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Mario Villalobos, Bruno Lanson, Alain Manceau, Brandy Toner, Garrison Sposito. Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *American Mineralogist*, Mineralogical Society of America, 2006, 91, pp.489-502. <10.2138/am.2006.1925>. <hal-00193592>

**HAL Id: hal-00193592**

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Submitted on 4 Dec 2007

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Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*

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ABSTRACT

X-ray diffraction (XRD) and Mn K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy were combined to elaborate a structural model for phylломanganates (layer-type Mn oxide) lacking 3D ordering (turbostratic stacking). These techniques were applied to a sample produced by a common soil and freshwater bacterium (*Pseudomonas putida*) and to two synthetic analogs,  $\delta$ -MnO<sub>2</sub> and “acid birnessite”, obtained by the reduction of potassium permanganate with MnCl<sub>2</sub> and HCl, respectively. To interpret the diffraction and spectroscopic data, we applied an XRD simulation technique utilized previously for well-crystallized birnessite varieties, complementing this approach with single-scattering-path simulations of the Mn K-edge EXAFS spectra. Our structural analyses revealed that all three Mn oxides have an hexagonal layer symmetry with layers comprising edge-sharing Mn<sup>4+</sup>O<sub>6</sub> octahedra and cation vacancies, but no layer Mn<sup>3+</sup>O<sub>6</sub> octahedra. The proportion of cation vacancies in the layers ranged from 6 to 17 %, these vacancies being charge-compensated in the interlayer by protons, alkali metals, and Mn atoms, in amounts that vary with the phylломanganate species and synthesis medium. Both vacancies and interlayer Mn were

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31 most abundant in the biogenic oxide. The diffracting crystallites contained three to six  
32 randomly stacked layers, and have coherent scattering domains of 19-42 Å in the  $c^*$  direction,  
33 and 60-85 Å in the  $ab$  plane. Thus, the Mn oxides investigated here are nanoparticles that  
34 bear significant permanent structural charge resulting from cation layer vacancies and  
35 variable surface charge from unsaturated O atoms at layer edges.

36

37

## INTRODUCTION

38

39 Manganese 2+ oxidation occurs primarily through biological mediation in the oxic and  
40 oxic/anoxic transition zone of aqueous environments (Tipping et al. 1984; Nealson et al.  
41 1988; Tebo 1991; Ghiorse and Ehrlich 1992; Bartlett and James 1993; Wehrli et al. 1995;  
42 Tebo et al. 1997, Harvey and Fuller 1998; Tebo and He 1999; Marble et al. 1999; Morgan  
43 2000; Kay et al. 2001). The oxidation products are mainly insoluble  $Mn^{4+}$  oxides of the  
44 birnessite family (i.e., hydrous phylломanganates) comprising edge-sharing  $Mn-O_6$  octahedra  
45 with high negative permanent structural charge, due principally to vacant cation layer sites,  
46 and correspondingly high cation sorption capacities (Chukhrov et al. 1985; Strobel et al.  
47 1987; Drits et al. 1997; Silvester et al. 1997; Lanson et al. 2000; Bilinski et al. 2002).  
48 Todorokite, a Mn oxide with tunnel structure, has also been found associated with birnessites  
49 in natural settings, but, since the latter are believed to be precursors to formation of the  
50 former (Golden et al. 1987; Shen et al. 1993; Tian et al. 1997; Ching et al. 1999; Luo et al.  
51 1999; Feng et al. 2001), todorokite is probably not a direct product of microbial oxidation.

52

53 Natural Mn oxides often are poorly-crystalline solids (Tipping et al. 1984; Friedl et al. 1997;  
54 McKeown and Post 2001; Bilinski et al. 2002; Manceau et al. 2003, 2004) and rather few  
55 structural investigations of them have been performed (Chukhrov et al. 1985, 1989; Manceau

56 et al. 1992; Gorshkov et al. 1992). Mineralogical techniques that rely on the presence of  
57 long-range order, such as X-ray and electron diffraction, have been applied mainly to  
58 synthetic analogs of natural birnessites, most often with an enhanced three-dimensional (3D)  
59 ordering (Holland and Walker 1996; Drits et al. 1997; Silvester et al. 1997; Lanson et al.  
60 2000, 2002a; Post et al. 2002; Jurgensen et al. 2004). These techniques have revealed the  
61 presence of two-layer symmetries, orthogonal ( $a > b\sqrt{3}$ ) as in triclinic Na-birnessite, and  
62 hexagonal ( $a = b\sqrt{3}$ ) as in H-birnessite, depending on the predominant origin of the layer  
63 charge ( $\text{Mn}^{3+}$  for  $\text{Mn}^{4+}$  substitution, or vacant  $\text{Mn}^{4+}$  sites within the octahedral sheet,  
64 respectively). H-birnessite is formed under acidic pH conditions (Silvester et al. 1997). It  
65 has the hexagonal unit-cell parameters  $a = 4.940 \text{ \AA}$ ,  $b = a/\sqrt{3} = 2.852 \text{ \AA}$ ,  $c = 7.235 \text{ \AA}$ ,  $\alpha = \beta =$   
66  $\gamma = 90^\circ$ , with 0.833 Mn ions and 0.167 cation vacancies per layer octahedron, and 0.167  
67 interlayer  $\text{Mn}^{3+}$  ions located above or below layer vacancies in a triple-corner sharing  
68 configuration. The vacancies are long-range ordered, in that they appear in every third row of  
69 Mn cations along [100], with half of the Mn sites along these rows being vacant (Drits et al.  
70 1997). Water molecules associated with interlayer Mn cations provide for strong hydrogen  
71 bonds between the layers (Lanson et al. 2000).

72

73 Villalobos et al. (2003) characterized a set of analogs of natural birnessites showing a limited  
74 3D ordering, including a biogenic Mn oxide produced in culture by a common soil and  
75 freshwater bacterium, *Pseudomonas putida*. Based on comparison of their layer symmetry,  
76 Mn oxidation numbers, and other physicochemical properties, all of the Mn oxides  
77 investigated appeared to be more structurally related to hexagonal H-birnessite than to the  
78 triclinic Na-birnessite variety. Also, the biogenic Mn oxide was concluded to have reactive  
79 and structural properties intermediate between those of the synthetic c-disordered  
80 phyllomanganates  $\delta\text{-MnO}_2$  and “acid birnessite”, which are formed through the reduction of



81 permanganate with  $\text{MnCl}_2$  or  $\text{HCl}$ , respectively. More recently, Jurgensen et al. (2004)  
82 studied the structure of the Mn oxide produced by another bacterium species (*Leptothrix*  
83 *discophora*) by X-ray absorption fine structure (XAFS) spectroscopy and X-ray diffraction  
84 (XRD). They found that this compound consists of single octahedral-layer microcrystals  
85 composed of  $\text{Mn}^{4+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{2+}$  similarly to triclinic Na-birnessite. They also identified  
86 the possible location of some Mn octahedra in corner-sharing configuration with those from  
87 the layer plane, as in H-birnessite.

88  
89 The birnessite samples previously studied by Villalobos et al. (2003) appear to have simple  
90 layer structures made up almost entirely of  $\text{Mn}^{4+}$  octahedra, their complexity arising from the  
91 presence of layer vacancies and lack of 3D ordering. In the present paper, we extend our  
92 previous work with a detailed structural investigation of the same samples using quantitative  
93 XRD and extended XAFS (EXAFS) spectroscopy. To interpret the XRD data, we applied a  
94 simulation technique utilized previously for birnessites with an enhanced 3D ordering  
95 (Manceau et al. 1997; Drits et al. 1998a; Lanson et al. 2000, 2002a, b), complementing this  
96 approach with single-scattering-path analyses of Mn K-edge EXAFS spectra.

97

98

## EXPERIMENTAL METHODS

99

### 100 **Synthesis and Characterization of Mn Oxide Samples**

101

102 The biogenic Mn oxide and its two synthetic analogs were prepared using methods described  
103 in Villalobos et al. (2003). Briefly, the biogenic Mn oxide was produced in cultures of  
104 *Pseudomonas putida* strain MnB1 provided by Dr. B. M. Tebo (Scripps Institution of  
105 Oceanography). Bacteria were grown at 27 °C to the stationary phase of growth in a liquid

106 suspension rich in nutrients and in the presence (or absence, for a cell control sample) of total  
107 ( $\text{Mn}^{2+}$ ) = 1.0 mM. A sample of the biogenic oxide was cleaned of organic material by  
108 gradual iterative oxidation using 0.2 % NaOCl reagent, taking care not to oxidize  $\text{Mn}^{4+}$  or  
109  $\text{Mn}^{3+}$  in the sample.  $\delta$ - $\text{MnO}_2$  was prepared using a “redox” method with stoichiometric  
110 amounts of  $\text{KMnO}_4$  and  $\text{MnCl}_2$  reagents (Catts and Langmuir 1986; Mandernack et al. 1995;  
111 Luo and Suib 1997; Luo et al. 2000). Physicochemical characterization of the sample  
112 (Villalobos et al. 2003) indicated a composition exclusively of  $\text{Mn}^{4+}$  and a highly pH-  
113 dependent cation sorption capacity. Acid birnessite was prepared by reducing  $\text{KMnO}_4$  with  
114 concentrated HCl at boiling temperature (McKenzie 1971). The solids were oven-dried  
115 overnight at 70 °C, except for acid birnessite, which was freeze-dried, and a sample of  
116 uncleaned biogenic oxide, which was washed, centrifuged, and left as a wet paste for in-situ  
117 EXAFS spectroscopy.

118

119 Thermogravimetric analyses (TGA) were performed to determine the water content on ca. 20  
120 mg of the dried samples except for the uncleaned biogenic oxide. The weight loss was  
121 measured by heating the samples on a Pt tray from room temperature to ca. 250 °C at a rate  
122 of 10 °C/min (SDT 2960 apparatus from TA Instruments). Alumina powder was used as  
123 reference material for weight loss calibrations. Two peaks were obtained in plots of  
124 weight/temperature differentials vs. temperature for all samples. They were decomposed  
125 using Galactic Grams 32 (vol. 6) software to determine the fractions of loosely bound  
126 (removed at < 80 °C) and strongly sorbed water (retained up to 250 °C), but excluding  
127 structural water bound to interlayer Mn cations. Duplicate analyses per sample were  
128 performed and the results obtained were used to constrain the water contents in the XRD  
129 simulations. Results are listed in Table 1.

130

131

## 132 **X-ray Diffraction**

133

134 Dry samples were crushed in an agate mortar, and powder XRD patterns (CuK $\alpha$  radiation,  $\lambda =$   
135 1.5418 Å) were collected with a Bruker D5000 powder diffractometer equipped with a Kevex  
136 Si(Li) solid-state detector. Intensities were measured at 0.04 ° 2 $\theta$  intervals with 40s counting  
137 time per step.

138 Simulations of XRD patterns were performed following the trial-and-error procedure  
139 developed by Drits and Tchoubar (1990) and applied previously to both natural and synthetic  
140 birnessites (Chukhrov et al. 1985; Manceau et al. 1997; Drits et al. 1998a; Lanson et al. 2000,  
141 2002a, 2002b). Details on the programs used to simulate XRD patterns and on the fitting  
142 procedure are given by Drits and Tchoubar (1990), Drits et al. (1998a), and Plançon (2002).

143 As the main features of XRD profiles recorded for the three samples resemble those reported  
144 by Drits et al. (1997) for turbostratic birnessite, the experimental patterns were divided for the  
145 simulations in two angular domains containing different families of reflections. In the low-  
146 angle region (5-30 ° 2 $\theta$  CuK $\alpha$  – d-spacing >10 to 3.0 Å), 00 $l$  reflections were calculated to  
147 assess the validity of the lamellar structure proposed by Villalobos et al. (2003) for the  
148 synthetic oxides. In addition, the simulation of 00 $l$  reflections allowed quantification of the  
149 extent of coherent scattering domains (CSDs) along the axis perpendicular to the **ab** plane (**c\***  
150 axis) using a lognormal distribution of CSD sizes parameterized by an average number of  
151 layers ( $N_{Av}$  – Drits et al. 1998b). In the high-angle range (32-75 ° 2 $\theta$  CuK $\alpha$  –  $d$ -spacing 2.80-  
152 1.27 Å), the 20 $l$ , 11 $l$  and the 02 $l$ , 31 $l$  reflections (Miller indexing based on a C-centered unit  
153 cell) were calculated to determine the structure of both the octahedral layer and the interlayer  
154 region (atomic coordinates and occupancies of the different sites). CSDs in the **ab** plane were  
155 assumed to have a disk-like shape whose average radius was constrained by fitting the first of

156 the two high-angle maxima. For all samples, the background was assumed to decrease  
157 linearly over the angular range considered. The average Mn oxidation number along with the  
158 alkali metal and structural water content of the samples were used to constrain initial  
159 assumptions about the stoichiometry of interlayer species in the simulations. Quality of fit  
160 was assessed over the 34-75 ° 2 $\theta$  CuK $\alpha$  range assuming the commonly employed  $R_{wp}$  factor,  
161 and comparing it to the statistical error associated with measured intensities ( $R_{Exp}$ ) (Howard  
162 and Preston 1989).

163

### 164 **EXAFS Spectroscopy**

165

166 Manganese K-edge EXAFS spectra were measured at room temperature on wiggler beamline  
167 4-3 at the Stanford Synchrotron Radiation Laboratory in transmission mode. A Si(220)  
168 crystal pair was used to create monochromatic X-rays and a Pt-coated mirror was used to  
169 reject harmonic X-rays. A 1-mm vertical entrance slit located 17.2 m from the source was  
170 used to improve the energy resolution by reducing the beam divergence on the  
171 monochromator. Dry Mn oxide samples were mixed with LiCO<sub>3</sub> [Mn oxide:LiCO<sub>3</sub> (w/w)  
172  $\approx$ 1:10], to ensure an absorbance of the edge jump of 1 to 1.5, then mounted on 1-mm thick  
173 Teflon holders in 25 mm x 3 mm slots. Raw biogenic oxide with cellular material was  
174 centrifuged and mounted directly as wet paste into these holders. Samples were held in place  
175 with Kapton tape X-ray windows. Spectra were acquired over the energy range 6400 to 7400  
176 eV, with typically two to three runs per sample performed, each run taking approximately 30  
177 min. Either a permanganate solid (Mn<sup>7+</sup>) (absorption edge jump at 6543 eV set at the  
178 maximum of the first derivative of the edge) or a Mn metal foil (absorption edge jump at  
179 6539 eV) were used to calibrate the monochromator before every sample run. No beam-  
180 induced changes in Mn oxidation state were observed.

181  
182 The EXAFS data analysis was performed in the single-scattering approximation using home-  
183 made software for data normalization and Fourier transformation, and WinXAS (Ressler  
184 1998) for spectral simulations. Fourier transformations were done on the entire  $k^3\chi(k)$  curves  
185 shown in the Results section with a Kaiser-Bessel window ( $\tau = 3$ ). Transformation from  
186 reciprocal ( $k$ ) to real (R) space produces radial structure functions (RSFs) with peaks  
187 corresponding to average absorber-backscatterer distances, but deviating from the true R  
188 distance by  $\Delta R$  due to a phase shift. Spectral simulations were performed on Fourier-filtered  
189 data using Mn-O and Mn-Mn phase shift and amplitude functions calculated with FEFF v. 7  
190 (Zabinsky et al. 1995) for the  $\lambda$ -MnO<sub>2</sub> reference (Thackeray et al. 1993). The Mn-O and Mn-  
191 Mn Feff files were tested on the spectrum of the reference, and good agreement was found  
192 between EXAFS and crystallographic values.  $\Delta E$ , the difference between the experimental  
193 (taken to be the half-edge jump point) and theoretical origins for the energy scale (E), was  
194 treated as a single adjustable parameter for all sets of backscattering atoms, and  $S_0^2$ , the  
195 amplitude reduction factor, was calibrated using  $\lambda$ -MnO<sub>2</sub>. Since the EXAFS analysis in the  
196 present work is limited to single-scattering-path calculations, any interpretation of long  
197 distance Mn-Mn pairs shells ( $R + \Delta R > 3.5 \text{ \AA}$ ), which requires full multiple-scattering  
198 calculations, is semi-quantitative. Below this distance, multiple scattering (MS) contributions  
199 are negligible (see Figure 15 of Manceau et al. 1998).

200

## 201 **RESULTS AND DISCUSSION**

202

### 203 **XRD Patterns**

204 Figure 1 shows a maximum of four major XRD peaks for the Mn oxide samples studied,  
205 whose positions and relative intensities closely resemble those reported by Drits et al. (1997)

206 for turbostratic birnessite. From this positive comparison it is possible to hypothesize that the  
207 two peaks occurring at  $\sim 7.3$ - $8.0$  Å and  $3.6$ - $3.8$  Å correspond to 001 and 002 basal reflections,  
208 although they do not strictly define a rational series. In addition, these reflections are  
209 significantly shifted as compared to the positions of 00l reflections commonly reported for  
210 birnessite samples. The two peaks observed at higher angles ( $2.42$  -  $2.44$  and  $1.41$  -  $1.42$  Å)  
211 likely correspond to 20,11, and 02,31 bands, respectively, choosing a C-centered layer cell.  
212 The ratio of the  $d$  values of the two bands ( $1.720$  -  $1.725$ ) is close to the  $1.732 = \sqrt{3}$  value  
213 expected for layers having a hexagonal symmetry. These bands do not show significant  
214 modulations of the  $hkl$  reflections and instead exhibit a strong asymmetry on their high-angle  
215 side. This profile shape is characteristic of lamellar compounds with a turbostratic stacking,  
216 i.e., lacking well-defined displacement/rotation between successive layers (Brindley and  
217 Brown 1980). A broad “hump” is however visible at ca.  $50$ - $55^\circ$   $2\theta$   $\text{CuK}\alpha$  for all three  
218 samples (Figure 1). In comparison to the acid-birnessite (Fig. 1a), the first two maxima at  $\sim 8$   
219 and  $3.8$  Å for  $\delta$ - $\text{MnO}_2$  are broadened (Fig. 1b), and also significantly shifted relative to their  
220 ideal positions for a “ $7$  Å” lamellar compound. The broadening of the basal reflections of  $\delta$ -  
221  $\text{MnO}_2$  extends to the 20,11 and 02,31 bands, and the broad “hump” between  $50$  and  $55^\circ$   $2\theta$   
222  $\text{CuK}\alpha$  has a different shape from that of the acid birnessite pattern. The two low-angle  
223 maxima of the pattern for the biogenic oxide are at  $\sim 7.6$  and  $3.8$  Å, and have a shape  
224 intermediate between those of the two previous samples (Fig. 1c). The biogenic oxide pattern  
225 exhibits an additional shoulder on the low-angle side of the  $3.8$  Å maximum. This shoulder  
226 arises from the contribution of dead cells to the diffracted intensity, as shown on the XRD  
227 pattern from the bacteria alone (Fig. 1d). The admixture of bacterial cells does not modify  
228 significantly the pattern from the biogenic oxide component in the high-angle region. The  
229 two 20,11 and 02,31 bands are still observed for the biogenic oxide, but the high-angle tail of

230 the former is less pronounced than in the two other samples, and the hump is slightly shifted  
231 to higher  $2\theta$  values.

232

### 233 **Simulations of the Low-Angle Region (5-30° $2\theta$ CuK $\alpha$ )**

234

235 One objective of these simulations was to verify if the observed non-rationality and the  
236 significant positional shift of the two diffraction maxima observed in this low-angle range  
237 was related to the small dimensions of the CSDs along the  $c^*$  direction as described by Drits  
238 and Tchoubar (1990) for layer silicates. Calculations were performed assuming a lamellar  
239 structure for all three oxides considered. Elementary birnessite layers consist of the sheet of  
240 Mn octahedra itself, which possibly contains vacant layer sites, and of associated interlayer  
241 species, which include interlayer Mn and alkali cations and coordinated H<sub>2</sub>O molecules (see  
242 Equation 1 below). Atomic coordinates along the  $c^*$  direction were equal to those  
243 determined from the analysis of  $hkl$  bands. Upon fixing these values, the amplitude, width,  
244 and position of the experimental diffraction peaks in this region essentially depend on the size  
245 of the CSDs along  $c^*$  and, therefore, on the number of layers in the diffracting crystallites.  
246 Although the fits to the experimental data are not perfect, the main features of the diffraction  
247 patterns were fairly reproduced by the simulations (Fig. 2). In particular, for all three samples  
248 the calculated positions, widths, and relative intensities were similar to the experimental data,  
249 thus providing strong support for the assumed lamellar structure of the unknowns (Villalobos  
250 et al. 2003). For the biogenic sample, the scattering from dead bacterial cells was not  
251 included in the calculation and, hence, only the high-angle contribution of the 002 peak was  
252 reproduced. The average sizes of the CSDs estimated from the models equal 2.6 layers ( $\sim 1.9$   
253 nm) for  $\delta$ -MnO<sub>2</sub>, 2.8 layers ( $\sim 2.0$  nm) for the biogenic oxide, and 5.8 layers ( $\sim 4.2$  nm) for the  
254 acid birnessite (Table 2).

255

256 **Simulations of the high-angle region ( $>30^\circ 2\theta$  CuK $\alpha$ )**

257

258 The successful simulation of the low-angle peaks supports our indexing of the high-angle  
259 reflections as 20,11 and 02,31 bands. As compared to equivalent reflections for hydrous  
260 layer silicates (Manceau et al. 2000a,b), the profiles of the 20,11 reflections are modulated  
261 and their shapes are different from one sample to another, indicating a variation of the  
262 structure factors, and hence of the sample structures. As will be shown below, these  
263 modulations can be used to determine both the layer and interlayer structures of the  
264 phylломanganate samples despite the absence of any 3D ordering.

265 For all simulations the generic structural formula,

266



268

269 was assumed, where interlayer species are written to the left of the square brackets and  $tc$   
270 refers to interlayer Mn in triple corner-sharing positions above or below cation vacancies  
271 ( $vac$ ) in the layer (enclosed in square brackets, except for the oxygens). The stoichiometric  
272 coefficients were calculated from the average Mn oxidation number and the alkali metal  
273 content determined previously (Villalobos et al. 2003), and from the water content  
274 determined by TGA (Table 1). Parameters refined in the XRD simulations include the unit-  
275 cell dimensions in the **ab** plane, from the position of the two high-angle maxima, and the  
276 amount of vacant layer sites, the amount and position of interlayer Mn cations, the positions  
277 of interlayer alkali cations and of associated H<sub>2</sub>O molecules, and the size of the CSDs in the  
278 **ab** plane. All sample spectra were simulated assuming an hexagonal layer symmetry and  
279 choosing a C-centered unit-cell with parameters  $b = 2.838 \text{ \AA}$ ,  $a = b\sqrt{3} = 4.916 \text{ \AA}$ ,  $\gamma = 90^\circ$ , and

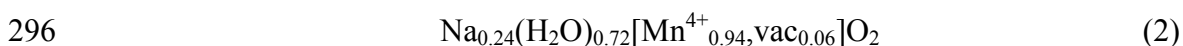


280 a basal  $d(001)$  distance of 7.20 Å. No parameters were used to define the layer-stacking  
281 mode, as layer stacking is random with  $W_R$ , the occurrence probability of random  
282 displacement/rotation between adjacent layers, being equal to 100 %. Optimal parameters  
283 obtained from the simulations are listed in Tables 2 and 3, and selected interatomic distances  
284 are reported in Table 4.

285

286  **$\delta$ -MnO<sub>2</sub>**. Since the average Mn oxidation number measured for this oxide is 4.0 (Table 1),  
287 the layer charge deficit was assumed to arise only from vacant layer sites. The optimal model  
288 had 6 % octahedral vacancies and did not contain interlayer Mn ( $t_c = 0$ ). Accordingly, the  
289 layer charge deficit was compensated by interlayer Na, whose fraction was constrained to be  
290 four times the refined fraction of vacant layer sites. The amount of interlayer H<sub>2</sub>O was  
291 assumed to be three times the amount of interlayer Na (Post and Veblen 1990), leading to a  
292 water content (12.7 %) consistent with the TGA value (15.8 %), although somewhat smaller.  
293 Thus, the structural formula corresponding to the optimum fit shown in Figure 3a ( $R_{WP} = 10.7$   
294 %,  $R_{EXP} = 3.5$  %) is:

295



297

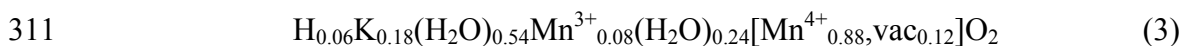
298 The coordinates of Na and H<sub>2</sub>O are (0.225, 0, 1/2) (Table 3a – Fig. 4) and the distance  
299 between water molecules and nearest layer oxygen atoms ( $O_{\text{layer}}$ ) is 2.65 Å, which is  
300 favorable to the formation of strong H-bonds (Table 4).

301

302 **Acid Birnessite**. The average Mn oxidation state of slightly lower than 4.0 (Table 1)  
303 suggests the occurrence of Mn<sup>3+</sup> cations, most likely above/below vacant layer sites, since the  
304 layer has an hexagonal symmetry. Thus, the amounts and positions of interlayer Mn were

305 optimized during the simulations, together with the amount of octahedral vacancies. The  
 306 amount of interlayer H<sub>2</sub>O was linked to that of alkali cations, as for the δ-MnO<sub>2</sub> simulation,  
 307 and their positions were also optimized. The refined structural formula, which yielded the  
 308 optimum match between the calculated scattering profile and data shown in Figure 3b (R<sub>wp</sub> =  
 309 9.3 %, R<sub>exp</sub> = 2.8 %), is:

310



312

313 This sample has a higher amount of vacant layer sites (0.12 per octahedron) than δ-MnO<sub>2</sub>,  
 314 and only two-thirds of the octahedral vacancies (0.08 per octahedron) are capped on one side  
 315 by octahedrally coordinated interlayer Mn<sup>3+</sup> cations (Fig. 4). The stoichiometric coefficient  
 316 of Mn<sup>3+</sup> is about half that of H-birnessite (Lanson et al. 2000). The average Mn oxidation  
 317 degree (3.92) determined by XRD agrees fairly well with the value determined by wet  
 318 chemistry (3.96 ± 0.02 – Villalobos et al. 2003), which provides confidence in the overall  
 319 consistency of our structural approach. The remaining layer charge is balanced by interlayer  
 320 K<sup>+</sup> cations and protons (0.18 and 0.06 per octahedron, respectively), the alkali metal content  
 321 (K/Mn = 0.19) being consistent with the K/Mn molar ratio measured by wet chemistry (0.20  
 322 ± 0.008 – Villalobos et al. 2003). The amount of structural water (9.6 %) is consistent with  
 323 the TGA value (7.5 % – Table 1), although somewhat larger. The position of the water  
 324 molecules (0.200, 0.0, 0.5 – Table 3b) is close to that determined for δ-MnO<sub>2</sub> (0.225, 0.0,  
 325 0.5), and again leads to a short <H<sub>2</sub>O-O<sub>layer</sub>> distance (2.68 Å) that is favorable to the  
 326 formation of strong H-bonds with O<sub>layer</sub>. However, the assumption of a common position for  
 327 K<sup>+</sup> and H<sub>2</sub>O did not yield optimal fits to the XRD pattern (R<sub>wp</sub> = 10.3 %). Best agreement  
 328 between calculation and experiment was obtained with K<sup>+</sup> at (-0.203, 0.0, 0.5), which is above  
 329 or below empty tridentate cavities of the layer surface at 2.97 Å from O<sub>layer</sub>. K atoms are

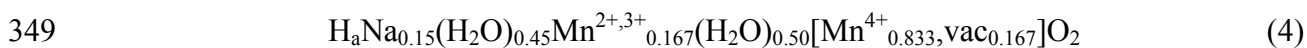
330 slightly shifted in the **ab** plane from the center of the cavity in the direction of the nearest  
331  $O_{\text{layer}}-O_{\text{layer}}$  edge of the Mn layer (Fig. 4). This position is close to that refined by Gaillot et  
332 al. (2003) (-0.229, 0.0, 0.5) for a birnessite single crystal having 11 % octahedral vacancies,  
333 of which two thirds were capped on one side by  $Mn^{3+}$  cations. The similar layer and interlayer  
334 structures found in the disordered birnessite synthesized at room temperature and in the single  
335 crystal form synthesized at 800°C suggest common structural principles despite the differing  
336 conditions of formation of the two species.

337

### 338 **Biogenic Oxide.**

339 As noted above, X-ray scattering from bacterial cells does not produce any significant  
340 modulations of the diffracted intensity over the analyzed angular range (Fig. 1d) and,  
341 consequently, all experimental features were interpreted as arising from the manganate  
342 admixture. As compared to the two previous samples, this oxide has an even lower Mn  
343 oxidation state ( $3.90 \pm 0.05$  – Table 1), thus suggesting a higher content of interlayer Mn, and  
344 possibly also of octahedral vacancies. Also, this sample has a lower alkali/Mn ratio ( $0.167$   
345  $\pm 0.003$ ), which suggests a higher proportion of vacant layer sites capped by interlayer Mn.  
346 Accordingly, the optimum fit to the XRD pattern of this oxide (Fig. 3c –  $R_{\text{WP}} = 9.8 \%$ ,  $R_{\text{EXP}} =$   
347  $3.1 \%$ ) was obtained for the following structural formula:

348



350

351 The amounts of vacancies and interlayer Mn are identical (0.167 per octahedron), and the  
352 same as in H-birnessite (Lanson et al. 2000). However, the short  $\langle Mn-O_{\text{layer}} \rangle$  distance (1.92  
353 Å – Table 4) pleads for the sole presence of  $Mn^{4+}$  within the octahedral layers in contrast to  
354 H-birnessite. In the optimized structural model, octahedrally coordinated interlayer Mn

355 atoms are slightly farther from the layer surface ( $z$ -coordinate = 2.15 Å – Table 3 c) than in  
356 the other birnessite samples, including H-birnessite ( $z$ -coordinate = 2.10 Å – Tables 3a, b –  
357 Lanson et al. 2000). This position results in a  $\langle \text{Mn}_{\text{interlayer}}\text{-O}_{\text{layer}} \rangle$  distance of 2.00 Å, that is  
358 significantly longer than usual (1.98 Å). This increase in distance is consistent with the likely  
359 presence of interlayer divalent Mn cations in the biogenic oxide. The residual layer charge is  
360 balanced by interlayer  $\text{Na}^+$  cations (0.15 per octahedron) and protons, the amount of which  
361 depends on the actual valency of interlayer Mn cations. The amount of interlayer Na  
362 estimated from our XRD model is consistent with the Na/Mn molar ratio ( $0.167 \pm 0.003$ )  
363 reported by Villalobos et al. (2003), and the amount of water bound to Na (8.2 %) is slightly  
364 smaller than the TGA value (10.0 %). Finally, the optimized atomic coordinates for Na and  
365  $\text{H}_2\text{O}$  are similar to those obtained for  $\delta\text{-MnO}_2$ , leading again to meaningful  $\langle \text{H}_2\text{O}\text{-O}_{\text{layer}} \rangle$  and  
366  $\langle \text{Na}\text{-O}_{\text{layer}} \rangle$  distances.

367

368 **Sensitivity of Calculated XRD Patterns to Structural Parameters.** As the optimum fits to  
369 the experimental data were obtained using a trial-and-error approach (making the assessment  
370 of uncertainties very difficult), the actual sensitivity of the XRD simulations to key structural  
371 parameters needs to be assessed. The sensitivity to the position of interlayer species will be  
372 illustrated by taking  $\delta\text{-MnO}_2$  as a case study. The optimum positions of Na and  $\text{H}_2\text{O}$  [(0.225,  
373 0.0, 0.5) and equivalent positions] are labeled “O3” in Figure 4. Placing the two interlayer  
374 species above or below an empty layer octahedron [position (0.0, 0.0, 0.5) – Alt. 1 in Fig. 4]  
375 modified the XRD profile considerably, especially the 20,11 band (Fig. 5a –  $R_{\text{WP}} = 21.9\%$ ).  
376 Even a small shift of these “light” species from their optimum (0.225, 0.0, 0.5) position to  
377 (0.333, 0.0, 0.5) (position “Alt. 2” in Fig. 4) changed significantly the calculated XRD profile  
378 relative to the best simulation (Fig. 5b –  $R_{\text{WP}} = 12.2\%$ ). Finally, when interlayer species are  
379 sitting above/below the tridentate cavities [Position “Alt. 3” in Fig. 4 with coordinates (-

380 0.167, 0.0, 0.5)], the calculated 20,11 band was broadened and differed greatly from  
381 experimental data (Fig. 5c -  $R_{\text{WP}} = 24.1 \%$ ).  
382 Figure 6 illustrates the sensitivity of the calculated XRD profiles to the mean radial  
383 dimension of the CSDs in the **ab** plane, taking again  $\delta\text{-MnO}_2$  as an example. In Figure 6a,  
384 this dimension has been increased from 6.0 nm, the optimum value (Table 2), to 10.0 nm. As  
385 a result, the 20,11 band peaks at lower  $2\theta$  value. In addition, the calculated band is sharper,  
386 leading to a poorer reproduction of the experimental profile ( $R_{\text{WP}} = 15.0 \%$ ). An opposite  
387 effect is observed when the mean CSD radial dimension is decreased from 6.0 to 3.0 nm (Fig.  
388 6b -  $R_{\text{WP}} = 11.6 \%$ ). Note that the CSD size does not affect the position of the modulation at  
389 about  $45^\circ 2\theta$   $\text{CuK}\alpha$ , which depends only on the layer structure.

390

391 The sensitivity of the calculated XRD profiles to the location and amount of interlayer Mn is  
392 illustrated next with the biogenic oxide (Fig. 7). Decreasing the stoichiometric coefficient  $t$   
393 (Equation 1) from its optimum 0.167 value to 0.100 modified the shape of the high-angle  
394 “tail” of the 20,11 band in a manner that smoothed the scattering dip at  $\sim 45^\circ 2\theta$   $\text{CuK}\alpha$   
395 rendering the calculated hump less pronounced (Fig. 7a -  $R_{\text{WP}} = 11.3 \%$ ) relative to the  
396 optimum fit (Fig. 3c -  $R_{\text{WP}} = 9.8 \%$ ). When both the proportion of interlayer Mn and layer  
397 vacancies were decreased from 0.167 to 0.100, the lineshape of the 20,11 band was  
398 broadened (Fig. 7b -  $R_{\text{WP}} = 14.6 \%$ ). As expected from the high sensitivity of the calculated  
399 XRD patterns to the position of “light” interlayer species, demonstrated previously with Na  
400 and  $\text{H}_2\text{O}$  in  $\delta\text{-MnO}_2$ , moving interlayer Mn from its optimal position dramatically modified  
401 the 20,11 lineshape, as observed when the 0.167 interlayer Mn atoms were located  
402 above/below the tridentate cavities (position Alt. 3 - Fig. 4; Fig. 7c -  $R_{\text{WP}} = 25.3 \%$ ).

403

## 404 EXAFS Spectra

405

406 The  $k^3$ -weighted Mn K-edge EXAFS spectra collected for the samples are shown in Figure  
407 8a. Frequencies for all the Mn oxides studied were similar, with differences between the  
408 samples arising mostly in the amplitudes. These amplitude differences are also evident in the  
409 corresponding radial structure functions (RSFs, uncorrected for phase shifts) shown in Figure  
410 8b. The uncleaned biogenic oxide sample shows a somewhat distinctive behavior at low  $k$   
411 values (Fig. 8a). These effects are probably a contribution of a relatively important  $Mn^{2+}$   
412 fraction (16-19 mole %) in this sample, which is absent from the others (Villalobos et al.  
413 2003).

414

415 The RSFs exhibit two principal peaks at similar interatomic distances for all samples (Fig.  
416 8b), including the uncleaned biogenic oxide. From a qualitative comparison with previously-  
417 reported spectra for layer type Mn oxides, it can be concluded that these two peaks arise  
418 mainly from single-scattering photoelectron interactions in the first Mn-O shell and in the  
419 second Mn-Mn shell, respectively (Manceau and Combes 1988; Manceau et al. 1992b;  
420 Silvester et al. 1997). Differences among the samples are observed mostly in the peak  
421 amplitudes, particularly for the Mn-Mn peak, and in the small feature that appears just  
422 beyond this peak at ca.  $R+\Delta R$  of 3 Å. This feature was used to elucidate important structural  
423 differences between the Mn oxides using single-scattering ab initio FEFF simulations.  
424 Specifically, the presence of a shoulder or a distinctive peak at  $R+\Delta R \sim 3$  Å for the uncleaned  
425 biogenic oxide may be indicative of Mn octahedra in different configurations from the edge-  
426 sharing octahedra in the layers, e.g. triple-corner (TC) sharing octahedra, as observed in H-  
427 birnessite and chalcophanite (Silvester et al. 1997) and in tectomanganates (Manceau and  
428 Combes 1988).

429

430 The EXAFS spectrum of the clean biogenic oxide clearly shows a shift in the  $\chi(k)$  frequencies  
431 in the region between 6 and 8  $\text{\AA}^{-1}$  (Fig. 8a.), which manifests itself in the disappearance of the  
432 feature at  $R+\Delta R \sim 3 \text{\AA}$  in real space (Fig. 8b). This spectral feature is very similar to that seen  
433 in the spectra of  $\delta$ -MnO<sub>2</sub> (Fig. 9) and acid birnessite (Fig. 10). In contrast, the spectrum for  
434 the unclean biogenic sample shows a strong similarity to that for H-birnessite, especially in  
435 the region between 6 and 7  $\text{\AA}^{-1}$  (Fig. 11a) and at  $R+\Delta R \sim 3 \text{\AA}$  (Fig. 11b – feature C).

436 Therefore, qualitatively, one may conclude that the biogenic sample as it is synthesized by the  
437 bacteria most likely contains interlayer Mn, in similar configuration to H-birnessite.

438

439 The peak caused by the third Mn layer shell at  $R+\Delta R \sim 5.2 \text{\AA}$  (Fig. 11b, feature D) is more  
440 intense than the peak of the second Mn layer shell at  $R+\Delta R \sim 4.5 \text{\AA}$ , although the two shells  
441 comprise six Mn atoms. The magnification of peak D has been attributed to a “focusing  
442 effect” between aligned cations in layer type metal oxides (O’Day et al. 1994).

443

#### 444 **Simulations of the EXAFS Spectra**

445

446  **$\delta$ -MnO<sub>2</sub>.** This layer Mn oxide appears to have a simple structure (Fig. 8) arising from the  
447 homogeneity of its Mn oxidation state (Villalobos et al. 2003). The FEFF simulations of the  
448  $k^3\chi(k)$  data filtered in the  $1.0 < R+\Delta R < 3.1 \text{\AA}$  interval are shown in Figure 12a and the  
449 corresponding optimized parameters are listed in Table 5. The first two shells correspond to  
450 Mn-O and Mn-Mn distances of 1.90  $\text{\AA}$  and 2.87  $\text{\AA}$ , respectively. The edge-sharing  
451 configuration of the Mn<sup>4+</sup> octahedra (six shared edges per octahedron) is isostructural with  
452 that in bivalent metal hydroxides of the brucite [Mg(OH)<sub>2</sub>] group, including pyrochroite  
453 [Mn(OH)<sub>2</sub>]. To reconcile the interatomic distances obtained by FEFF simulation with this

454 configuration in a crystallographic model, the  $\text{Mn}^{4+}$  octahedra must flatten slightly. To  
455 ensure a Mn-Mn distance of 2.87 Å between adjacent octahedra while keeping all Mn-O  
456 distances equal to 1.90 Å, the O-O distance along shared edges must shorten to 2.49 Å (Fig.  
457 13, inset). The O-O distances along the unshared edges in this configuration are effectively  
458 equal to the interatomic Mn-Mn distance of 2.87 Å.

459

460 An idealized octahedral sheet for  $\delta\text{-MnO}_2$  may now be constructed (Fig. 13) in which all Mn  
461 near neighbor distances are determined by geometry alone. For example, a second O shell  
462 [O(2)] is expected at 3.45 Å, and further Mn layer shells are expected at 4.97 Å (dotted lines  
463 in Fig. 13) and 5.74 Å. The O(2) shell at 3.45 Å from Mn is within the range of influence of  
464 the edge-sharing Mn shell [Mn(1)], and of the triple-corner sharing Mn shell [Mn(tc)], when  
465 present, and, consequently, it was included in the spectral fits for all sample spectra.

466 However, spectral simulations showed that adding the Mn-O(2) electronic wave improves the  
467 fit in the 4-6 Å<sup>-1</sup>  $k$  interval but does not modify significantly the EXAFS parameters from the  
468 Mn(1) and Mn(tc) shells because these shells have a maximum amplitude at higher  $k$   
469 (Manceau and Combes 1988; Schlegel et al. 2001).

470

471 According to the ideal hexagonal layer model of  $\delta\text{-MnO}_2$ , and in the absence of  
472 configurations other than edge-sharing octahedra, six near neighbors of Mn centers are  
473 expected for all shells (Fig. 13). The optimized fit for the O(1) shell indeed yielded  $N$  very  
474 close to 6 (Table 5). However, the Mn(1) shell fit produced a considerably lower value of  $N$ ,  
475 even when taking into account the commonly accepted precision of 20 % in this parameter.  
476 Two factors may predominate in causing this reduction: vacant cation sites (i.e., the absence  
477 of some Mn near neighbors per Mn center present) and the contribution of particle-edge



478 octahedra that have an incomplete shell of near neighbors, a contribution that is important  
479 because of the small size of the layers in our samples.

480

481 Based on a Mn-Mn(1) distance of 2.87 Å as obtained from analysis of the first Mn shell  
482 (Table 5), and on a layer size estimate from our XRD simulations of  $\delta$ -MnO<sub>2</sub> (from the  
483 coherent scattering domain radial dimensions – Table 2), a rough estimate of the contribution  
484 of layer-edge octahedra may be performed: one sheet of a square particle of dimensions 85 ×  
485 85 Å<sup>2</sup> yields a total of  $(85/2.87)^2 = 900$  octahedra, of which  $4 \times (85/2.87) = 120$  occur at the  
486 edges. The latter represents 13 % of the total. Assuming smooth edges, we estimate that ca.  
487 4 Mn near-neighbors occur for every edge octahedron (Fig. 13). Thus the average number of  
488 nearest Mn neighbors for all Mn atom centers in the 85 × 85 Å<sup>2</sup> particle is about  $0.13 \times 4 +$   
489  $(1-0.13) \times 6 = 5.74$ ; i.e., a reduction of less than 5 % from the ideal value. Therefore, the low  
490 coordination number (28 % difference) observed by EXAFS spectral fitting must be due  
491 primarily to the presence of vacant Mn sites. Unfortunately, the uncertainty of the predicted  
492 *N* value by EXAFS is too high to render a useful quantitative estimate of the vacancy content  
493 by this method. However, it provides a convincing qualitative explanation for the occurrence  
494 of Mn *N* values significantly lower than the theoretical value of 6 (Fig. 13).

495

496 **Hexagonal birnessite with an Enhanced 3D Ordering.** The H-birnessite (HBi) studied by  
497 Silvester et al. (1997) has a more complex structure than  $\delta$ -MnO<sub>2</sub> because of the presence of  
498 significant Mn<sup>3+</sup> in the layer and at interlayer sites in TC octahedra above cation vacancies.

499 The significant increase by 0.01 Å of the Mn-Mn(1) distance relative to  $\delta$ -MnO<sub>2</sub> (Table 5) is  
500 indicative of the presence of Mn<sup>3+</sup> in the layer, whereas the Mn shell at 3.49 Å with an  
501 effective coordination number of 2.8 is characteristic of corner-sharing linkages between  
502 layer and interlayer octahedra.

503

504 **Acid Birnessite.** As expected from the average Mn oxidation number of 3.96 for this oxide  
505 (Villalobos et al. 2003) and from the RSF (Fig. 8b) and XRD data, FEFF simulations gave  
506 optimized structural parameters very similar to those for  $\delta$ -MnO<sub>2</sub> (Fig. 12b, Table 5). The  
507 main difference between the two structures lies in the larger size of the diffracting crystallites  
508 (CSD) in acid birnessite.

509

510 **Biogenic Oxide.** Simulation of the NaOCl-cleaned sample of the biogenic oxide produced  
511 shells and optimized structural parameters different from the uncleaned sample (Fig. 14), but  
512 very similar to those of  $\delta$ -MnO<sub>2</sub> and acid birnessite (Figs. 9, 10, 12c, Table 5). Figures 11a  
513 and 15a show that HBi has a higher wave frequency than the biogenic oxide, which translates  
514 in real space to a shift to higher  $R+\Delta R$  values of peaks B and D (Fig. 11b). Accordingly,  
515 Table 5 shows that the Mn-Mn(1) distance is greater by 0.02 Å in HBi. This is due to the  
516 presence of layer Mn<sup>3+</sup> in the latter, and its absence in the biogenic oxide. Matching the  
517 simulation of HBi (Fig. 15b), the prominent shoulder at ca. 3 Å in the RSF of the uncleaned  
518 sample (peak C in Fig. 11b) was successfully simulated with a TC Mn shell at 3.49 Å (Fig.  
519 15c, Table 5). The oxidation state of this interlayer Mn species is different in the biogenic  
520 oxide [Mn<sup>2+</sup>] from that in HBi [Mn<sup>3+</sup>], however, the Mn-Mn(tc) EXAFS distance is the same  
521 for both (Table 5). This may be explained as a trade-off between the larger radius of Mn<sup>2+</sup>  
522 compared to Mn<sup>3+</sup>, and the need for Mn<sup>2+</sup> to approach the layer at a closer distance to  
523 compensate for a similar negative layer charge. This type of behavior has been reported in  
524 chalcophanite, in which Zn is octahedrally-coordinated but has Zn-O<sub>layer</sub> distances  
525 characteristic of a tetrahedral coordination owing to the lowering of the Zn position in the  
526 direction of the layer (Wadsley 1955).

527

528 Additionally, note that  $N$  predicted for the O(1) shell of both is lower than for the other  
529 samples (Table 5). This difference occurs because the high proportion of low-valent Mn in  
530 the sample causes a higher disorder in the Mn-O EXAFS frequency, manifested in a decrease  
531 from what would be observed for pure  $\text{Mn}^{4+}$ -O pairs. This situation is illustrated in Figure  
532 16, which shows an EXAFS simulation for a hypothetical system consisting of 80 %  $\text{Mn}^{4+}$ -O  
533 and 20 %  $\text{Mn}^{2+}$ -O pairs. In such a system, the frequency of the shorter  $\text{Mn}^{4+}$ -O pair  
534 dominates the EXAFS spectrum (Fig. 16a) and, therefore, the RSF peak for the composite  
535 Mn valency spectrum appears at the same distance as that for the pure  $\text{Mn}^{4+}$  spectrum, but  
536 with a lower amplitude (Fig. 16b).

537

## 538 **General Discussion**

539

### 540 **Ability of the trial-and-error XRD modeling approach to determine the structure of**

541 **turbostratic compounds.** The ability of the trial-and-error approach used in the present  
542 study to unravel the structure of defect-bearing compounds has been amply demonstrated in  
543 recent studies of different birnessite varieties with an enhanced 3D ordering (Manceau et al.  
544 1997; Drits et al. 1998a; Lanson et al. 2000, 2002a, b; Gaillot et al. 2003, 2004). Based on  
545 the above fits to the experimental data and the subsequent sensitivity analysis, it is clear that  
546 this trial-and-error approach can also be applied to build meaningful structure models for  
547 extremely defective (turbostratic stacking – 100 % of random stacking faults) layered  
548 compounds. The symmetry and cation occupancy of the octahedral layer, and to some extent  
549 the amounts and positions of interlayer species, were well constrained. Specifically, it was  
550 possible to assess the presence and the number of interlayer Mn cations associated with  
551 vacant layer sites, and to determine their position with a reasonable precision (e.g., Figs. 3c  
552 and 7). The position and, to a lesser extent, the amount of “light” interlayer species, such as

553 Na<sup>+</sup> and H<sub>2</sub>O molecules, were also obtained by this approach (e.g., Figs. 3a and 5). Our  
554 modeling procedure also provided estimates of the CSD sizes in the **ab** plane for these  
555 compounds (e.g., Figs. 3a and 6).

556 The high sensitivity of XRD profiles to the structure of highly defective phyllomanganates  
557 contrasts with the limited effect reported previously for other layered compounds having a  
558 turbostratic stacking, such as smectites. For example, Manceau et al. (2000a,b) used a similar  
559 modeling approach to determine average cation occupancy in nontronite for which the layer  
560 and interlayer structures were reasonably well known, a few parameters being left to refine.  
561 For this purpose these authors used the relative intensities of 02,11 and 20,13 bands because  
562 no modulations were observed for the two diffraction bands. For turbostratic layer  
563 compounds, calculated XRD patterns hold information only on the structure of the layer,  
564 including interlayer species, and give an estimate of the lateral extension of these layers.  
565 However, no information is provided on the layer stacking mode, which is assumed to be  
566 totally random. In the present case, modulations of the two *hkl* bands, and especially of the  
567 20,11 band, were observed and successfully reproduced by computation assuming a  
568 turbostratic stacking. As the position and profile of the bands depend on the amount and  
569 atomic coordinates of both layer and interlayer species, they may be used for structural  
570 chemistry determination. Similar modulations can result from the partial ordering of the layer  
571 stacking (e.g., Ben Brahim et al. 1983; Ben Brahim et al. 1984; Drits & Tchoubar 1990; Viani  
572 et al. 2002). Special attention should thus be paid to the structural interpretation of these  
573 modulations, and, in this respect, verifying the structural XRD model with independent data  
574 from another structural technique, such as EXAFS spectroscopy, is always warranted.

575

576 **Particle size considerations.** The small coherent scattering dimensions obtained from XRD  
577 simulations provided estimates for the size of the diffracting crystallites in the nanometer

578 range. The implications of this small particle size include the exposure at the surface of a  
579 large proportion of the total structure. Therefore, edge surface sites, which contain  
580 unsaturated singly- and doubly-coordinated oxygen groups (Fig. 13), are expected to hold a  
581 relatively high proportion of the total particle charge and thus contribute palpably to ion  
582 sorption capacity. Other implications of small particle size may be relevant not only to  
583 reactivity studies, but also to structural characterization using wet-chemistry and  
584 spectroscopic techniques, such as those employed by Villalobos et al. (2003). For example,  
585 the molar ratio,  $[\text{Mn(IV)} + \text{vacancies}] / \text{O}$  is no longer expected to be 0.5, as in infinitely large  
586 octahedral layers. The total charge will depend on both the vacancy content and the number  
587 of unsaturated oxygen bonds at the edges of the particles. Small particle size in the radial  
588 direction has the potential to create “border effects” that may influence characterization based  
589 on spectroscopic techniques that have been calibrated using samples having much larger  
590 particle size.

591 **Comparisons between Mn oxides studied.** Complementary information obtained from  
592 simulations of XRD patterns and Mn K-edge EXAFS spectra has led to more accurate  
593 determination of the structures of the biogenic Mn oxide and its two synthetic analogs  
594 investigated by Villalobos et al. (2003). Hexagonal layer symmetry was established for all  
595 three Mn oxides studied, with differences occurring mainly in the number of layer vacancies,  
596 in the cation interlayer content, and in particle size (coherent scattering domain radial  
597 dimensions and number of randomly stacked sheets per crystallite). The uncleaned sample of  
598 the biogenic Mn oxide seems to be structurally related to synthetic HBi, including similar  
599 vacancy contents and the presence of low-valency interlayer Mn in TC configuration.  
600 However, the biogenic phase’s octahedral layer is composed of tetravalent Mn only, in  
601 contrast to HBi, but in close similarity with  $\delta\text{-MnO}_2$  and acid birnessite. Thus, the layer  
602 charge originates only from the presence of vacant layer sites. Another characteristic of the

603 biogenic oxide is the presence of  $Mn^{2+}$  in the interlayer, whereas HBi has  $Mn^{3+}$ , and  $\delta$ - $MnO_2$   
604 and acid birnessite have no  $Mn^{2+}$ . This  $Mn^{2+}$  is most likely a remnant of unoxidized  $Mn^{2+}$   
605 added to the system initially. A recent X-ray absorption study of the oxidation product of a  
606 *Leptothrix* bacterium (Jurgensen et al. 2004) detected both  $Mn^{2+}$  and  $Mn^{3+}$  in the birnessite-  
607 like biogenic oxide, suggesting that  $Mn^{3+}$  may be a structural component of certain biogenic  
608 oxides. In yet another study on biogenic oxides,  $Mn^{3+}$  was detected by Scanning  
609 Transmission X-ray Microscopy (STXM) (Pecher et al. 2003; Toner et al. 2004), but this  
610 species was assigned an intermediate role in the bacterial oxidation process to  $Mn^{4+}$ .

611

## 612 **Acknowledgments**

613

614 The first author would like to thank Philip N. Ross (Materials Science Divison, Lawrence  
615 Berkeley National Laboratory) for use of a TGA-DTA apparatus, and John Bargar for  
616 facilitating EXAFS measurements and providing technical assistance at the beamline. The  
617 third author expresses gratitude to the Division of Ecosystem Sciences, University of  
618 California at Berkeley, for its hospitality during a sabbatical leave visit. This research was  
619 funded in part (M.V., B.T., G.S.) by the National Science Foundation, Collaborative Research  
620 Activities in Environmental Molecular Science (CRAEMS) program (CHE-0089208) and in  
621 part (A. M.) by a LDRD grant through the Advanced Light Source, Lawrence Berkeley  
622 National Laboratory. SSRL is a national user facility operated on behalf of the U.S. DOE,  
623 Office of Basic Energy Sciences.

624

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## 832 FIGURES

833

834 **Fig. 1.** Experimental XRD patterns of the Mn oxide samples. (a) acid birnessite, (b)  $\delta$ -  
835  $\text{MnO}_2$ , (c) biogenic oxide with cell material, (d) cell material without the biogenic oxide.

836

837 **Fig. 2.** Comparison between experimental ('+' symbols) and calculated (solid line) XRD  
838 patterns for the various Mn oxide samples. Structural parameters used for calculations are  
839 listed in Tables 2 and 3. Calculations are limited to the 00 $l$  reflections occurring below 35°2 $\theta$   
840  $\text{CuK}\alpha$ . (a) acid birnessite, (b)  $\delta$ - $\text{MnO}_2$ , (c) biogenic oxide with cell material. The lower gray  
841 trace in (c) is the experimental XRD pattern for cell material without the biogenic oxide.

842

843 **Fig. 3.** Comparison between experimental and calculated XRD patterns for the various Mn  
844 oxide samples. Patterns as for Figure 2. Structural parameters used for calculations are listed  
845 in Tables 2 and 3. Calculations are performed for the 20,11 and for the 02,31 bands (maxima  
846 at ~37 and 66°2 $\theta$   $\text{CuK}\alpha$ , respectively). (a)  $\delta$ - $\text{MnO}_2$ , (b) acid birnessite, (c) biogenic oxide.

847

848 **Fig. 4.** Structure model for the various Mn oxide samples. (a) Projection on the **ab** plane.  
849 The upper surface of the layer is shown as light shaded triangles.  $\text{O}_{\text{layer}}$  atoms of this upper  
850 surface are shown as solid circles, whereas  $\text{Mn}_{\text{layer}}$  atoms are not shown. Large open circles



851 represent  $\text{Na}^+$  cations and  $\text{H}_2\text{O}$  molecules in  $\delta\text{-MnO}_2$  [(0.225,0,0.5) – Position O3]. K  
852 represents the position of interlayer  $\text{K}^+$  cations in the acid birnessite sample. Positions labeled  
853 Alt.n (n = 1, 2, 3) represent test positions to assess the sensitivity of calculated XRD patterns  
854 to the position of interlayer species. The dashed triangle outlines the upper surface of the  
855  $\text{Mn}_{\text{interlayer}}$  coordination octahedron which is defined by three  $\text{H}_2\text{O}_{\text{interlayer}}$  (small open circles).  
856 (b) Projection along the **b** axis. Open and solid symbols indicate atoms at  $y = 0$  and  $y = \pm\frac{1}{2}$ ,  
857 respectively. Large circles represent  $\text{O}_{\text{layer}}$  atoms, small circles represent Mn atoms. The solid  
858 squares represents a vacant layer site. The dashed line outlines the  $\text{Mn}_{\text{interlayer}}$  coordination  
859 octahedron which is defined by  $\text{O}_{\text{layer}}$  and  $\text{H}_2\text{O}_{\text{interlayer}}$ .

860

861 **Fig. 5.** Comparison between experimental and calculated XRD patterns for  $\delta\text{-MnO}_2$ .

862 Patterns as for Figure 2. Structural parameters used for calculations are listed in Tables 2 and  
863 3a. Calculations are performed for the  $20l,11l$  and for the  $02l,31l$  sets of reflections (maxima  
864 at  $\sim 37$  and  $66^\circ 2\theta$   $\text{CuK}\alpha$ , respectively). (a) Interlayer  $\text{Na}^+$  cations and  $\text{H}_2\text{O}$  molecules are  
865 located above or below layer octahedra [position (0.0, 0.0, 0.5) – Alt. 1 in Fig. 4] rather than  
866 in the optimum O3 position (0.225, 0.0, 0.5) (Fig. 3a). (b) Interlayer  $\text{Na}^+$  cations and  $\text{H}_2\text{O}$   
867 molecules are located in (0.333, 0.0, 0.5) (position Alt. 2 in Fig. 4) rather than in the optimum  
868 O3 position (0.225, 0.0, 0.5). (c) Interlayer  $\text{Na}^+$  cations and  $\text{H}_2\text{O}$  molecules are located  
869 above/below the tridentate cavities at the layer surface [Position “Alt. 3” in Fig. 4 with  
870 coordinates (-0.167, 0.0, 0.5)] rather than in the optimum O3 position (0.225, 0.0, 0.5).

871

872 **Fig. 6.** Comparison between experimental and calculated XRD patterns for  $\delta\text{-MnO}_2$ .

873 Patterns as for Figure 2. Structural parameters used for calculations are listed in Tables 2 and  
874 3a. Calculations are performed for the  $20l,11l$  and for the  $02l,31l$  sets of reflections (maxima  
875 at  $\sim 37$  and  $66^\circ 2\theta$   $\text{CuK}\alpha$ , respectively). (a) Mean radial dimension of the CSD in the **ab** plane

876 is increased from the optimum 5.8 nm (Fig. 3a) to 10.0 nm. (b) Mean radial dimension of the  
877 CSD in the **ab** plane is decreased from the optimum 5.8 nm to 3.0 nm.

878

879 **Fig. 7.** Comparison between experimental and calculated XRD patterns for the biogenic  
880 oxide. Patterns as for Figure 2. Structural parameters used for calculations are listed in  
881 Tables 2 and 3c. Calculations are performed for the  $20l,11l$  and for the  $02l,31l$  sets of  
882 reflections (maxima at  $\sim 37$  and  $66^\circ 2\theta$  CuK $\alpha$ , respectively). (a) Amounts of vacant layer sites  
883 and of interlayer Mn cations are assumed to be 0.167 and 0.100, as compared to the optimum  
884 0.167 and 0.167 values (Fig. 3c), respectively. (b) Amounts of vacant layer sites and of  
885 interlayer Mn cations are assumed to be 0.100 and 0.100, as compared to the optimum 0.167  
886 and 0.167 values, respectively. (c) Interlayer Mn cations are located above/below the  
887 tridentate cavities at the layer surface [Position “Alt. 3” in Fig. 4 with coordinates (-0.167,  
888 0.0, 0.299)] rather than in the optimum position (0.0, 0.0, 0.299).

889

890 **Fig. 8.** (a)  $k^3$ -weighted Mn K-edge EXAFS spectra of Mn oxides lacking 3D ordering and of  
891 H-birnessite. (b) Magnitude of the Fourier transform (uncorrected for phase shifts).

892

893 **Fig. 9.** Comparison between  $k^3$ -weighted Mn K-edge EXAFS spectra of (a) the cleaned  
894 biogenic Mn oxide and  $\delta$ -MnO<sub>2</sub>, (b) the cleaned biogenic Mn oxide and acid birnessite, and  
895 (c) the uncleaned biogenic Mn oxide and H-birnessite. The arrow denotes the area where the  
896 biogenic oxide and H-birnessite overlap (Manceau et al. 1997).

897

898 **Fig. 10.** Comparison between the magnitude and imaginary part of the Fourier transforms  
899 (uncorrected for phase shifts) for (a) the cleaned biogenic Mn oxide and  $\delta$ -MnO<sub>2</sub>, (b) the  
900 cleaned biogenic Mn oxide and acid birnessite, and (c) the uncleaned biogenic Mn oxide and

901 H-birnessite. The letters refer to the four different shells identified. A indicates the peak due  
902 to Mn-O(1) distance, B to the Mn-Mn(1) distance, C mostly to the Mn-Mn(tc) distance, and  
903 D to the third Mn layer shell distance. The latter was not modeled with the single scattering  
904 model employed in the spectral simulations. The arrow denotes the area where the biogenic  
905 oxide and H-birnessite overlap (Manceau et al. 1997).

906

907 **Fig. 11.** Fourier-filtered experimental EXAFS spectra and FEFF simulations of the  $1.0 <$   
908  $R + \Delta R < 3.1 \text{ \AA}$  region for (a)  $\delta$ -MnO<sub>2</sub>, (b) acid birnessite, (c) NaOCl-cleaned biogenic Mn  
909 oxide, according to the parameters listed in Table 5.

910

911 **Fig. 12.** Idealized hexagonal layer structure of edge-sharing Mn<sup>4+</sup>-O<sub>6</sub> octahedra (inset at left)  
912 for  $\delta$ -MnO<sub>2</sub>.

913

914 **Fig. 13.** Comparison between the EXAFS data of the cleaned and uncleaned biogenic Mn  
915 oxide. (a)  $k^3$ -weighted Mn K-edge EXAFS spectra. (b) Magnitude and imaginary part of the  
916 Fourier transforms (uncorrected for phase shifts).

917

918 **Fig. 14.** Fourier-filtered experimental EXAFS spectra of the  $1.0 < R + \Delta R < 3.1 \text{ \AA}$  region for  
919 (a) H-birnessite and the uncleaned biogenic Mn oxide; and FEFF simulations for (b) H-  
920 birnessite, and (c) the uncleaned biogenic Mn oxide, according to the parameters listed in  
921 Table 5.

922

923 **Fig. 15.** EXAFS contribution of the Mn-O(1) shell for a theoretical Mn oxide composed of  
924 80 % Mn<sup>4+</sup> and 20 % Mn<sup>2+</sup>, which shows that despite the widely differing  $\chi(k)$  frequencies (a)

925 obtained, and corresponding radial structure functions (b), the dominant  $\chi(k)$  function and  
926 RSF of the mixture is that of the shorter Mn<sup>4+</sup>-O distance, with amplitude reductions.  
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**Table 1.** Physicochemical properties of the Mn oxides investigated

Mn oxide	H <sub>2</sub> O content (% w/w) (± 0.02)	Average Mn Oxidation Number (± 0.02) <sup>†</sup>	Structural Alc*/Mn <sub>tot</sub> (mol %) <sup>†</sup>
Biogenic <sup>#</sup>	10.0	3.90 ±0.05	(pH 8.1) 16.7 ±0.3
Acid Birnessite	7.5	3.96	(pH 5.6) 20.4 ±0.8
δ-MnO <sub>2</sub>	15.8	4.02	(pH 8.1) 25.3 ±0.1

Note: <sup>†</sup>From Villalobos et al. (2003); \* Alc refers to the alkaline counterion, which is K<sup>+</sup> for “acid birnessite” and Na<sup>+</sup> for the others; <sup>#</sup>From *Pseudomonas putida*.

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933 **Table 2.** Optimum structural parameters used for the simulation of the three experimental X-  
 934 ray diffraction profiles (cf. Figs. 2, 3).

935

Atom	$\delta$ -MnO <sub>2</sub>	Acid birnessite	Biogenic oxide
a (Å)	4.916	4.916	4.916
b (Å)	2.838	2.838	2.838
<i>d</i> (001) (Å)	7.20	7.20	7.20
Average CSD size (along the <b>c*</b> axis)	2.6	5.8	2.8
Average CSD size (in the <b>ab</b> plane)	60	70	85

*Note:* Optimal values were determined by trial-and-error fitting of the experimental XRD patterns. *a* and *b* parameters were determined from the simulation of the *hkl* bands whereas the *c* parameter was estimated from the simulation of the 00*l* reflections. Coherent scattering domain (CSD) sizes along **c\*** are expressed as number of layers, whereas the average radius of the CSDs in the **ab** plane is expressed in Å. The latter values have been determined to fit the 20,11 band.

936

937

937 **Table 3a.** Optimum structural parameters used for the simulation of  $\delta$ -MnO<sub>2</sub> X-ray  
 938 diffraction profile (cf. Fig. 3a).

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Atom	$x$	$y$	$\zeta$	Occ.	$x$	$y$	$\zeta$	Occ.
Mn <sub>layer</sub>	0	0	0	0.94	-	-	-	-
O <sub>layer</sub>	0.333	0	1.00	1.00	-0.333	0	-1.00	1.00
Mn <sub>interlayer</sub>	-	-	-	0.00	-	-	-	0.00
H <sub>2</sub> O <sub>interlayer</sub>	-	-	-	0.00	-	-	-	0.00
Na <sub>interlayer</sub>	0.225	0	3.60	0.04	-0.225	0	-3.60	0.04
Na <sub>interlayer</sub>	-0.1125	0.3375	3.60	0.04	-0.1125	-0.3375	3.60	0.04
Na <sub>interlayer</sub>	0.1125	0.3375	-3.60	0.04	0.1125	-0.3375	-3.60	0.04
H <sub>2</sub> O <sub>interlayer</sub>	0.225	0	3.60	0.12	-0.225	0	-3.60	0.12
H <sub>2</sub> O <sub>interlayer</sub>	-0.1125	0.3375	3.60	0.12	-0.1125	-0.3375	3.60	0.12
H <sub>2</sub> O <sub>interlayer</sub>	0.1125	0.3375	-3.60	0.12	0.1125	-0.3375	-3.60	0.12

*Note:* Optimal values were determined by trial-and-error fitting of the experimental XRD patterns.  $x$ , and  $y$  coordinates are expressed as fractions of the  $a$  and  $b$  parameters, respectively. Coordinates along the  $\mathbf{c}^*$  axis,  $\zeta$ , are expressed in Å to emphasize the thickness of layer and interlayer polyhedra. Un-refined thermal  $B$  factors are 0.5 for Mn<sub>layer</sub>, 1.0 for O<sub>layer</sub> and Mn<sub>interlayer</sub>, and 1.5 for interlayer H<sub>2</sub>O molecules associated with Mn<sub>interlayer</sub>, and 2.0 for other interlayer species (alkali cations and H<sub>2</sub>O molecules)

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941 **Table 3b.** Optimum structural parameters used for the simulation of acid birnessite X-ray  
 942 diffraction profile (cf. Fig. 3b).

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Atom	$x$	$y$	$\zeta$	Occ.	$x$	$y$	$\zeta$	Occ.
Mn <sub>layer</sub>	0	0	0	0.88	-	-	-	-
O <sub>layer</sub>	0.333	0	1.00	1.00	-0.333	0	-1.00	1.00
Mn <sub>interlayer</sub>	0	0	2.15	0.04	0	0	-2.15	0.04
H <sub>2</sub> O <sub>inter.</sub>	-0.333	0	3.35	0.12	0.333	0	-3.35	0.12
K <sub>interlayer</sub>	-0.203	0	3.60	0.03	0.203	0	-3.60	0.03
K <sub>interlayer</sub>	-0.4167	0.125	3.60	0.03	-0.4167	-0.125	3.60	0.03
K <sub>interlayer</sub>	0.4167	0.125	-3.60	0.03	0.4167	-0.125	-3.60	0.03
H <sub>2</sub> O <sub>inter.</sub>	0.200	0	3.60	0.09	-0.200	0	-3.60	0.09
H <sub>2</sub> O <sub>inter.</sub>	-0.100	0.300	3.60	0.09	-0.100	-0.300	3.60	0.09
H <sub>2</sub> O <sub>inter.</sub>	0.100	0.300	-3.60	0.09	0.100	-0.300	-3.60	0.09

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945 **Table 3c.** Optimum structural parameters used for the simulation of the biogenic oxide X-ray  
 946 diffraction profile (cf. Fig. 3c).

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Atom	$x$	$y$	$\zeta$	Occ.	$x$	$y$	$\zeta$	Occ.
Mn <sub>layer</sub>	0	0	0	0.833	-	-	-	-
O <sub>layer</sub>	0.333	0	1.00	1.00	-0.333	0	-1.00	1.00
Mn <sub>interlayer</sub>	0	0	2.15	0.0833	0	0	-2.15	0.0833
H <sub>2</sub> O <sub>inter.</sub>	-0.333	0	3.35	0.25	0.333	0	-3.35	0.25
Na <sub>interlayer</sub>	0.225	0	3.60	0.04	-0.225	0	-3.60	0.04
Na <sub>interlayer</sub>	-0.1125	0.3375	3.60	0.04	-0.1125	-0.3375	3.60	0.04
Na <sub>interlayer</sub>	0.1125	0.3375	-3.60	0.04	0.1125	-0.3375	-3.60	0.04
H <sub>2</sub> O <sub>inter.</sub>	0.225	0	3.60	0.12	-0.225	0	-3.60	0.12
H <sub>2</sub> O <sub>inter.</sub>	-0.1125	0.3375	3.60	0.12	-0.1125	-0.3375	3.60	0.12
H <sub>2</sub> O <sub>inter.</sub>	0.1125	0.3375	-3.60	0.12	0.1125	-0.3375	-3.60	0.12

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949 **Table 4.** Typical inter-atomic distances calculated from the optimum atomic coordinates.

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Atomic pair	$\delta$ -MnO <sub>2</sub>	Acid birnessite	Biogenic oxide
Mn <sub>layer</sub> -O <sub>layer</sub>	1.920 Å	1.920 Å	1.920 Å
Mn <sub>inter.</sub> -O <sub>layer</sub>	-	2.00 Å	2.00 Å
Mn <sub>inter.</sub> -H <sub>2</sub> O	-	2.03 Å	2.03 Å
*Alc <sub>inter.</sub> -O <sub>layer</sub>	2.65 Å	2.97 Å	2.65 Å
*Alc <sub>inter.</sub> -H <sub>2</sub> O	2.838 Å	2.93 x1 / 2.99 x2 / 3.02x2 Å	2.838 Å
H <sub>2</sub> O <sub>inter.</sub> -O <sub>layer</sub>	2.65 Å	2.68 Å	2.65 Å

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952 \* Alc<sub>inter</sub> refers to the alkaline interlayer counterion, which is K<sup>+</sup> for “acid birnessite” and Na<sup>+</sup>  
 953 for the others. Inter-atomic distances from interlayer species to O<sub>layer</sub> are calculated with  
 954 respect to a unique layer, without adjacent layer whose actual position is unknown as a result  
 955 of the turbostratic stacking.

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**Table 5.** Optimized simulation parameters of K-edge Mn EXAFS for biogenic Mn oxide and synthetic analogs.

Sample	Mn-O (1)			Mn-O (2) <sup>‡</sup>			Shells <sup>†</sup>			Mn-Mn (tc)			$\Delta E$
	R(Å)	N	$\sigma^2$ (Å <sup>2</sup> )	R(Å)	N	$\sigma^2$ (Å <sup>2</sup> )	R(Å)	N	$\sigma^2$ (Å <sup>2</sup> )	R(Å)	N	$\sigma^2$ (Å <sup>2</sup> )	
$\delta$ -MnO <sub>2</sub>	1.90	5.7	0.0042	3.49	6*	0.0167	2.88	4.3	0.0042	-	-	-	0.6
Acid Birnessite	1.90	5.3	0.0038	3.50	6*	0.0134	2.88	4.6	0.0045	-	-	-	0.8
H-birnessite	1.91	4.5	0.0032	3.61	6*	0.0049	2.89	4.8	0.0051 <sup>#</sup>	3.49	2.8	0.0051 <sup>#</sup>	1.6
Biogenic (clean)	1.90	5.1	0.0035	3.42	6*	0.0149	2.87	2.9	0.0033	-	-	-	0.4
Biogenic (unclean)	1.91	4.8	0.0030	3.61	6*	0.0049	2.87	4.8	0.0051 <sup>#</sup>	3.49	2.8	0.0051 <sup>#</sup>	3.6
$\lambda$ -MnO <sub>2</sub> (standard)	1.91	6.0	0.0025	3.52	6*	0.0088	2.85	6.0	0.0028				1.5

961Note: <sup>†</sup>S<sub>0</sub><sup>2</sup> values used for the amplitude normalization were 0.73 for the O(1) shell and 0.80  
962for the Mn shells. Typical uncertainty on Mn-O (1), Mn-Mn (1), and Mn-Mn (tc)

963interatomic distances and coordination numbers are 0.02 Å and ± 1.5, respectively.

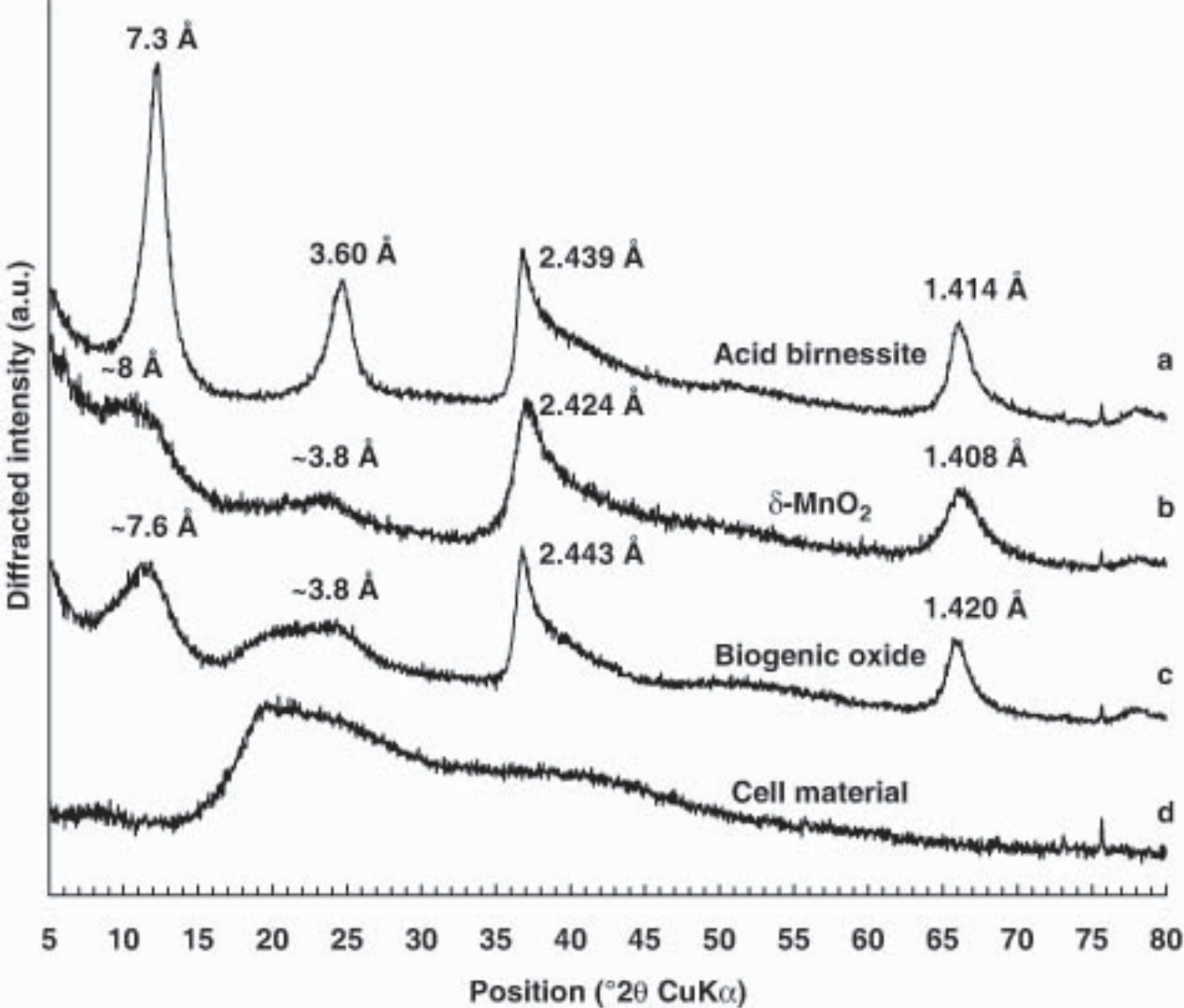
964<sup>‡</sup> The Mn-O(2) shell contribution is very weak and thus a high correlation occurs between  
965the optimized frequency and  $\Delta E$ , resulting in a low precision of the predicted parameters.

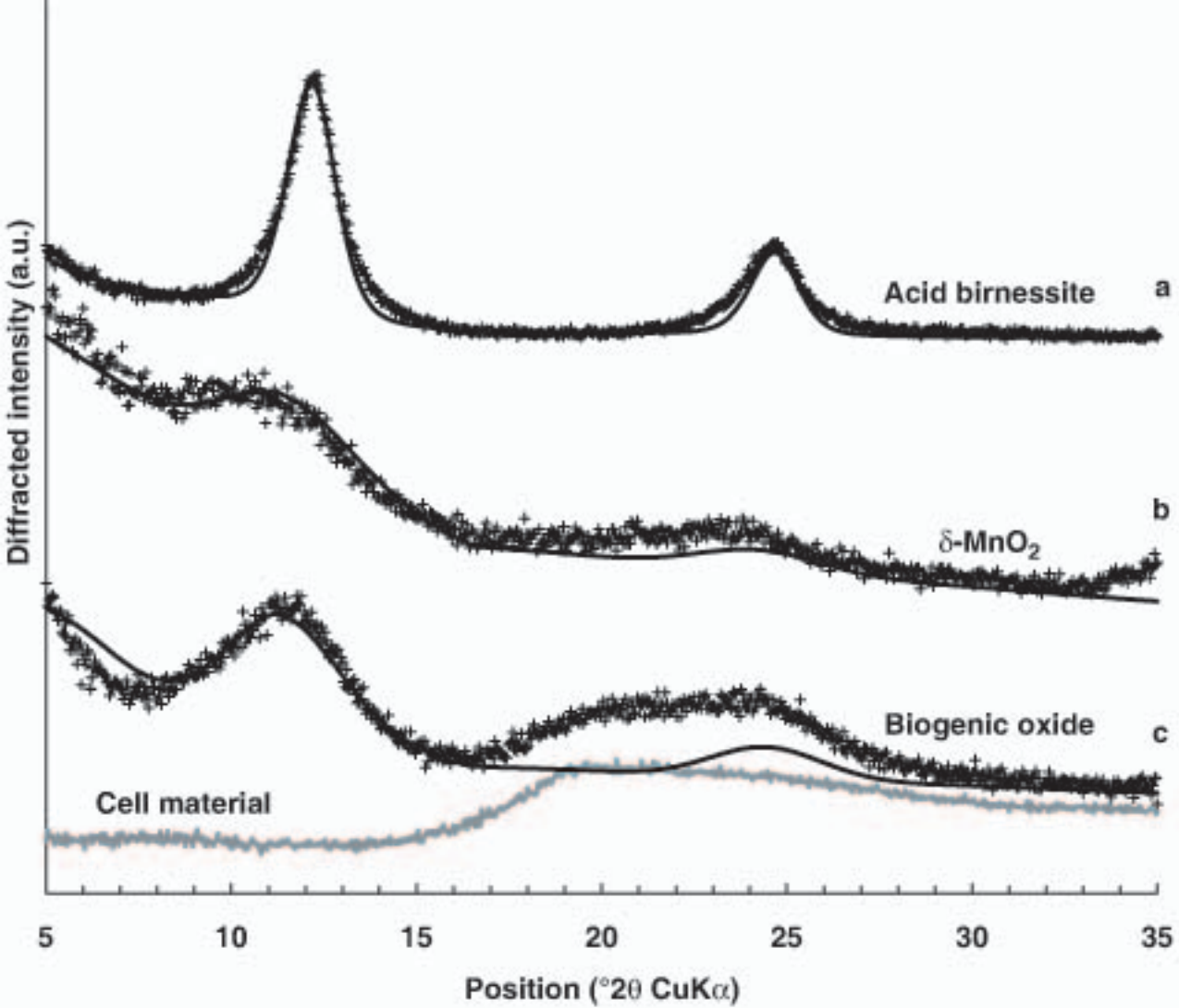
966\*Fixed value in the optimization procedure.

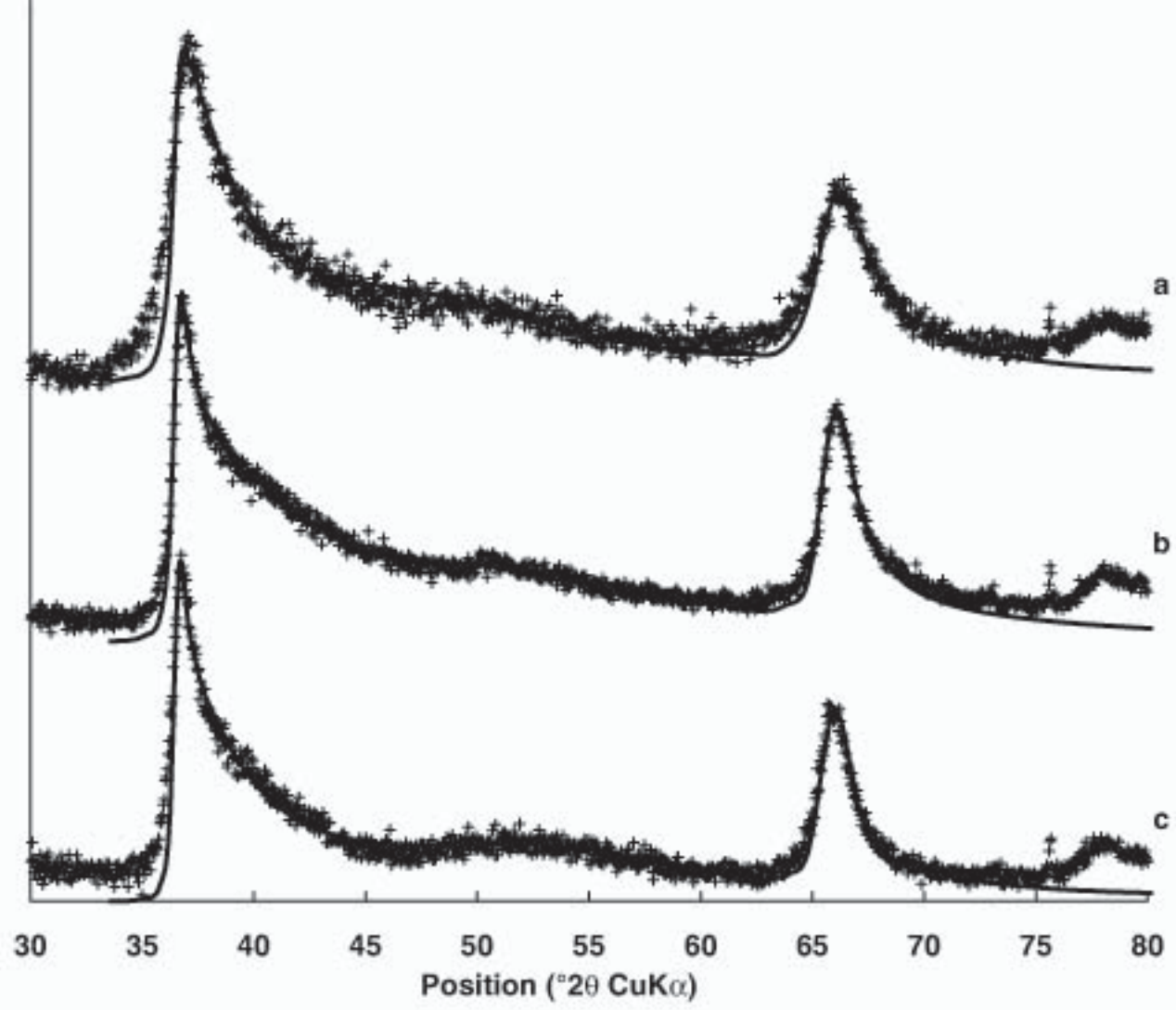
967<sup>#</sup> $\sigma$  values for the Mn(1) and Mn(tc) shells were floated but kept identical.

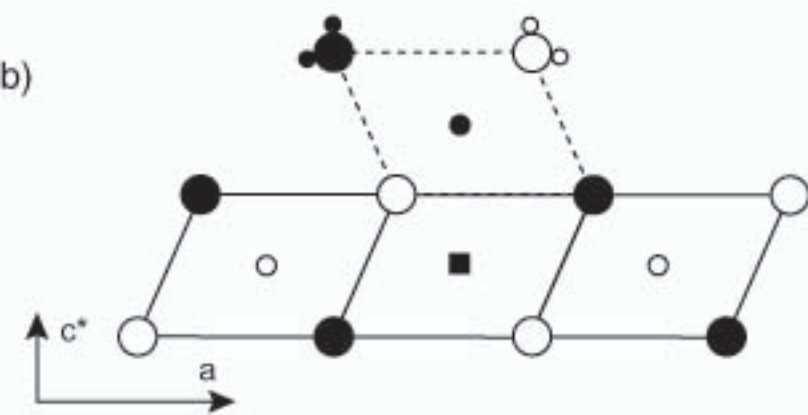
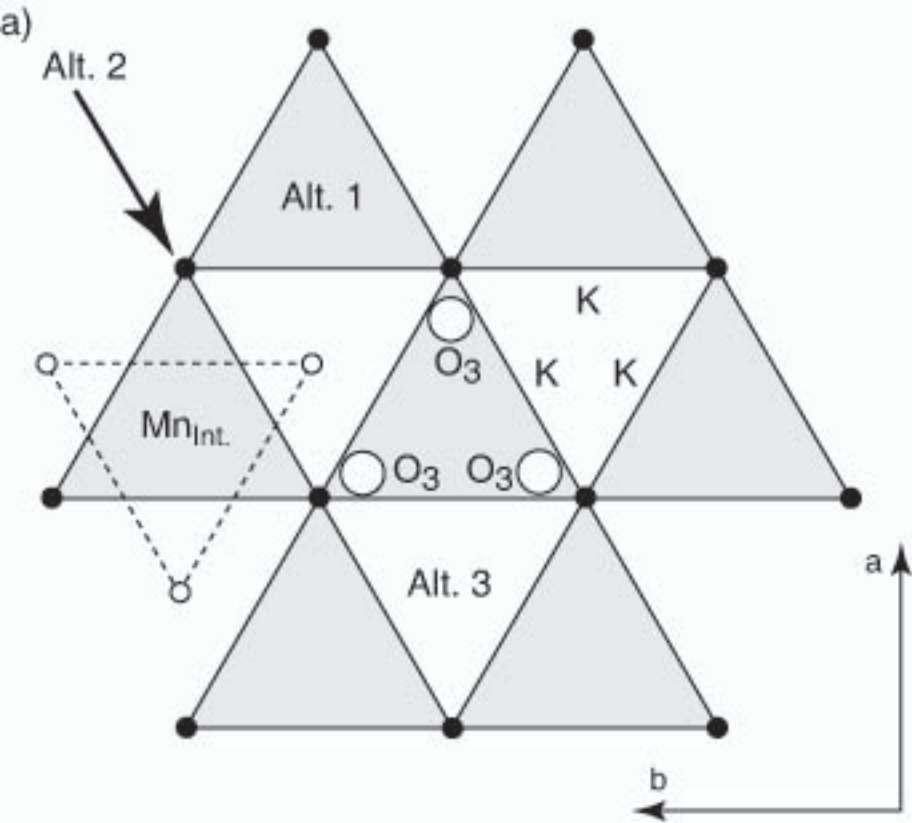
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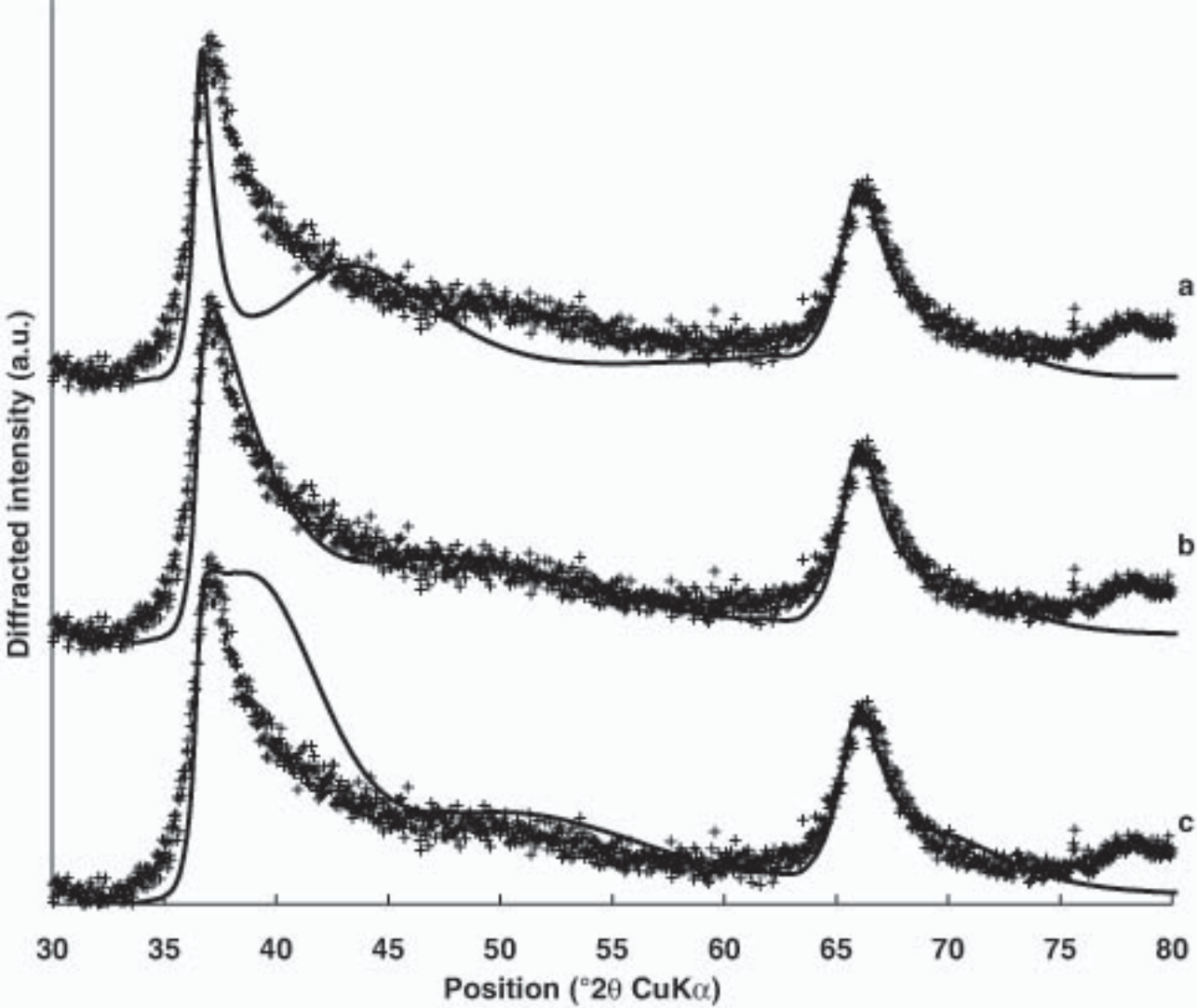
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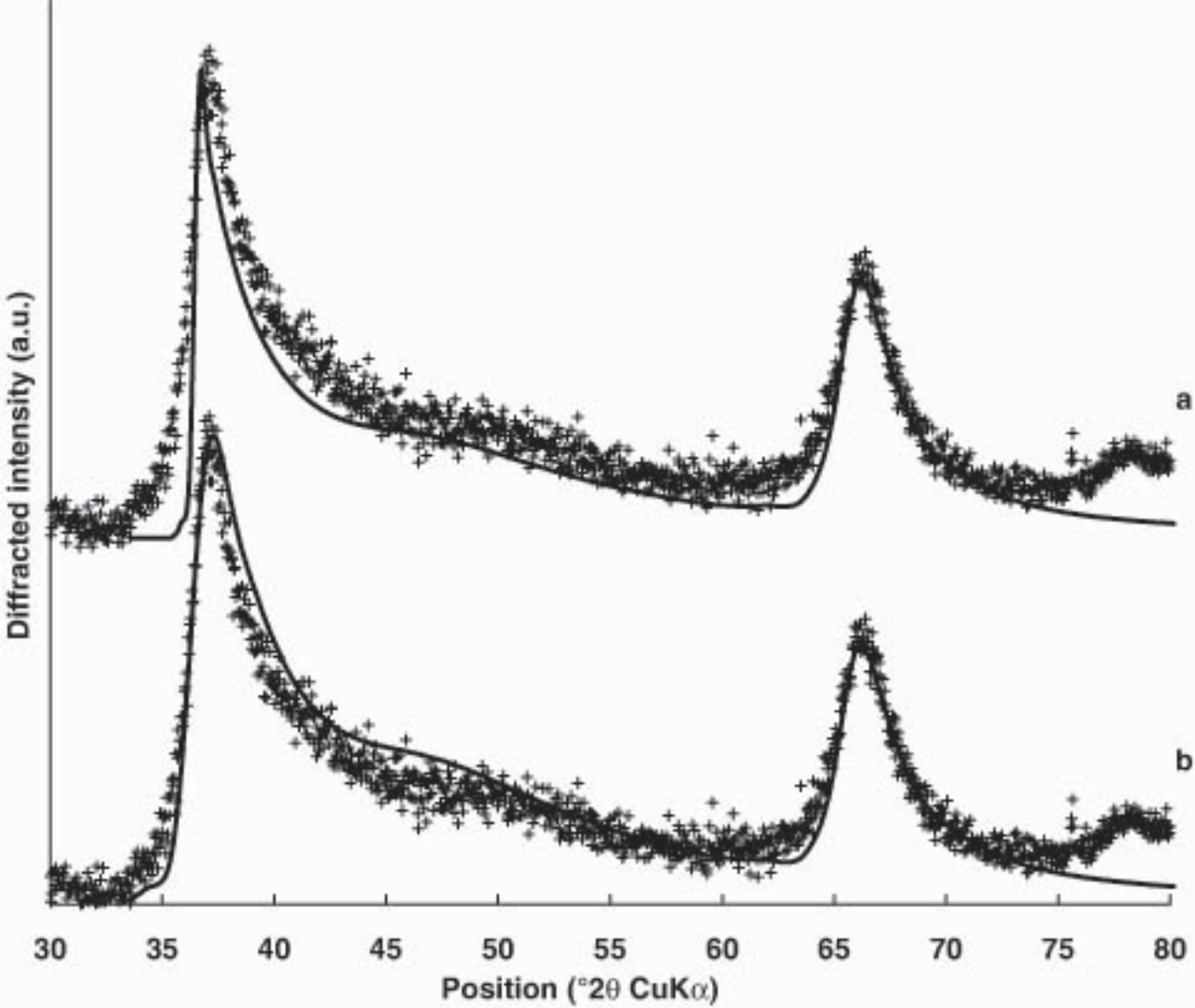


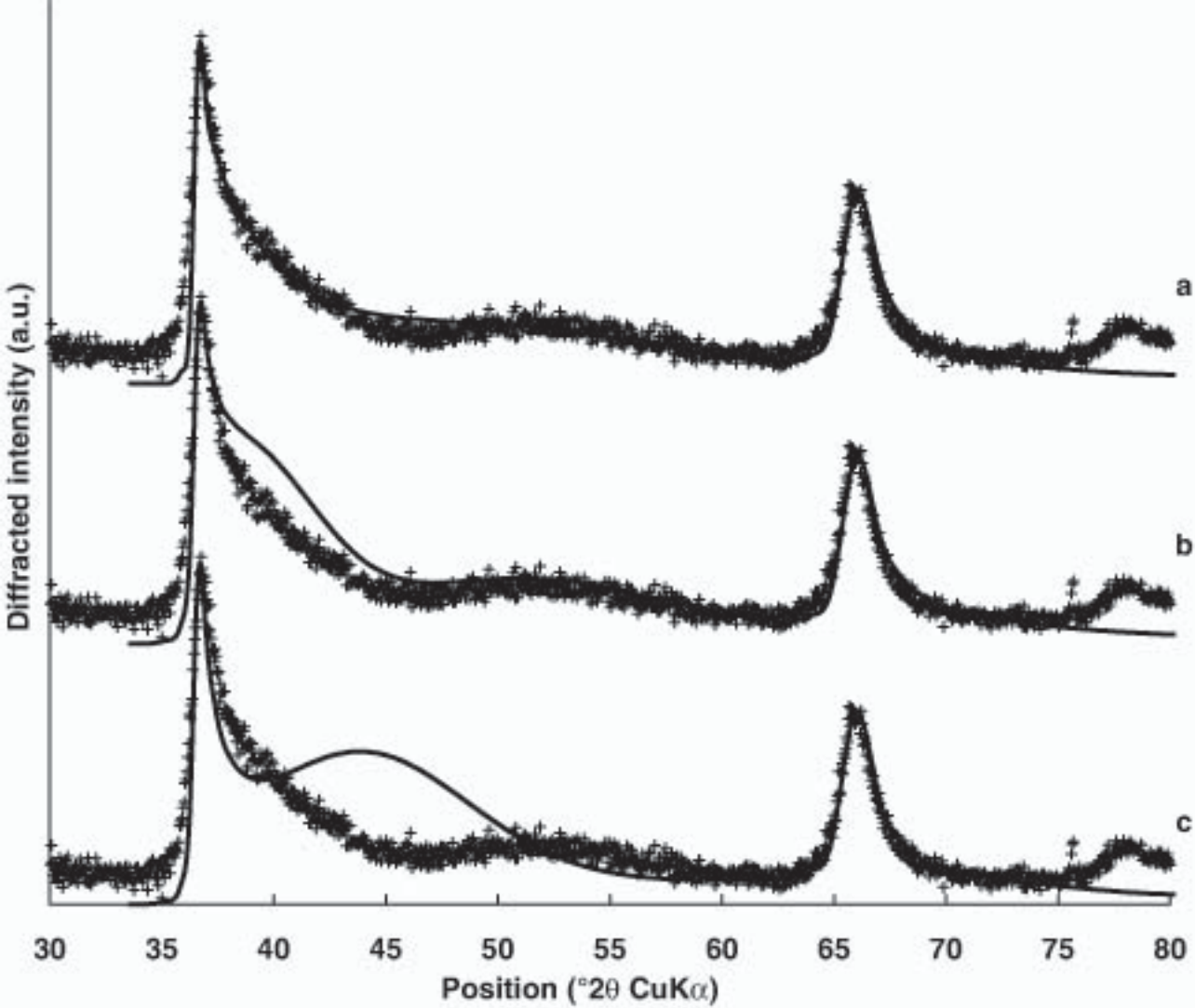


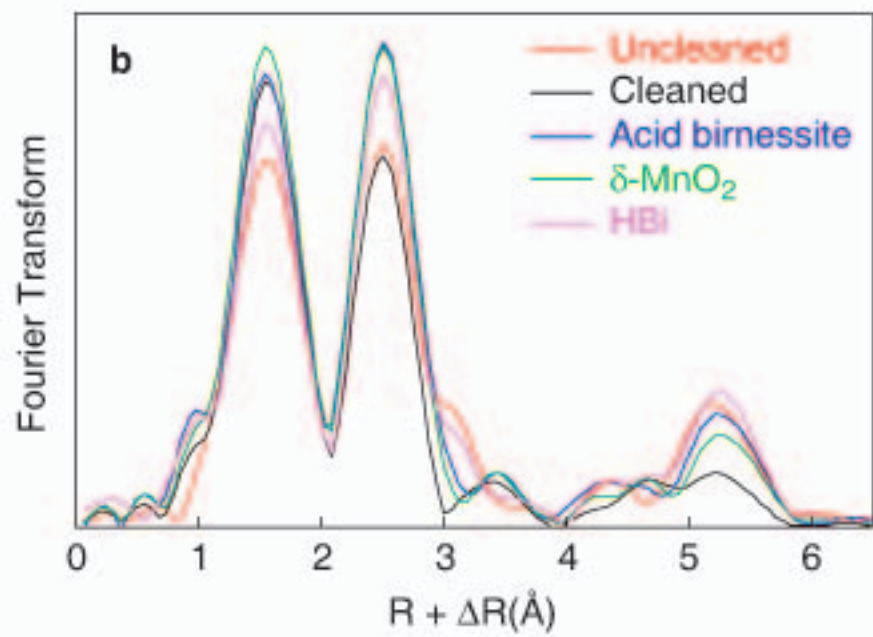
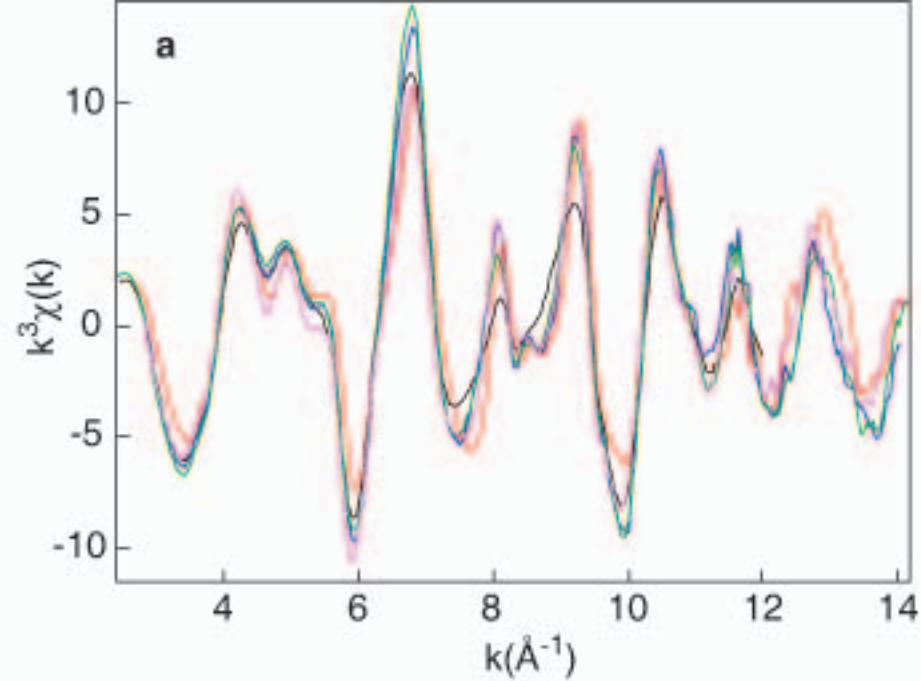


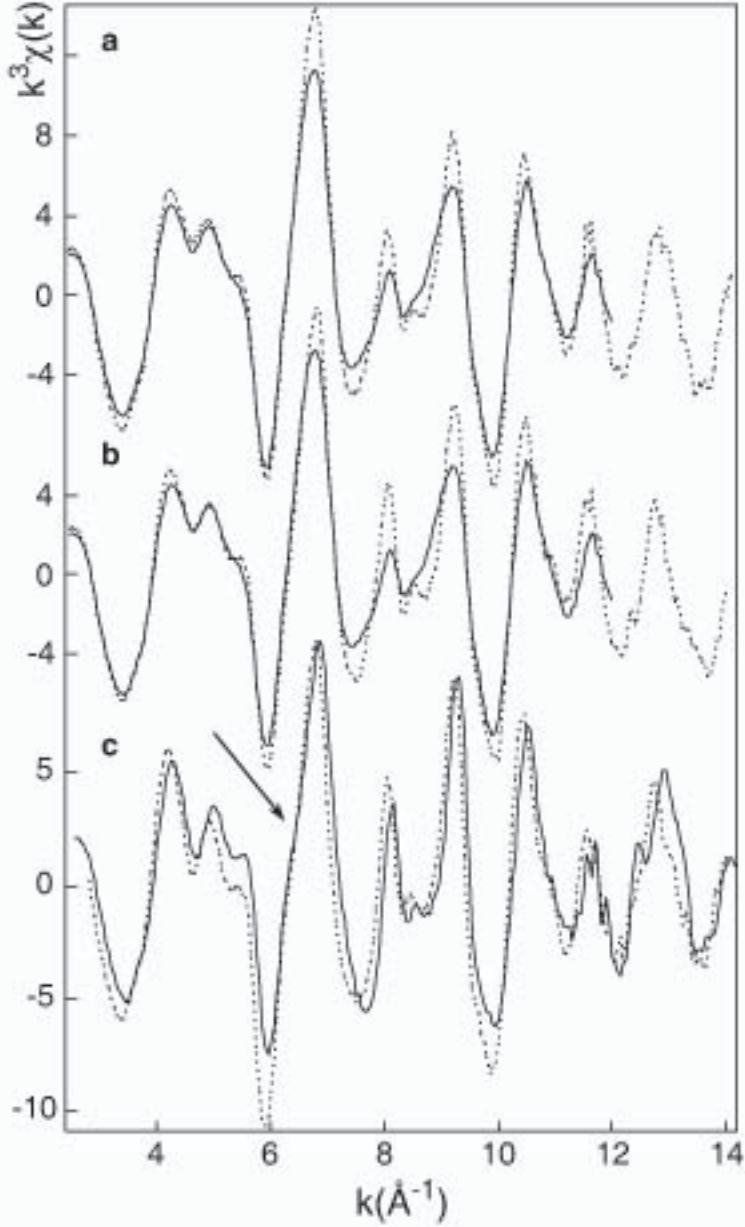


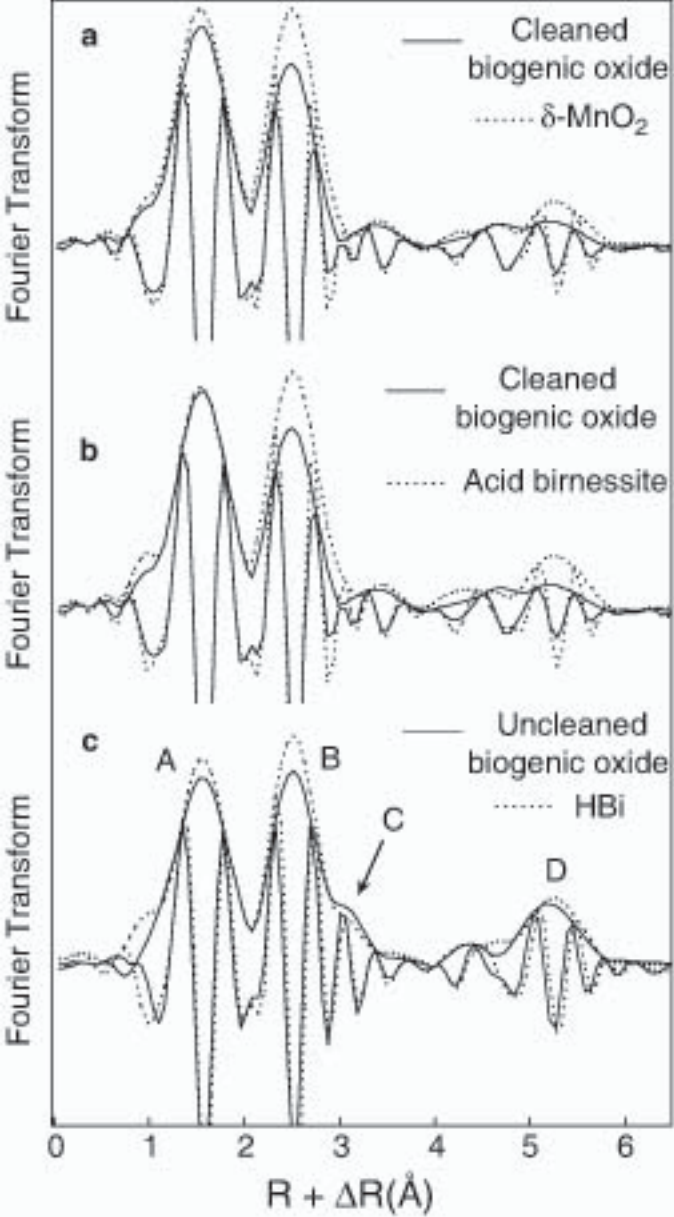


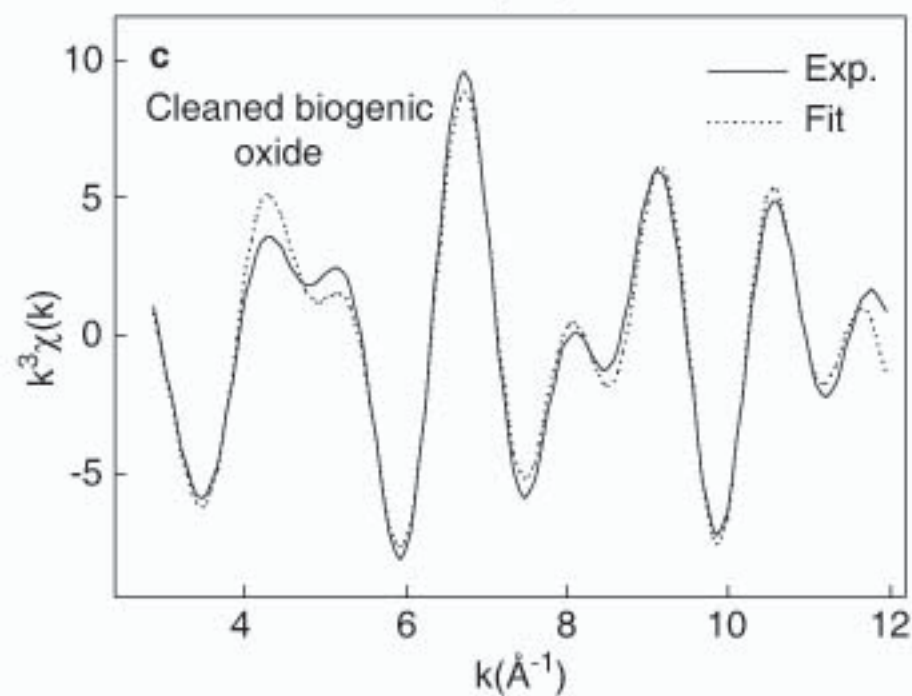
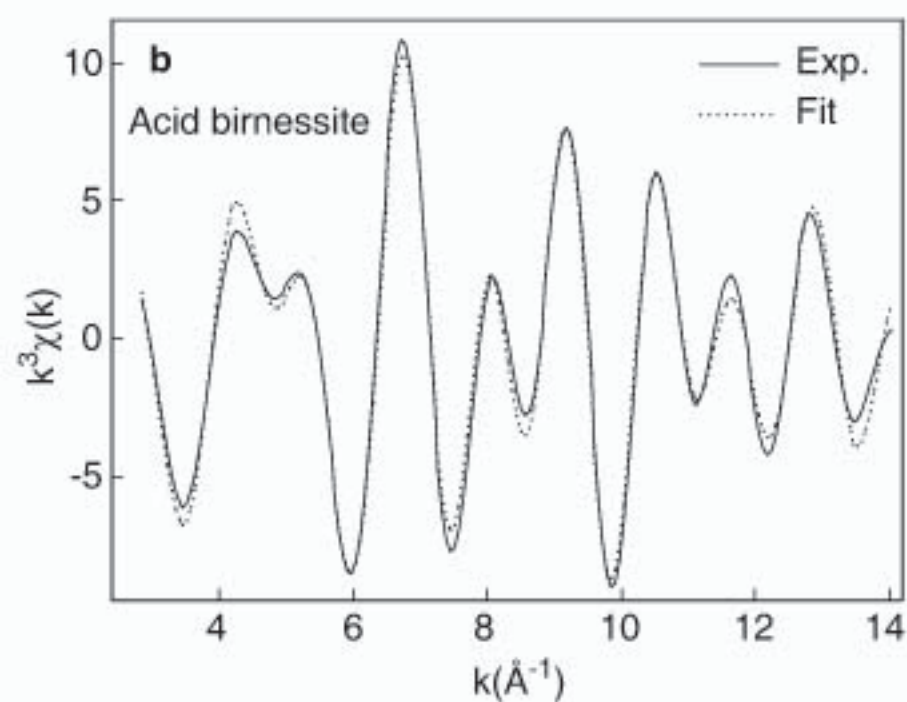
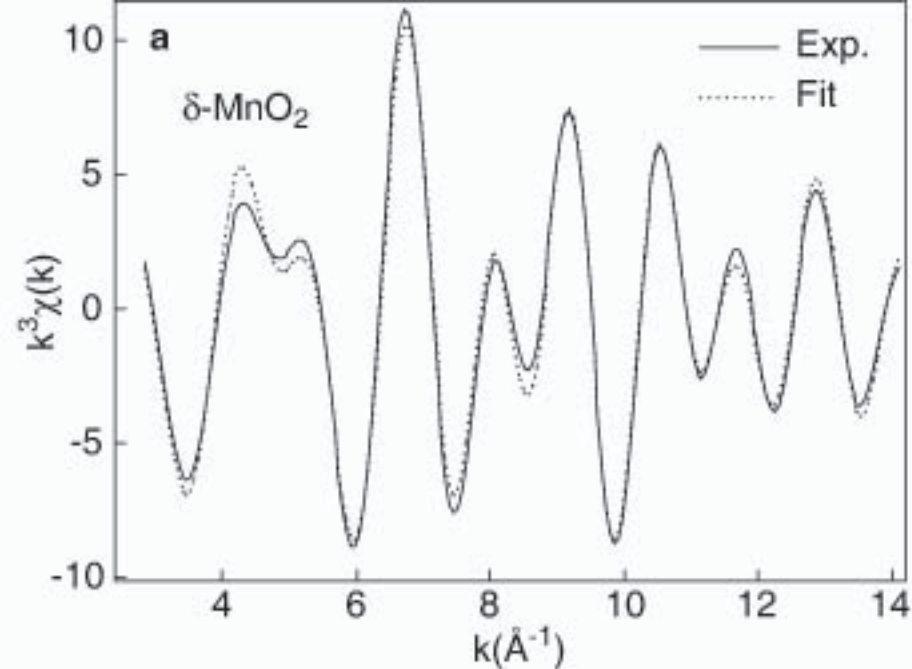














Side view of structural unit:

