) of Mn oxide minerals without layer or tunnel structure as well as Mn(III) oxy-
1134   hydroxides, carbonate, phosphate, and silicate minerals, organic Mn(II/III) compounds, and
1135   adsorbed Mn(II) species. The spectrum numbers match the numbers in Table 1: 15 - bixbyite,
1136   16 - bixbyite (syn), 17 - hausmannite, 18 - manganosite, 19 - feitknechtite (syn), 20 - groutite,
1137   21 - manganite (syn), 22 - braunite, 23 - hendricksite, 24 - masutomilite, 25 - rhodochrosite,
1138   26 - triplite, 27 - Mn(II) acetate tetrahydrate (syn), 28 - Mn(II) oxalate dihydrate (syn), 29 -
1139   Mn(III) acetate dihydrate (syn), 30 - Mn(II) ads. illite pH7, 31 - Mn(II) ads. peat pH5, 32 -
1140   Mn(II) ads. peat pH7.
1141
1142   **Figure 4.** Linear regression (solid line) between average oxidation state (AOS) of Mn ob-
1143   tained from redox titrations against Mn AOS determined by XANES LCF. Confidence and
1144   prediction bands (95%) are indicated by dark and light blue color, respectively. Data for
1145   hausmannite and triplite (out of range) were excluded from analysis.
1146
1147   **Figure 5.** Stacked k^3-weighted Mn K-edge EXAFS spectra (left) as well as corresponding
1148   Fourier-transform magnitudes and real parts (right) of selected Mn reference compounds: 1 -
1149 δ-MnO_2 (syn), 2 - hollandite s.s., 3 - hausmannite, 4 - feitknechtite, 5 - rhodochrosite, 6 -
1150   Mn(II) oxalate dihydrate, 7 - Mn(II) ads. peat pH5. Solid lines represent experimental data
1151   and dotted lines model fits. EXAFS parameters are summarized in Table 4. The fits of other
1152   Mn compounds are displayed in Figures S3 and S4.
1153
1154   **Figure 6.** Stacked k^3-weighted Mn K-edge EXAFS spectra of phyllo- and tectomanganates.
1155   1 - acid Na-birnessite (hex, syn), 2 - δ-MnO_2 (syn), 3 - Na-birnessite (tricl, syn), 4 - lithiopho-
1156   rite, 5 - todorokite, 6 - todorokite (syn), 7 - romanèchite (nat), 8 - romanèchite (Ba-free, syn),
1157   9 - hollandite s.s., 10 - cryptomelane (nat), 11 - cryptomelane (syn), 12 - ramsdellite, 13 - py-
1158   rolusite (nat), 14 - pyrolusite (syn). Vertical lines and black arrows indicate important spectral
1159   features (see text for details).
1160
1161
1162

1163   **Figure 7.** Interatomic distances between Mn and near-neighbor atoms in Mn reference com-
1164   pounds obtained from this study (colored symbols) and the literature (gray symbols). Litera-
1165   ture references are listed in Table S4. In masutomilite, first-shell O could also be F and third-
1166   shell Al could be Si. In triplite and hendricksite, second-shell Mn may also be Fe. Horizontal
1167   lines separate the seven different Mn species groups (see text for further details).

1168

1169   **Figure 8.** Pearson correlation matrix for k^2-weighted Mn K-edge EXAFS spectra (k = 2.0-
1170   11.5 Å^{-1}, E_0 = 6,563 eV) of Mn reference compounds. Only significant correlations (p <0.05)
1171   are reported.

1172

1173   **Figure 9.** Loading plot of the first two PCs obtained from PCA of k^2-weighted Mn K-edge
1174   EXAFS spectra (k = 2.0-11.5 Å^{-1}, E_0 = 6,563 eV) of Mn reference compounds. Species are
1175   colored according to their XANES-derived Mn AOS.

1176

1177   **Figure 10.** Unsupervised tree clustering of k^2-weighted Mn K-edge EXAFS spectra (k = 2.0-
1178   11.5 Å^{-1}, E_0 = 6,563 eV) of Mn reference compounds using Ward′s method. Five clusters are
1179   indicated at a linkage distance of 18.

1180

Table 1. Manganese reference compounds studied by XAS

No.	Reference	Mineral formula (nominal / empirical)[a]	Remarks	Mn (wt.%)[b]	Spectrum source
Phyllomanganates					
1	Acid Na-birnessite (hex, syn)	$H_{0.06}K_{0.18}(H_2O)_{0.54}Mn^{3+}_{0.08}(H_2O)_{0.24}(Mn^{4+}_{0.88},vac_{0.12})_{\Sigma1.00}O_2$		54	This study
2	δ-MnO$_2$ (syn)	$(Mn^{4+},Fe^{3+},Ca,Na)_{\Sigma1.00}(O,OH)_2 \cdot nH_2O$		49	This study
3	Lithiophorite	$(Al,Li)Mn^{4+}_2O_2(OH)_2 / Al_2LiMn^{4+}_2Mn^{3+}O_6(OH)_6$		39[c]	McKeown and Post (2001)
4	Na-birnessite (tricl, syn)	$Na_{0.26}(Mn^{4+}_{0.74}Mn^{3+}_{0.26})_{\Sigma1.00}O_2$		55	This study
Tectomanganates					
5	Cryptomelane	$K(Mn^{4+},Mn^{3+})_8O_{16} / (K_{0.78}Na_{0.06}Si_{0.05}Ca_{0.04}Zn_{0.03}Sr_{0.02})_{\Sigma0.98}(Mn^{4+}_{6.73}Mn^{3+}_{1.22}Al_{0.06})_{\Sigma8.01}O_{16}$	2×2 tunnel	57	This study
6	Cryptomelane (syn)	$K(Mn^{4+},Mn^{3+})_8O_{16} / (K_{0.89}Pb_{0.01})_{0.90}(Mn^{4+}_{6.79}Mn^{3+}_{1.31})_{\Sigma8.10}O_{16}$	2×2 tunnel	62	This study
7	Hollandite s.s.	$Ba(Mn^{4+},Mn^{3+})_8O_{16} / (Ba_{0.75}Pb_{0.16})_{0.91}(Mn^{4+}Mn^{3+}Fe)_{\Sigma8.00}O_{16}$	2×2 tunnel	n.d.	McKeown and Post (2001)
8	Pyrolusite	$β-Mn^{4+}O_2 / (Mn^{4+}_{0.99}Al_{0.01})_{\Sigma1.00}O_2$	1×1 tunnel	61	This study
9	Pyrolusite (syn)	$β-Mn^{4+}O_2$	1×1 tunnel	61[c]	This study
10	Ramsdellite	$R-Mn^{4+}O_2 / (Mn^{4+}_{0.99}Al_{0.01})_{\Sigma1.00}O_2$	1×2 tunnel	62	This study
11	Romanèchite	$(Ba,H_2O)_2(Mn^{4+},Mn^{3+})_5O_{10} / Ba_{0.66}(Mn^{4+}_{3.68}Mn^{3+}_{1.32})_{\Sigma5.00}O_{10} \cdot 1.34H_2O$	2×3 tunnel	50[c]	McKeown and Post (2001)
12	Romanèchite (Ba-free, syn)	$(Na,H_2O)_2(Mn)_{10}O_{20} / Na_{1.08}(Mn^{4+}_{4.17}Mn^{3+}_{0.74})_{\Sigma4.91}O_{10} \cdot H_2O$	2×3 tunnel	60	This study
13	Todorokite	$(Mn^{2+},Ca,Na,K)(Mn^{4+},Mn^{2+},Mg)_6O_{12} \cdot 3H_2O / (Mn^{2+}_{0.18}Ca_{0.22}Na_{0.22}Sr_{0.14}K_{0.11}Zn_{0.08}Ba_{0.03}Si_{0.02})_{\Sigma0.99}(Mn^{4+}_{5.15}Mn^{2+}_{0.62}Mg_{0.23})_{\Sigma6.00}O_{12} \cdot 3H_2O$	3×3 tunnel	52	This study
14	Todorokite (syn)	$(Mn^{2+},Ca,Na,K)(Mn^{4+},Mn^{2+},Mg)_6O_{12} \cdot 3H_2O / Mn_{6.1}Mg_{0.7}O_{12} \cdot 3H_2O$	3×3 tunnel	56[c]	Peacock and Moon (2012)
Oxide minerals without layer or tunnel structure					
15	Bixbyite	$(Mn^{3+},Fe^{3+})_2O_3 / (Mn^{3+}_{1.74}Fe^{3+}_{0.21}Al_{0.05})_{\Sigma2.00}O_3$		60	This study
16	Bixbyite (syn)	$Mn^{3+}_2O_3$		70[c]	This study
17	Hausmannite	$(Mn^{2+},Mn^{3+})_3O_4 / (Mn^{3+}_{1.97}Mn^{2+}_{1.00}Fe^{3+}_{0.02})_{\Sigma3.00}O_{4.00}$	Spinel	70	This study
18	Manganosite (syn)	$Mn^{2+}O$		77[c]	This study
Mn(III) oxyhydroxides					
19	Feitknechtite (syn)	$β-Mn^{3+}O(OH)$		62[c]	Lefkowitz et al. (2013)
20	Groutite	$α-Mn^{3+}O(OH) / α-(Mn^{3+}_{0.98}Mg_{0.1})_{\Sigma0.99}O(OH)$		60	This study
21	Manganite (syn)	$γ-Mn^{3+}O(OH) / γ-Mn^{3+}_{1.00}O(OH)$		66	This study
Carbonate, phosphate, and silicate minerals					
22	Braunite	$Mn^{3+}Mn^{2+}_6O_8SiO_4 / (Mn^{3+}_{6.08}Mn^{2+}_{0.80}Ca_{0.15}Al_{0.01})_{\Sigma7.04}O_8Si_{0.95}O_4$	Nesosilicate	61	This study
23	Hendricksite	$K(Zn,Mg,Mn^{2+})_3Si_3AlO_{10}(OH)_2 / (K_{0.93}Na_{0.07})_{\Sigma1.00}(Zn_{1.28}Mg_{0.76}Mn^{2+}_{0.76}Fe^{2+}_{0.28}Ba_{0.01}Ti_{0.01})_{\Sigma3.10}(Si_{2.83}Al_{1.17})_{\Sigma4.00}O_{10}(F_{0.03}(OH)_{1.97})_{\Sigma2.00}$	Trioctahedral mica	8.3	This study
24	Masutomilite	$K(Li,Al,Mn^{2+})_3(Si,Al)_4O_{10}(F,OH)_2 / (K_{0.85}Na_{0.04})_{\Sigma0.89}(Li_{1.53}Al_{1.23}Mn^{2+}_{0.18})_{\Sigma2.94}(Si_{3.43}Al_{0.57})_{\Sigma4.00}O_{9.93}(F_{2.06}Cl_{0.01})_{\Sigma2.07}$	Trioctahedral mica	2.4	This study
25	Rhodochrosite	$Mn^{2+}CO_3 / (Mn^{2+}_{0.94}Zn_{0.03}Ca_{0.02}Mg_{0.01})_{\Sigma1.00}CO_3$	Carbonate	43	This study
26	Triplite	$(Mn^{2+},Fe^{2+},Ca,Mg)_2(PO_4)(F,OH) / (Mn^{2+}_{1.10}Fe^{2+}_{0.74}Ca_{0.10}Mg_{0.05})_{\Sigma2.00}(P_{0.99}O_{3.96})(F_{0.79}(OH)_{0.21})_{\Sigma1.00}$	Phosphate	27	This study
Organic Mn(II/III) compounds					
27	Mn(II) acetate tetrahydrate (syn)	$Mn^{2+}(CH_3COO)_2 \cdot 4H_2O$		22[c]	Ehlert et al. (2014)
28	Mn(II) oxalate dihydrate (syn)	$Mn^{2+}C_2O_4 \cdot 2H_2O$		31[c]	This study
29	Mn(III) acetate dihydrate (syn)	$Mn^{3+}(CH_3COO)_3 \cdot 2H_2O$		20[c]	This study
Adsorbed Mn(II) species					
30	Mn(II) ads. illite pH7	$K_{0.65}Al_{2.0}(Al_{0.65}Si_{3.35}O_{10})(OH)_2 \cdots Mn^{2+}_x$	Phyllosilicate	0.7	This study
31	Mn(II) ads. peat pH7		Organic sediment	0.9	This study
32	Mn(II) ads. peat pH5		Organic sediment	1.2	This study

[a] Nominal mineral formulas after Anthony et al. (2003). Empirical formulas of birnessites and δ-MnO$_2$ are taken from Villalobos et al. (2003, 2006), those of hollandite, lithiophorite, and romanèchite 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.

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

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

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

No.	Reference	Absorption		First derivative				
		1	2	1	2	3	4	5
Phyllomanganates								
1	Acid Na-birnessite (hex, syn)	6562.5		6540.5		6553.5	6558.0	6560.0
2	δ-MnO$_2$ (syn)	6561.8		6539.8		6552.5	6556.5	
3	Lithiophorite	6560.4		6539.5	6541.7	6551.5	6557.5	
4	Na-birnessite (tricl, syn)	6560.9		6539.7		6549.2	6553.6	6558.2
Tectomanganates								
5	Cryptomelane	6562.0		6540.8		6556.8		
6	Cryptomelane (syn)	6562.0		6540.6		6557.6		
7	Hollandite s.s	6561.2		6540.0	6542.0	6551.5	6556.0	
8	Pyrolusite	6561.0		6541.0		6552.3	6558.2	
9	Pyrolusite (syn)	6560.3		6540.6	6542.2	6552.7	6558.5	
10	Ramsdellite	6560.9		6540.6	6542.4	6552.2	6558.3	
11	Romanèchite	6561.7		6539.8	6541.7	6551.5	6556.5	
12	Romanèchite (Ba-free, syn)	6561.4		6539.8		6550.7	6557.3	
13	Todorokite	6562.1		6540.6		6551.1	6557.8	
14	Todorokite (syn)	6560.4		6538.9		6549.0	6556.2	
Oxide minerals without layer or tunnel structure								
15	Bixbyite	6558.2		6539.4		6547.9	6549.9	6553.4
16	Bixbyite (syn)	6559.5		6539.8		6548.4	6550.7	6553.8
17	Hausmannite	6559.1		6539.8		6546.8	6550.8	6556.8
18	Manganosite (syn)	6555.0	6568.6	6539.8		6544.5	6550.2	6554.0
Mn(III) oxyhydroxides								
19	Feitknechtite (syn)	6559.7		6539.5		6549.2	6555.5	
20	Groutite	6560.4		6539.0		6549.1	6555.1	
21	Manganite (syn)	6560.7		6539.4		6549.3	6556.1	
Carbonate, phosphate, and silicate minerals								
22	Braunite	6556.4		6540.0		6548.1	6553.0	
23	Hendricksite	6551.9	6556.4	6539.0		6546.9	6550.3	6555.3
24	Masutomilite	6552.3	6557.5	6539.3		6546.1	6551.1	6556.3
25	Triplite	6552.7		6540.1		6547.4	6548.1	
26	Rhodochrosite	6551.1	6562.4	6539.4		6548.9	6559.9	
Organic Mn(II/III) compounds								
27	Mn(II) acetate tetrahydrate (syn)	6551.9		6539.4		6548.4	6564.7	
28	Mn(II) oxalate dihydrate (syn)	6553.3		6539.0		6547.0	6551.5	
29	Mn(III) acetate dihydrate (syn)	6560.8		6539.0		6552.0	6557.5	
Adsorbed Mn(II) species								
30	Mn(II) ads. illite pH7	6552.2		6539.1		6547.4	6551.0	
31	Mn(II) ads. peat pH7	6552.8		6539.8		6549.3		
32	Mn(II) ads. peat pH5	6553.1		6539.5		6549.0		

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

No.	Reference	AOS[a] (nominal)	AOS[b] (titration)	AOS (XANES)	Mn^{2+}	Mn^{3+}	Mn^{4+}	Fit sum	R-factor[c] ($\times 10^5$)
Phyllomanganates									
1	Acid Na-birnessite (hex, syn)	3.92	3.94(0)	3.86	0.04	0.05	0.91	0.99	5
2	δ-MnO₂ (syn)	4.00	3.98(2)	3.90	0.01	0.08	0.91	0.99	11
3	Lithiophorite	3.70	n.d.	3.49	0.02	0.47	0.51	0.97	36
4	Na-birnessite (tricl, syn)	3.57	3.69(1)	3.84	0.03	0.10	0.87	0.97	22
Tectomanganates									
5	Cryptomelane	3.88	3.85(1)	3.84	0.04	0.08	0.88	0.99	9
6	Cryptomelane (syn)	3.88	3.88(2)	3.95	0.00	0.05	0.95	1.02	18
7	Hollandite s.s.	3.75	n.d.	3.75	0.08	0.09	0.83	0.96	42
8	Pyrolusite	4.00	4.03(2)	3.98	0.01	0.00	0.99	0.98	31
9	Pyrolusite (syn)	4.00	4.03(0)	4.00	0.00	0.00	1.00	1.00	21
10	Ramsdellite	4.00	4.02(1)	3.98	0.01	0.00	0.99	1.00	9
11	Romanèchite	3.50	n.d.	3.82	0.02	0.14	0.84	0.98	10
12	Romanèchite (Ba-free, syn)	3.84	3.76(1)	3.91	0.03	0.03	0.94	1.04	8
13	Todorokite	3.67	3.77(2)	3.77	0.01	0.21	0.78	1.02	6
14	Todorokite (syn)	3.67	3.70(2)	3.74	0.04	0.17	0.79	0.99	9
Oxide minerals without layer or tunnel structure									
15	Bixbyite	3.00	3.11(3)	3.08	0.16	0.61	0.24	1.00	17
16	Bixbyite (syn)	3.00	3.05	3.07	0.08	0.78	0.15	1.02	10
17	Hausmannite	2.67	2.72(1)	3.35	0.19	0.27	0.54	0.93	32
18	Manganosite (syn)	2.00	2.04(0)	2.12	0.94	0.00	0.06	1.00	118
Mn(III) oxyhydroxides									
19	Feitknechtite (syn)	3.00	n.d.	3.02	0.02	0.93	0.04	0.97	58
20	Groutite	3.00	3.05(1)	3.17	0.03	0.78	0.20	0.99	14
21	Manganite (syn)	3.00	3.07(3)	3.01	0.02	0.96	0.03	1.02	16
Carbonate, phosphate, and silicate minerals									
22	Braunite	2.86	2.98(4)	2.99	0.10	0.80	0.10	0.98	57
23	Hendricksite	2.00	2.32(11)	2.21	0.79	0.21	0.00	0.96	655
24	Masutomilite	2.00	2.41(13)	2.49	0.51	0.49	0.00	0.98	1130
25	Rhodochrosite	2.00	2.06(1)	2.08	0.96	0.00	0.04	0.99	38
26	Triplite	2.00	1.39(5)	2.01	0.99	0.01	0.00	0.99	62
Organic Mn(II/III) compounds									
27	Mn(II) acetate tetrahydrate (syn)	2.00	n.d.	2.00	1.00	0.00	0.00	0.96	45
28	Mn(II) oxalate dihydrate (syn)	2.00	2.04(1)	2.05	0.95	0.05	0.00	1.01	133
29	Mn(III) acetate dihydrate (syn)	3.00	3.00(0)	3.06	0.00	0.94	0.06	1.02	202
Adsorbed Mn(II) species									
30	Mn(II) ads. illite pH7	2.00	2.48	2.35	0.69	0.26	0.05	1.01	11
31	Mn(II) ads. peat pH5	2.00	n.d.	2.00	1.00	0.00	0.00	1.01	218
32	Mn(II) ads. peat pH7	2.00	n.d.	2.00	1.00	0.00	0.00	1.02	280

[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 = $\Sigma_i (data_i - fit_i)^2 / \Sigma_i data_i^2$.

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

No.	Reference	R-factor[b]	χ_v^{2b}	N_{idp}[c] k-range	N_{var}[c] R-range	ΔE_0(eV)[d]	CN[e] σ^2(Å²)[f]	R(Å)[g]	CN σ^2(Å²)	R(Å)	CN σ^2(Å²)	R(Å)	CN σ^2(Å²)	R(Å)	CN σ^2(Å²)	R(Å)
Phyllomanganates																
1	Acid Na-birnessite (hex, syn)	0.005	856	14.4 2.8-13.2	6 1.0-3.2	2.2(6)	O: 6.2(6) 0.0049(3)	1.90(0)	Mn: 5.3(4) 0.0046(1)	2.89(0)	Mn: 1.2(4) 0.0046	3.49(1)				
2	δ-MnO$_2$ (syn)	0.007	793	16.1 2.9-13.1	6 1.0-3.5	3.0(7)	O: 5.6(6) 0.0042(3)	1.90(0)	Mn: 4.7(3) 0.0044(2)	2.87(0)	Mn: 1.0 0.0044	3.44(2)				
3	Lithiophorite	0.009	74	14.7 3.5-11.3	8 1.0-4.0	-0.8(11)	O: 4.1(5) 0.0022(3)	1.92(1)	Mn: 6.0 0.0067(3)	2.92(1)	O: 4.0 0.0082(38)	3.56(3)	Mn: 4.0 0.0082	4.14(12)		
4	Na-birnessite (tricl, syn)	0.006	781	12.7 2.6-11.8	5 1.0-3.2	6.1(8)	O: 5.3(5) 0.0030(3)	1.92(0)	Mn: 6.8(8) 0.0066(3)	2.89(0)						
Tectomanganates																
5	Cryptomelane	0.008	769	16.2 2.7-13.0	6 1.0-3.5	0.8(7)	O: 5.0(4) 0.0025(3)	1.90(0)	Mn: 3.7(3) 0.0032(2)	2.88(0)	Mn: 4.0(4) 0.0032	3.44(0)				
6	Cryptomelane (syn)	0.016	351	17.8 2.7-13.0	6 1.0-3.5	1.4(10)	O: 5.8(7) 0.0024(7)	1.91(0)	Mn: 3.7(4) 0.0026(4)	2.89(1)	Mn: 4.2(6) 0.0026	3.45(1)				
7	Hollandite	0.006	142	13.6 3.5-11.3	7 1.0-3.8	-0.7(9)	O: 4.3(5) 0.0032(3)	1.91(0)	Mn: 3.6(4) 0.0062(4)	2.91(1)	Mn: 3.5(5) 0.0062	3.48(1)	Mn: 1.9(5) 0.0062	3.75(1)		
8	Pyrolusite	0.013	290	18.28 2.6-12.3	9 1.0-4.0	-5.5(9)	O: 5.6(8) 0.0028(4)	1.88(1)	Mn: 2.1(4) 0.0018(2)	2.87(1)	Mn: 5.6(6) 0.0018	3.43(1)	O: 8.0 0.0102(35)	4.01(5)	Mn: 4.0 0.0102	4.42(4)
9	Pyrolusite (syn)	0.013	53	23.0 2.7- 4.2	9 1.0-4.2	-5.3(7)	O: 5.6(6) 0.0023(3)	1.88(0)	Mn: 1.9(2) 0.0020(2)	2.88(1)	Mn: 7.1(6) 0.0020	3.43(0)	O: 8.0 0.0030(8)	3.93(2)	Mn: 4.0 0.0030	4.41(1)
10	Ramsdellite	0.006	70	69.3 2.7-13.8	7 1.0-3.6	-6.2(6)	O: 5.6(4) 0.0026(2)	1.89(0)	Mn: 3.2(4) 0.0026(2)	2.88(0)	Mn: 3.8(5) 0.0010(2)	3.43(0)				
11	Romanèchite	0.005	309	10.2 2.8-10.2	6 1.0-3.2	-2.9(10)	O: 4.7(9) 0.0025(4)	1.90(1)	Mn: 4.6(18) 0.0077(6)	2.90(1)	Mn: 2.8(13) 0.0077	3.47(2)				
12	Romanèchite (Ba-free, syn)	0.013	1548	14.5 2.9-11.8	6 1.0-3.6	-2.5(10)	O: 5.7(8) 0.0035(4)	1.90(1)	Mn: 4.4(8) 0.0044(4)	2.88(1)	Mn: 2.4(7) 0.0044	3.44(1)				
13	Todorokite	0.011	1593	18.5 2.6-13.9	9 1.0-3.6	0.4(8)	O: 5.3(5) 0.0032(3)	1.92(0)	Mn: 4.2(7) 0.0049(3)	2.87(0)	Mn: 2.7 0.0027(10)	3.43(1)	O: 6.0 0.0024(21)	3.71(3)		
14	Todorokite (syn)	0.011	834	18.3 2.7-13.9	9 1.0-3.6	-2.1(9)	O: 4.7(4) 0.0033(3)	1.92(0)	Mn: 3.8(8) 0.0055(4)	2.88(1)	Mn: 2.7 0.0069(19)	3.44(2)	O: 6.0 0.0072(43)	3.72(7)		
Oxide minerals without layer or tunnel structure																
15	Bixbyite[h]	0.011	667	14.2 2.6-11.0	5 1.0 - 3.7	-4.3(12)	O1: 4.0(5) 0.0070(6) / O2: 1.7(4) 0.0070	1.92(1) / 2.24(1)	Mn: 5.2(10) 0.0053(3)	3.11(1)	Mn: 6.0 0.0118(13)	3.57(1)				
16	Bixbyite (syn)[h]	0.020	204	15.9 2.7-12.1	5 1.0-3.7	-6.8(13)	O1: 4.0(6) 0.0059(7) / O2: 1.3(6) 0.0059	1.90(1) / 2.23(1)	Mn: 5.1(12) 0.0057(4)	3.09(1)	Mn: 6.0 0.0086(9)	3.54(1)				
17	Hausmannite	0.002	66	16.8 2.9-11.8	10 1.0-4.0	0.4(11)	O1: 4.1(3) 0.0071(3) / O2: 1.9(3) 0.0071	1.95(1) / 2.27(1)	Mn1: 1.3(1) 0.0028(5) / Mn2: 2.7(2) 0.0028	2.88(1) / 3.10(0)	Mn: 8.1(8) 0.0082	3.44(1)	Mn: 7.7(7) 0.0082(3)	3.73(1)		

Table 4. (continued)

No.	Reference	R-factor[b]	χ_v^{2b}	N_{idp}^c k-range	N_{var}^c R-range	ΔE_0 (eV)[d]	CN^e σ^2 (Å²)[f]	R (Å)[g]	CN σ^2 (Å²)	R (Å)	CN σ^2 (Å²)	R (Å)	CN σ^2 (Å²)	R (Å)	CN σ^2 (Å²)	R (Å)
Oxide minerals without layer or tunnel structure																
18	Manganosite (syn)[h]	0.010	29	21.8 2.3-13.6	5 1.0-3.6	-2.8(6)	O: 5.8(10) 0.0063(9)	2.22(0)	Mn: 12.0 0.0048(2)	3.13(0)	O: 8.0 0.0164(92)	3.84(0)				
Mn(III) oxyhydroxides																
19	Feitknechtite (syn)	0.002	8	14.2 2.7-11.1	10 1.0-3.7	0.3(7)	O1: 4.0(2) 0.0052(1) O2: 2.0(2) 0.0052	1.91(0) 2.22(1)	Mn1: 1.9(3) 0.0074(4) Mn2: 3.8(11) 0.0074	2.83(1) 2.99(0)	Mn: 4.0 0.0141(1)	3.33(1)	O: 8.0 0.0141	3.60(2)		
20	Groutite	0.008	113	19.1 2.8-13.7	12 1.0-3.8	3.6(11)	O1: 4.2(4) 0.0040(4) O2: 0.9(4) 0.0040 O3: 1.4(3) 0.0040	1.93(1) 2.15(4) 2.34(2)	Mn: 2.1(4) 0.0028(3)	2.88(1)	Mn: 2.0 0.0115(36)	3.38(3)	Mn: 4.0 0.0035(7) O: 8.0 0.0035	3.61(1) 3.77(2)		
21	Manganite (syn)	0.005	214	16.2 2.8-12.4	11 1.1-3.8	1.7(9)	O1: 4.7(4) 0.0062(3) O2: 2.0(3) 0.0062	1.93(0) 2.28(1)	Mn1: 1.0(1) 0.0021(6) Mn2: 1.0(1) 0.0021	2.77(1) 2.98(2)	O: 8.4(18) 0.0062 Mn: 4.0 0.0075(18)	3.61(2) 3.69(1)	Mn: 4.0 0.0075(14)	3.83(2)		
Carbonate, phosphate, and silicate minerals																
22	Braunite	0.011	26	14.9 2.9-11.4	8 1.0-3.8	5.4(10)	O1: 2.6(2) 0.0045(5) O2: 2.1(3) 0.0045 O3: 0.9(3) 0.0045	1.94(1) 2.25(1) 2.55(3)	Mn: 1.9(5) 0.0038(5)	3.17(1)	O: 5.3(18) 0.0063	3.77(2)				
23	Hendricksite	0.017	22	12.1 2.6-11.4	5 1.1-3.3	3.9(13)	O: 4.9(9) 0.0042(8)	2.16(1)	Mn/Fe: 2.0 0.0037(4) Zn: 2.5 0.0037	3.14(1) 3.14						
24	Masutomilite	0.022	52	12.1 2.1-10.5	6 1.0-3.3	4.2(15)	O/F: 4.9(7) 0.0027(1)	2.15(1)	Al: 2.5 0.0100 Mn: 0.4 0.0100	3.02(5) 3.02	Al/Si: 4.0 0.0100	3.24(3)	O: 4.0 0.0100	3.47(3)		
25	Rhodochrosite	0.012	42	21.7 2.2-11.5	12 1.1-4.8	2.7(9)	O: 6.3(8) 0.0050(5)	2.19(1)	C: 6.0 0.0034	3.08(2)	O: 6.0 0.0033(14)	3.28(1)	Mn: 6.0 0.0048	3.79(1)	O1: 6.0 0.0048(4) O2: 4.0 0.0048 Mn: 6.0 0.0032(1)	4.10(3) 4.58(1) 4.75(1)
26	Triplite	0.008	91	12.4 2.3-10.6	7 1.0-3.4	3.6(8)	F: 1.6 0.0067 O: 4.4 0.0067(1)	2.05(3) 2.15(1)	Mn/Fe: 1.0(4) 0.0073(13)	2.93(2)	P: 2.8(7) 0.0073	3.55(1)				

Table 4. (continued)

No.	Reference	R-factor[b]	χ_v^{2b} k-range	N_{idp}^{c} R-range	N_{var}^{c}	ΔE_0 (eV)[d]	CN^e σ^2 (Å²)[f]	R (Å)[g]	CN σ^2 (Å²)	R (Å)	CN σ^2 (Å²)	R (Å)	CN σ^2 (Å²)	R (Å)	CN σ^2 (Å²)	R (Å)
Organic Mn(II/III) compounds																
27	Mn(II) acetate tetrahydrate (syn)	0.015	175 13.2 2.3-11.1	6.0 1.0-3.4		2.1(10)	O:5.9(7) 0.0045(0)	2.18(1)	C: 5.2 0.0112(62)	3.19(4)	Mn: 1.6 0.0060(20)	3.40(2)				
28	Mn(II) oxalate dihydrate (syn)	0.029	476 19.0 2.8-12.3	8.0 1.0-4.2		6.9(9)	O: 6.5(6) 0.0041(4)	2.18(1)	C: 4.0 0.0041	2.95(2)	O-C[i]: 8.0 0.0062	3.11(12)	O: 6.0 0.0040	3.93(2)	C-O-C[i]: 4.0 0.0083	4.08(4)
															C-O[i]: 8.0 0.0062	4.23(2)
29	Mn(III) acetate dihydrate (syn)	0.013	703 24.2 2.7-13.7	9 0.9-4.4		5.7(8)	O1: 5.2(5) 0.0041(0) O2: 1.5(5) 0.0041	1.93(0) 2.20(1)	C: 4.0 0.0077(24)	2.98(2)	Mn: 2.0 0.0014(3)	3.40(0)	O: 2.0 0.0068(40)	4.37(5)		
Adsorbed Mn(II) species																
30	Mn(II) ads. illite pH7	0.005	5 9.9 2.5-10.5	5 1.0-3.0		-2.4(9)	O1: 2.0 0.0123(18) O2: 4.0 0.0123	1.92(1) 2.16(1)								
31	Mn(II) ads. peat pH5	0.016	540 14.4 2.0-10.5	5 1.3-4.0		3.3(9)	O: 6.0 0.0057(0)	2.18(1)	C: 1.0 0.0057	3.20(7)	C-O[i]: 8.0 0.0086	4.48(5)				
32	Mn(II) ads. peat pH7	0.017	266 14.4 2.0-10.5	5 1.3-4.0		3.4(10)	O: 6.0 0.0051(5)	2.18(1)	C: 1.0 0.0051	3.21(8)	C-O[i]: 8.0 0.0077	4.49(5)				

[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 = $\Sigma_i(\text{data}_i-\text{fit}_i)^2/\Sigma_i\text{data}_i^2$ and reduced $\chi^2 = (N_{idp}/N_{pts})\Sigma_i((\text{data}_i-\text{fit}_i)/\varepsilon_i)^2/(N_{idp}-N_{var})$, 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 CNs set in the final fit), and ε_i is the uncertainty of the ith data point.

[c]Number of independent points and fit variables in final fit, respectively.

[d]Energy-shift parameter.

[e]Coordination number (path degeneracy). Coordination numbers with assigned errors were fit individually and subsequently set in the final fit.

[f]Debye-Waller parameter. If no uncertainties are indicated, parameters were constrained.

[g]Mean half path length.

[h]A volumetric lattice expansion parameter was used to calculate atomic distances in bixbyites and manganosite (cubic crystal system).

[i]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 σ^2(Mn-O1)+0.5σ^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 σ^2(Mn-C)+σ^2(Mn-O1) and σ^2(Mn-C)+0.5σ^2(Mn-O1), respectively. For Mn(II) adsorbed to peat, the Debye-Waller parameter of the obtuse triangle MS path was defined as 1.5σ^2(Mn-O).
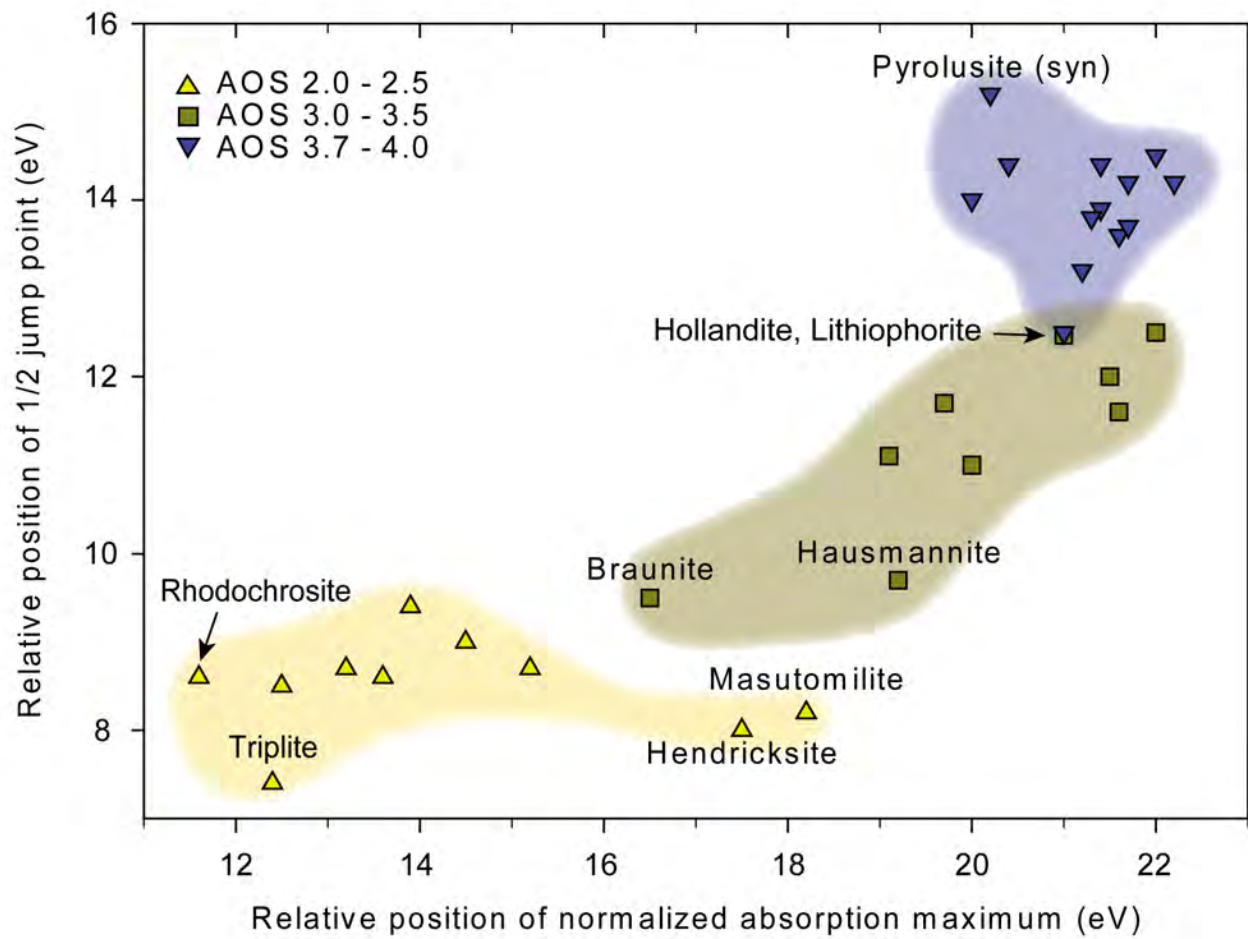
Figure 1

Figure 2

Figure 3
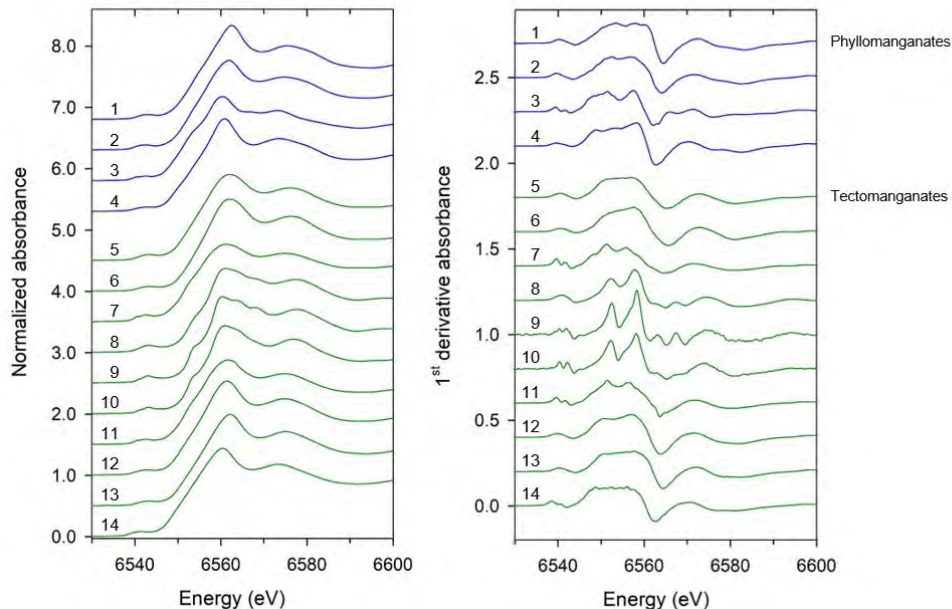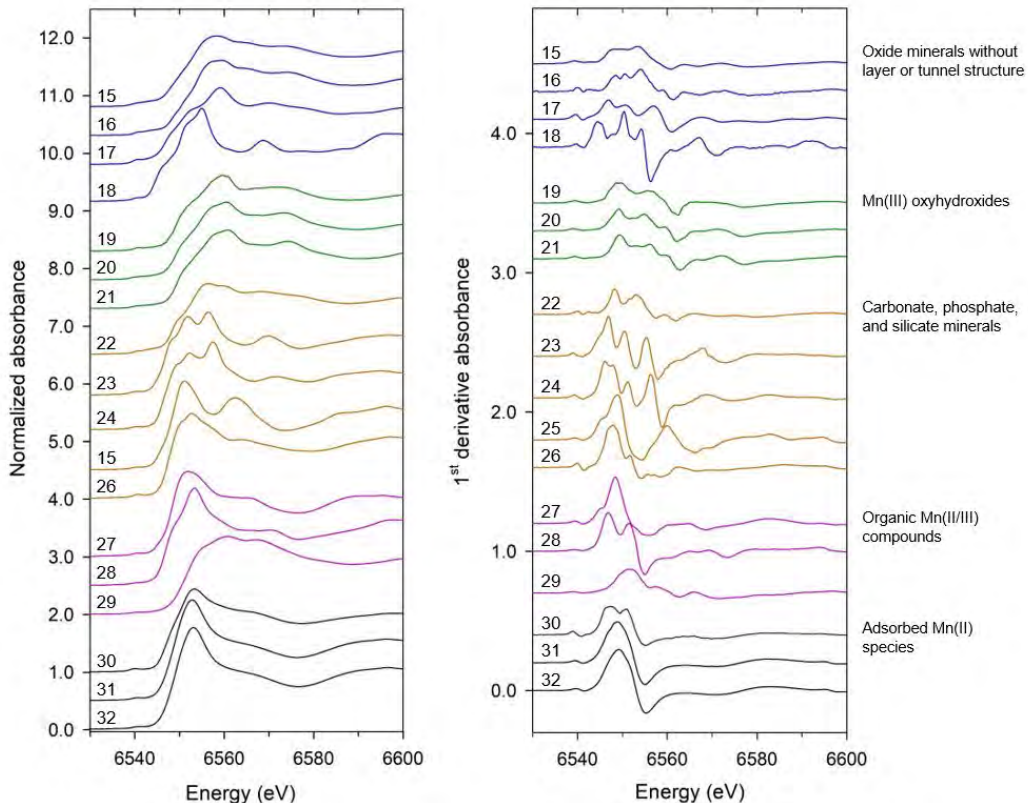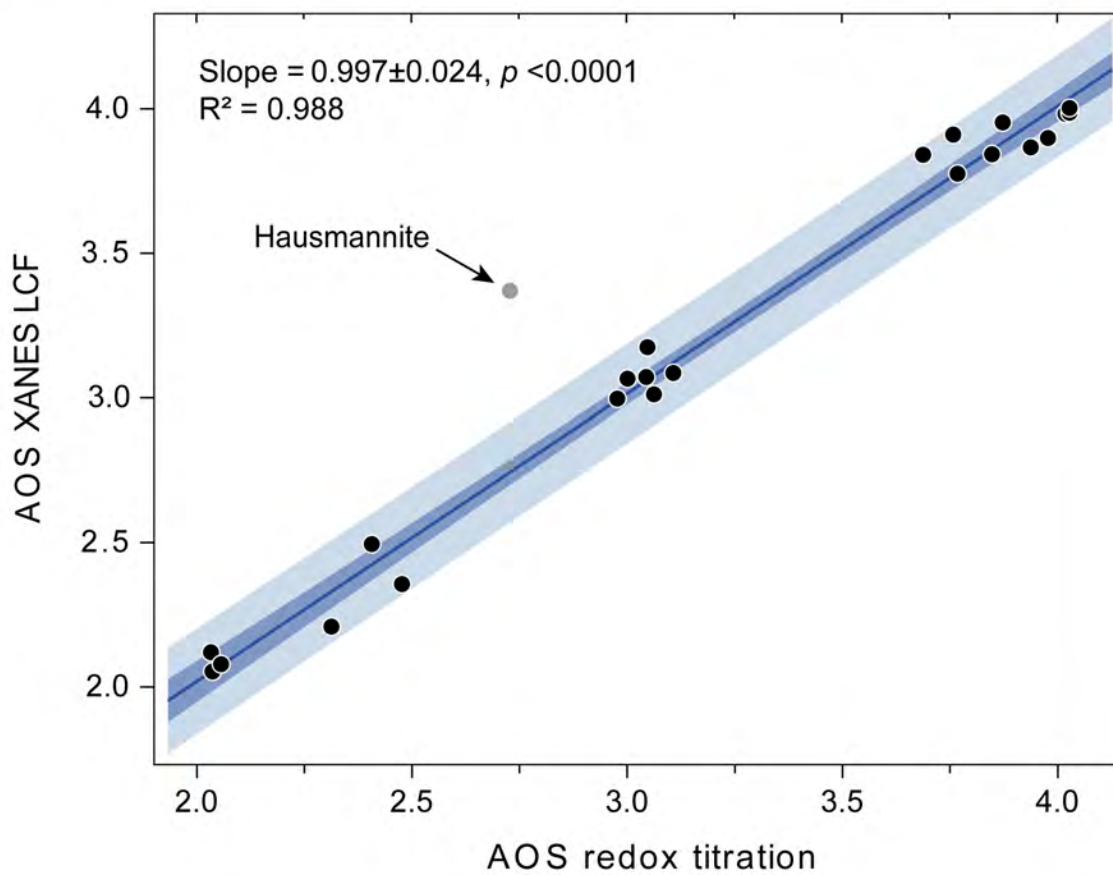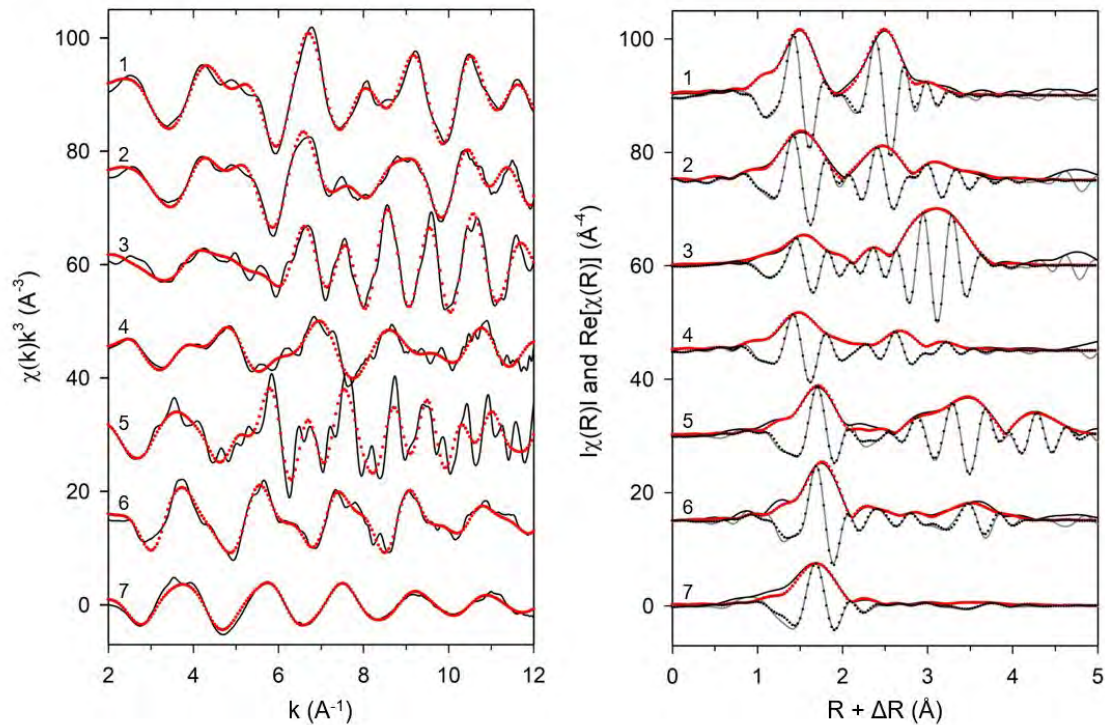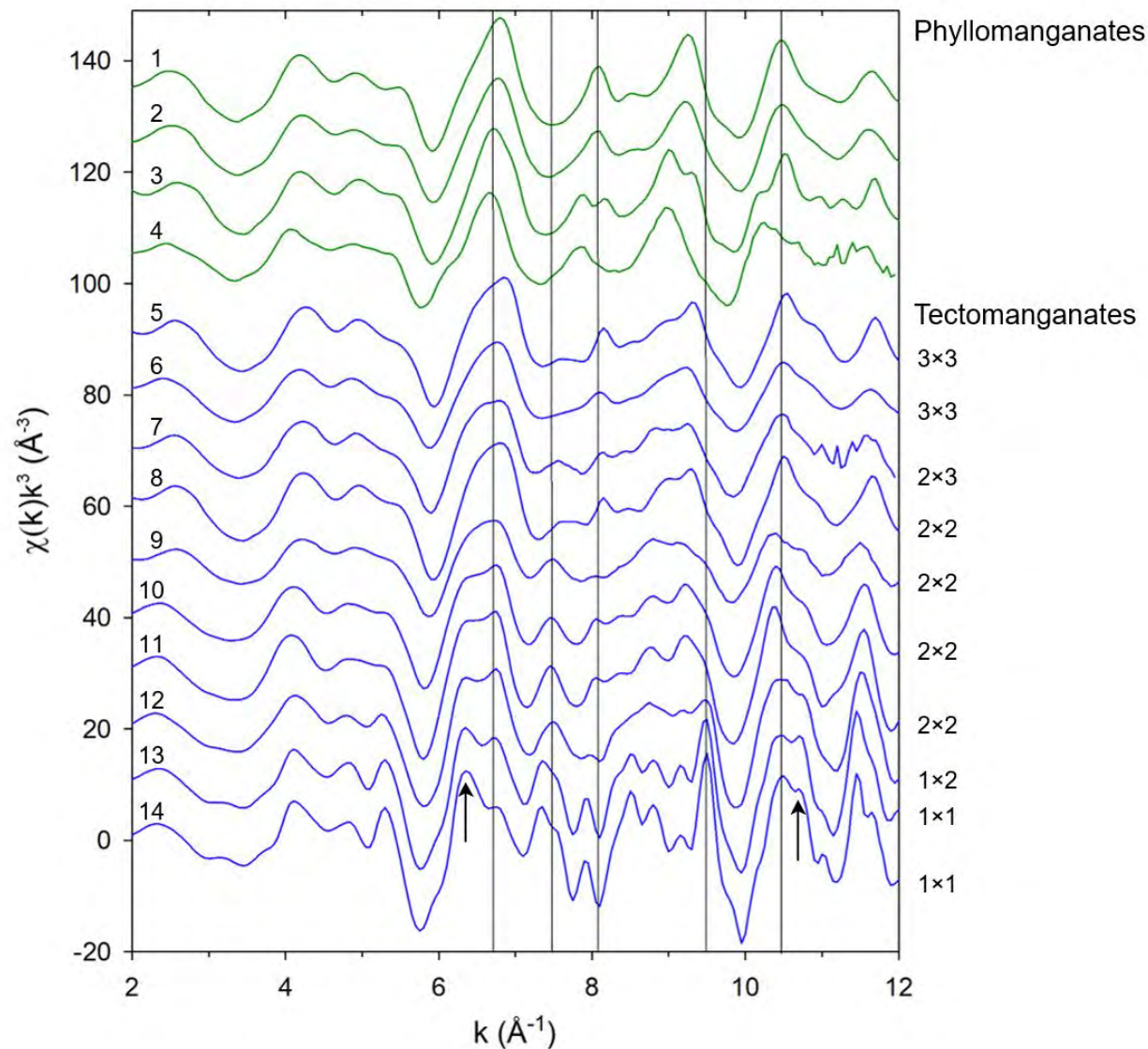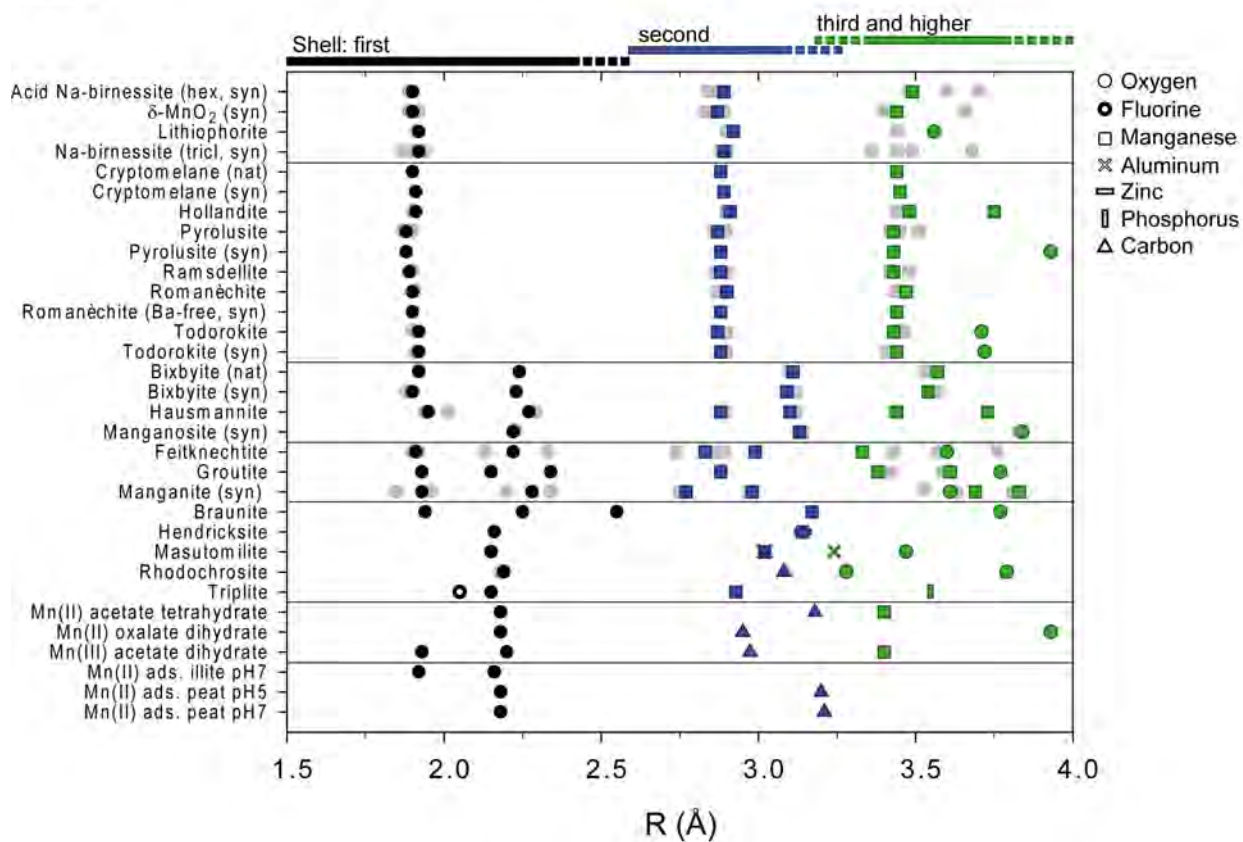
Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Correlation matrix (lower triangular). Column/row index key:
1 = Acid Na-birnessite (hex, syn); 2 = δ-MnO₂ (syn); 3 = Lithiophorite; 4 = Na-birnessite (tricl, syn); 5 = Cryptomelane; 6 = Cryptomelane (syn); 7 = Hollandite; 8 = Pyrolusite; 9 = Pyrolusite (syn); 10 = Ramsdellite; 11 = Romanèchite (Ba-free, syn); 12 = Romanèchite; 13 = Todorokite; 14 = Todorokite (syn); 15 = Bixbyite; 16 = Bixbyite (syn); 17 = Hausmannite; 18 = Manganosite (syn); 19 = Feitknechtite (syn); 20 = Groutite; 21 = Manganite (syn); 22 = Braunite; 23 = Hendricksite; 24 = Masutomilite; 25 = Rhodochrosite; 26 = Triplite; 27 = Mn(II) acetate tetrahydrate; 28 = Mn(II) oxalate dihydrate; 29 = Mn(III) acetate dihydrate; 30 = Mn(II) ads. illite pH7; 31 = Mn(II) ads. peat pH5; 32 = Mn(II) ads. peat pH7.

Group annotations: PM* (Phyllomanganates); Tectomanganates; Oxide minerals without layer or tunnel structure; Mn(III) oxyhydroxides; Carbonate, phosphate, and silicate minerals; Organic Mn(II/III) compounds; Adsorbed Mn(II) species.

Row	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
1 Acid Na-birnessite (hex, syn)																															
2 δ-MnO₂ (syn)	0.99																														
3 Lithiophorite	0.73	0.80																													
4 Na-birnessite (tricl, syn)	0.86	0.90	0.88																												
5 Cryptomelane	0.92	0.94	0.78	0.88																											
6 Cryptomelane (syn)	0.91	0.93	0.77	0.87	1.00																										
7 Hollandite	0.84	0.88	0.90	0.87	0.94	0.94																									
8 Pyrolusite	0.76	0.78	0.58	0.70	0.90	0.90	0.81																								
9 Pyrolusite (syn)	0.69	0.72	0.53	0.65	0.84	0.85	0.76	0.98																							
10 Ramsdellite	0.86	0.88	0.69	0.80	0.96	0.96	0.87	0.96	0.92																						
11 Romanèchite (Ba-free, syn)	0.92	0.94	0.78	0.96	0.95	0.95	0.89	0.82	0.76	0.90																					
12 Romanèchite	0.90	0.93	0.89	0.89	0.95	0.95	0.98	0.79	0.73	0.88	0.91																				
13 Todorokite	0.95	0.95	0.73	0.92	0.95	0.94	0.86	0.82	0.77	0.90	0.99	0.90																			
14 Todorokite (syn)	0.94	0.97	0.82	0.96	0.95	0.94	0.91	0.80	0.74	0.89	0.98	0.94	0.98																		
15 Bixbyite							0.20				0.20																				
16 Bixbyite (syn)							0.22				0.21				0.99																
17 Hausmannite	0.34	0.38	0.37	0.30	0.52	0.52	0.55	0.57	0.57	0.50	0.39	0.50	0.37	0.40	0.37	0.36															
18 Manganosite (syn)	-0.24	-0.30	-0.47	-0.42	-0.26	-0.27	-0.33	-0.19	-0.23	-0.26	-0.31	-0.30	-0.26	-0.32	0.38	0.31															
19 Feitknechtite (syn)	0.54	0.56	0.49	0.43	0.48	0.44	0.56	0.41	0.39	0.45	0.43	0.59	0.49	0.54	0.64	0.62	0.43														
20 Groutite	0.80	0.82	0.77	0.73	0.68	0.65	0.71	0.48	0.41	0.60	0.69	0.78	0.69	0.77	0.16	0.15	0.26	-0.22	0.66												
21 Manganite (syn)	0.52	0.56	0.55	0.50	0.42	0.39	0.49	0.34	0.31	0.42	0.43	0.55	0.47	0.54	0.34	0.34	0.27	-0.17	0.84	0.72											
22 Braunite	0.35	0.38	0.32	0.26	0.37	0.35	0.42	0.29	0.26	0.33	0.29	0.43	0.34	0.37	0.75	0.73	0.48	0.29	0.75	0.39	0.49										
23 Hendricksite	-0.42	-0.47	-0.55	-0.58	-0.47	-0.48	-0.51	-0.40	-0.42	-0.47	-0.52	-0.48	-0.50	-0.53	0.33	0.28	0.03	0.63		-0.39	-0.27	0.12									
24 Masutomilite	-0.37	-0.41	-0.30	-0.42	-0.38	-0.37	-0.38	-0.39	-0.40	-0.40	-0.43	-0.37	-0.45	-0.45					-0.46	-0.39	-0.38	-0.35	0.57								
25 Rhodochrosite	-0.34	-0.37	-0.35	-0.36	-0.29	-0.27	-0.34	-0.16	-0.14	-0.21	-0.35	-0.37	-0.37	-0.40			-0.33	-0.34	-0.37	-0.44	-0.26	-0.24	0.31	0.46							
26 Triplite	-0.62	-0.63	-0.48	-0.64	-0.58	-0.56	-0.57	-0.47	-0.43	-0.53	-0.67	-0.58	-0.70	-0.69	-0.29	-0.29	-0.16	0.16	-0.50	-0.45	-0.46	-0.37	0.50	0.72	0.56						
27 Mn(II) acetate tetrahydrate	-0.44	-0.49	-0.46	-0.50	-0.44	-0.43	-0.49	-0.32	-0.30	-0.37	-0.49	-0.50	-0.49	-0.53	-0.31	-0.34	-0.22	0.22	-0.48	-0.50	-0.47	-0.42	0.54	0.76	0.70	0.77					
28 Mn(II) oxalate dihydrate	-0.43	-0.45	-0.35	-0.43	-0.40	-0.39	-0.42	-0.31	-0.29	-0.36	-0.47	-0.43	-0.51	-0.51	-0.27	-0.29	-0.25	0.20	-0.42	-0.33	-0.45	-0.33	0.44	0.60	0.48	0.84	0.80				
29 Mn(III) acetate dihydrate	0.64	0.70	0.71	0.63	0.75	0.74	0.80	0.71	0.72	0.76	0.64	0.80	0.66	0.71	0.29	0.30	0.56	-0.28	0.71	0.63	0.64	0.54	-0.49	-0.46	-0.25	-0.41	-0.49	-0.38			
30 Mn(II) ads. illite pH7	-0.37	-0.40	-0.30	-0.45	-0.40	-0.40	-0.41	-0.36	-0.36	-0.38	-0.49	-0.38	-0.50	-0.48	-0.18	-0.19		0.25	-0.29	-0.25	-0.23	-0.22	0.63	0.81	0.60	0.86	0.85	0.81	-0.35		
31 Mn(II) ads. peat pH5	-0.55	-0.59	-0.50	-0.57	-0.56	-0.55	-0.59	-0.48	-0.47	-0.53	-0.61	-0.58	-0.63	-0.64	-0.29	-0.30	-0.27	0.26	-0.49	-0.47	-0.45	-0.41	0.61	0.80	0.65	0.87	0.94	0.87	-0.57	0.92	
32 Mn(II) ads. peat pH7	-0.53	-0.57	-0.48	-0.56	-0.54	-0.54	-0.57	-0.46	-0.46	-0.51	-0.59	-0.56	-0.62	-0.63	-0.29	-0.30	-0.25	0.27	-0.49	-0.45	-0.45	-0.40	0.61	0.80	0.65	0.88	0.94	0.87	-0.55	0.93	1.00

Legend: 1 | >0.9 | >0.8 | >0.7 | >0.6 | ≤0.6

*PM = Phyllomanganates

Figure 9

Figure 10