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1 **Crystal structure of Ni-sorbed synthetic vernadite: A powder X-ray diffraction study**

2

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4

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9

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11 diffraction, crystal chemistry, Ni sorption

12

13 Running title: Structure of Ni-sorbed vernadite

14

## ABSTRACT

15

16

17 Vernadite is a nanocrystalline turbostratic phyllosilicate ubiquitous in the environment,  
18 which contains nickel in specific settings such as oceanic sediments. To improve our  
19 understanding of nickel uptake in this mineral, two series of synthetic analogs to vernadite ( $\delta$ -  
20  $\text{MnO}_2$ ) were prepared with Ni/Mn atomic ratios ranging from 0.002 to 0.105 at pH 4 and from  
21 0.002 to 0.177 at pH 7, and their structures characterised using X-ray diffraction (XRD). The  
22  $\delta$ - $\text{MnO}_2$  nano-crystals are essentially monolayers with coherent scattering domain sizes of  
23  $\sim 10$  Å perpendicular to the layer and of  $\sim 55$  Å in the layer plane. The layers contain an  
24 effective proportion of  $\sim 18\%$  vacant octahedral sites, regardless of the Ni content. At Ni/Mn  
25 ratios  $< 1\%$ , XRD has no sensitivity to Ni, and the layer charge deficit is apparently entirely  
26 balanced by interlayer Mn, Na, and protons. At higher Ni/Mn ratios, Ni occupies the same site  
27 as interlayer Mn above and/or below layer vacancies together with sites along the borders of  
28 the  $\text{MnO}_2$  layers, but the layer charge is balanced differently at the two pH values. At pH 4,  
29 Ni uptake is accompanied by a decrease in structural Na and protons, whereas interlayer Mn  
30 remains strongly bound to the layers. At pH 7, interlayer Mn is less strongly bound and partly  
31 replaced by Ni. The results also suggest that the number of vacant layer sites and multivalent  
32 charge-compensating interlayer species are underestimated in the current structure models for  
33  $\delta$ - $\text{MnO}_2$ .

34

35 **Introduction**

36

37 The phylломanganate vernadite, like its synthetic analog  $\delta$ -MnO<sub>2</sub> (McMurdie, 1944), is a  
38 nanosized and turbostratic variety of birnessite, that is a layered manganese oxide consisting  
39 of randomly stacked layers composed of MnO<sub>6</sub> octahedra (Bricker, 1965; Giovanoli, 1980). In  
40 the structure model presently available for  $\delta$ -MnO<sub>2</sub> (Villalobos *et al.*, 2006), the nano-sized  
41 layers contain only Mn<sup>4+</sup> cations and vacant octahedral sites (6%), whose charge is  
42 compensated for by interlayer Na<sup>+</sup> (Na<sub>0.24</sub>(H<sub>2</sub>O)<sub>0.72</sub>[Mn<sup>4+</sup><sub>0.94</sub>vac<sub>0.06</sub>]O<sub>2</sub>). Vernadite likely  
43 forms, at least in part, from the biologically-mediated oxidation of Mn(II) (Tebo *et al.*, 2004).  
44 For example, different strains of fungi and bacteria have been shown to produce vernadite-  
45 like oxides (Mandernack *et al.*, 1995; Jurgensen *et al.*, 2004; Tebo *et al.*, 2004, 2005; Webb *et*  
46 *al.*, 2005; Miyata *et al.*, 2006; Villalobos *et al.*, 2006). Their high metal sorption capacities  
47 result from the combination of small particle size, which induces a high number of border  
48 sites, and of vacant layer sites, which create a locally strong charge deficit.

49 As a result of this reactivity, vernadite has a key influence on the mobility of metals in a  
50 variety of environments. For example, Ni and other trace metals were reported to be  
51 associated with vernadite-like minerals in oceanic and lake ferromanganese nodules and  
52 crusts (Aplin and Cronan, 1985; Bogdanov *et al.*, 1995; Koschinsky and Halbach, 1995; Lei  
53 and Boström, 1995; Exon *et al.*, 2002; Koschinsky and Hein, 2003; Bodei *et al.*, 2007;  
54 Peacock and Sherman, 2007a; Manceau *et al.*, 2007a). Similarly, in manganese coatings  
55 deposited on water-processing filtration sands nickel is essentially bound to vernadite  
56 (Manceau *et al.*, 2007b). Understanding the reactivity of vernadite with nickel and the  
57 stability of Ni-complexes requires gaining insights into the metal-mineral interactions  
58 occurring at the atomic scale. The ability of usual diffraction methods, such as the Rietveld

59 method, is however impaired by the minute size and extreme stacking disorder of these  
60 compounds.

61 This article reports structure models for Ni-sorbed  $\delta$ -MnO<sub>2</sub> using X-ray diffraction  
62 (XRD), and chemical data. The layer and interlayer crystal structure and the mean number of  
63 stacked layers were determined from the trial-and-error simulation of the *hk* scattering bands  
64 and of the *00l* reflections (Drits and Tchoubar, 1990; Plançon, 2002). This modelling  
65 approach was applied previously on synthetic and natural phyllomanganates differing in  
66 chemical composition and density of structural defects (Chukhrov *et al.*, 1985; Lanson *et al.*,  
67 2000, 2002a, 2002b, 2008; Gaillot *et al.*, 2003, 2005, 2007; Villalobos *et al.*, 2006). The  
68 validity of the structure models was assessed from the comparison with Ni K-edge extended  
69 X-ray absorption fine structure (EXAFS) data and from bond valence calculations. Finally,  
70 structural mechanisms for the sorption of Ni onto  $\delta$ -MnO<sub>2</sub> crystals are proposed from the  
71 integration of all results.

72

### 73 **Experimental methods**

#### 74 *Synthesis of $\delta$ -MnO<sub>2</sub> and Ni sorption protocol*

75 The sample preparation was described previously (Manceau *et al.*, 2007b). Briefly,  
76 suspensions of Na-rich  $\delta$ -MnO<sub>2</sub> were prepared following the protocol of Villalobos *et al.*  
77 (2003), kept hydrated for several days, and then equilibrated at pH 4 or pH 7 and enriched  
78 afterwards in Ni at constant pH by the slow (0.4 mL/min) dropwise addition of a  $5 \times 10^{-4}$  mol/L  
79 Ni(NO<sub>3</sub>)<sub>2</sub> solution. After 12 h of equilibration, the suspensions were filtered, rinsed with a  
80 few mL of deionized water, and freeze-dried. The samples are named as in the previous study  
81 (Table 1).

82

83

84 *Chemical analysis*

85 The mean oxidation degree of manganese was determined by potentiometric titration using  
86 Mohr salt  $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)]$  and  $\text{Na}_4\text{P}_2\text{O}_7$  (Lingane and Karplus, 1946; Vetter and Jaeger,  
87 1966). Three measurements were made on each sample, and a reference was measured after  
88 each sample to ensure the absence of bias due to titrant ageing. Total Mn, Ni and Na contents  
89 were determined with a Perkin-Elmer Optima 3000 ICP-AES (Inductively Coupled Plasma –  
90 Atomic Emission spectrometer) on aliquots of solutions prepared from ~5 mg powder  
91 digested in ~15 mL  $\text{NH}_3\text{OHCl}$  (0.7 mol/L, pH 1.9) for 1 minute. Results are reported in  
92 Table 1.

93

94 *X-ray diffraction*

95 Powder X-ray diffraction (XRD) patterns were recorded over the 5-80 °2 $\theta$  angular range  
96 (17.6 Å – 1.20 Å) with a 0.04 °2 $\theta$  angular step and 40 seconds counting time per step, using a  
97 D5000 diffractometer equipped with a SolX solid-state detector from Baltic Scientific  
98 Instruments and  $\text{CuK}\alpha$  radiation. Simulations were performed successively on the high- (30-  
99 80 °2 $\theta$   $\text{CuK}\alpha$ ) and low-angle (5-30 °2 $\theta$   $\text{CuK}\alpha$ ) regions of the diffractograms. The high-angle  
100 region is dominated by the scattering from two-dimensional  $hk$  bands,  $hkl$  reflections being  
101 unresolved owing to the random layer stacking (random rotations and/or translations in the  $a$ -  
102  $b$  plane are systematic between adjacent layers). The in-plane unit-cell parameters ( $a$  and  $b$ )  
103 were determined from the position of the band at ~1.41 Å (31,02 band using a C-centered  
104 unit-cell, in which  $a$  and  $b$  axes are orthogonal), which is little affected by other structural  
105 parameters. The unit-cell parameters relative to the layer stacking ( $c$  parameter, and  $\alpha$  and  $\beta$   
106 angles) and the space group were not determined because of the turbostratic stacking which  
107 leads to the lack of any 3D periodicity. Despite the intrinsic structural disorder, atomic  
108 coordinates and site occupancies for layer (Mn) and interlayer (Na, Ni, Mn) cations were

109 however obtained from the simulation of the 11,20 band (at  $\sim 2.42$  Å), because its profile is  
110 strongly modulated by the crystal structure factor (Villalobos *et al.*, 2006; Drits *et al.*, 2007;  
111 Lanson *et al.*, 2008). The size of the coherent scattering domains (CSDs), which are supposed  
112 to have a disk-like shape in the *a-b* plane, also was derived from the modelling of the 11,20  
113 band profile. The low-angle region, which contains 00*l* reflections, was used to verify the  
114 lamellar character of the samples and to calculate the size of the CSDs along the  $c^*$  direction  
115 (i.e. the mean number of layers stacked coherently) and the  $d(001)$  basal distance. Atomic  
116 positions and occupancies were constrained to be identical for the simulation of the two sets  
117 of reflections.

118 The background was supposed to decrease linearly over the two angular ranges. The  
119 quality of fit was evaluated with the  $R_{wp}$  and GoF (Goodness of fit =  $R_{wp}^2/R_{exp}^2$ ) parameters  
120 (Attfield *et al.*, 1988; Howard and Preston, 1989). The uncertainty on the different structure  
121 parameters could not be determined quantitatively because the trial-and-error approach,  
122 required by the turbostratic nature of the samples investigated, does not allow the calculation  
123 of a covariance matrix. However, the uncertainty on interlayer cation site occupancy can be  
124 estimated to  $\pm 1\%$  from the comparison of experimental and calculated XRD patterns  
125 (Manceau *et al.*, 1997). Further qualitative assessment of uncertainties is provided by  
126 Villalobos *et al.* (2006) and Lanson *et al.* (2008) using sensitivity tests.

127

## 128 **Results**

### 129 *Qualitative description of XRD profiles*

130 The diffractograms of Ni-sorbed  $\delta$ -MnO<sub>2</sub> are typical of turbostratic birnessite-like crystals  
131 (Fig. 1 – Drits *et al.*, 1997; Villalobos *et al.*, 2006). The peaks at  $\sim 7.6$  Å and  $\sim 3.7$  Å  
132 correspond to basal reflections 001 and 002, although they do not form a strictly rational  
133 series (Lanson *et al.*, 2008). The broad and asymmetric scattering maxima at  $\sim 2.42$  Å,

134  $\sim 1.41 \text{ \AA}$  and  $\sim 1.22 \text{ \AA}$  are indexed as 11,20, 31,02 and 22,40 bands, respectively, using a C-  
135 centred unit cell (Drits *et al.*, 1997, 2007; Webb *et al.*, 2005; Villalobos *et al.*, 2006; Lanson  
136 *et al.*, 2008). For all samples, the  $d$ -spacings of the 11,20 and 31,02 bands are in a ratio  
137 ( $\sim 1.72$ ) close to  $\sqrt{3}$ , indicative of a hexagonal layer symmetry. The symmetry of the 31,02  
138 band profile also supports a layer unit cell that is hexagonal. If the layer unit cell were  
139 orthogonal this band would split into separate 31 and 02 bands and appear asymmetric (Drits  
140 *et al.*, 2007; Lanson *et al.*, 2008).

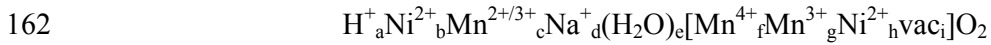
141 At first glance, all XRD patterns look similar, with the systematic presence of poorly  
142 defined  $00l$  reflections in the low-angle region, and of  $hk$  bands exhibiting similar relative  
143 intensities in the high-angle one. Upon closer examination, it appears however that only  
144 NidBi2-4 and NidBi11-4, and NidBi2-7 and NidBi11-7, are statistically indistinguishable  
145 (Fig. 1). Therefore, in the following NidBi11-4 and NidBi11-7 are omitted. The  $00l$   
146 reflections are more intense at pH 7 than pH 4, and decrease with increasing Ni content for  
147 the pH 4 series. The broad hump at  $50\text{-}55^\circ 2\theta$  becomes more pronounced as the Ni content  
148 increases in the two pH series (Fig. 1).

149 As shown by Drits *et al.* (2007), the modulations of the 11,20 band can be interpreted in  
150 structural terms. Specifically, XRD data resemble computations performed assuming  
151 hexagonal layer symmetry and  $\sim 17\%$  vacant layer sites capped by interlayer  $\text{Mn}^{2+/3+}$  in triple-  
152 corner sharing position (TC linkage, Fig. 2 – Manceau *et al.*, 2002). The above described  
153 “hump” is indeed characteristic of a high number ( $>10\%$ ) of layer vacancies capped by  
154 “heavy” cations (Figs. 13a, b in Drits *et al.*, 2007). Furthermore, “heavy” interlayer cations  
155 are located mainly in TC rather than TE (triple edge sharing – Fig. 2) position (see Fig. 13c in  
156 Drits *et al.*, 2007). We can thus hypothesize as a starting model, that all Ni-sorbed  $\delta\text{-MnO}_2$   
157 samples are turbostratic phyllosulfates, whose layers have a hexagonal symmetry and



158 bear significant amount of vacancies (>10%) capped mainly by “heavy” interlayer species  
159 (Mn or Ni) in TC or DC sites.

160 Combining this tentative structure model and the chemical data reported in Table 1, the  
161 following generic structural formula can be proposed:



163 where species between square brackets are located within the octahedral layer (vac stands for  
164 vacant layer sites) and those to the left of the brackets are interlayer species. The number of  
165 adjustable variables can be substantially reduced by physical and chemical constrains. First,  
166 EXAFS showed that Ni is predominantly located at TC and DC sites at pH 4 and pH 7 and  
167 Ni/Mn > 1% (Manceau *et al.*, 2007b –  $\langle d(\text{Ni-O}) \rangle \sim 2.05 \pm 0.02 \text{ \AA}$ ). At lower Ni concentration,  
168 Ni partly fills vacant layer sites (E sites) in proportions which depend on the pH. This fraction  
169 was ignored in XRD simulations ( $h = 0$ ) because it is minor (< 1%) compared to the number  
170 of Mn atoms in the manganese layers, and because Mn and Ni have similar scattering factors.  
171 Interlayer Mn cations are octahedrally coordinated as consistently reported in similar  
172 structures (Chukhrov *et al.*, 1985; Silvester *et al.*, 1997; Villalobos *et al.*, 2006; Lanson *et al.*,  
173 2008). In the simulations, sodium was coordinated to three water molecules as reported  
174 previously (Post and Veblen, 1990; Villalobos *et al.*, 2006). Finally, relative amounts of  $\text{Mn}^{4+}$ ,  
175  $\text{Mn}^{3+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Na}^+$  were constrained to their chemical values (Table 1), and protons were  
176 eventually introduced to ensure the electro-neutrality of the structure. Parameters adjusted  
177 during the fitting process were thus limited to the distribution of  $\text{Mn}^{3+}$  cations between layer  
178 and interlayer sites, the position of interlayer  $\text{Na}^+$  and coordinated  $\text{H}_2\text{O}$  molecules, and the  
179 coordinates of interlayer Mn, Ni, and associated  $\text{H}_2\text{O}$  molecules along the  $c^*$  axis.

180

181

182 *Simulation of the high-angle (30-80 °2θ Cu-Kα) region*

183 In a first attempt, atomic coordinates were assumed to be identical for all samples, as the  
184 synthesis and sorption procedures were analogous, and only site occupancies were adjusted,  
185 together with unit-cell parameters and CSD sizes. Once the main features of all XRD patterns  
186 were satisfactorily reproduced, atomic coordinates were adjusted for each sample, but the fit  
187 to the data could not be improved significantly. Atomic positions are thus identical for all  
188 samples which differ only by their respective unit-cell parameters, CSD sizes, and their  
189 contents of the various interlayer species (Tables 2, 3). The best fits to the XRD data are  
190 shown in Figure 3. The plausibility of the proposed models was assessed by calculating the  
191 valence of all atoms in the structure (Table 4 – Brown, 1996), which is an efficient way to  
192 constrain the model (Gaillot *et al.*, 2003).

193 The crystals are systematically nanosized (50-56 Å in diameter in the layer plane).  
194 Layers contain a significant amount (16-18.5%) of vacant sites, which are capped on one or  
195 the two sides by octahedrally coordinated Mn<sup>3+</sup> and/or Ni<sup>2+</sup>, depending on the Ni/Mn loading  
196 and on the equilibration pH. Na<sup>+</sup> and H<sup>+</sup> compensate for the remainder of the negative layer  
197 charge. With increasing Ni loading, the number of Ni complexes increases at the expense of  
198 Na<sup>+</sup> and/or interlayer Mn, depending on the pH series. At pH 4, Ni preferentially replaces  
199 Na<sup>+</sup>, the number of <sup>55</sup>Mn remaining constant within error, whereas Ni replaces both Na<sup>+</sup>,  
200 <sup>55</sup>Mn, and <sup>54</sup>Mn at pH 7.

201 Interlayer Mn<sup>3+</sup> and Ni<sup>2+</sup> are octahedrally coordinated and located either above/below  
202 vacant layer sites or in TE sites. Sodium is located in the interlayer mid-plane coordinated to  
203 three water molecules at 2.30 Å, 2.89 Å and 2.95 Å (Fig. 4). The first distance is shorter than  
204 commonly observed (i.e. ~2.45 Å – Angeli *et al.*, 2000) but has already been reported in the  
205 literature (Brown, 1977). The prevalence of monolayers precludes oxygen atoms from  
206 adjacent layers to provide bond valence to Na, and thus favours strong interactions with

207 interlayer H<sub>2</sub>O molecules. The first coordination sphere of Na<sup>+</sup> is limited to ~3.0 Å, consistent  
208 with theoretical studies (Delville, 1992). However, the sum of bond valence with H<sub>2</sub>O  
209 molecules (O6) and layer oxygen (O1) is not sufficient to fully compensate the Na<sup>+</sup> charge  
210 (Table 4), as discussed in the following section. The position of H<sub>2</sub>O molecules coordinated to  
211 interlayer Na<sup>+</sup> allows for the formation of strong H-bonds with layer oxygen atoms (O<sub>layer</sub>),  
212 with  $d(\text{H}_2\text{O}-\text{O}_{\text{layer}}) = 2.71 \text{ \AA}$ .

213 To match the measured mean oxidation degree of Mn, Mn<sup>3+</sup> cations have to be included  
214 in the octahedral layers, but the number of <sup>E</sup>Mn<sup>3+</sup> remains limited, peaking at ~9% of layer  
215 octahedra for sample NidBi2-4 (Table 1). This low number is consistent with the hexagonal  
216 symmetry of the layer (Gaillot *et al.*, 2005, 2007; Manceau *et al.*, 2005). The in-plane *b* unit-  
217 cell parameter ( $2.835 \text{ \AA} \leq b \leq 2.840 \text{ \AA}$ ) are similar to those reported previously for δ-MnO<sub>2</sub>  
218 ( $2.838 \text{ \AA}$  – Villalobos *et al.*, 2006). The sensitivity to this parameter was assessed with sample  
219 NidBi105-4 from the variation of R<sub>wp</sub> as a function of the *b* parameter ( $a = \sqrt{3} \times b$  – Fig. 5).  
220 The estimated error on *b* is ±0.001 Å.

221

### 222 *Simulation of the low-angle (5-30 °2θ) region*

223 The position, amplitude, and width of the two 00*l* reflections present over this low-angle  
224 region were simulated using the optimal structure models and adjusting only the out-of-plane  
225 *d*(001) parameter and CSD size along the *c*<sup>\*</sup> direction. Experimental data were fitted with  
226 mean CSD sizes of  $9.5/7.3 = 1.3$  to  $15.3/7.3 = 2.1$  layers (Table 2, Fig. 6). Thus, most crystals  
227 consist of isolated layers. When a diffracting crystallite contains two or more layers, its layer  
228 stacking is random (i.e., turbostratic) as no significant modulations are visible on *hk* bands  
229 (see Lanson *et al.*, 2008, for a discussion). The *d*(001) basal distance determined (7.3 Å) is  
230 slightly higher than usually reported for both ordered and disordered birnessites (7.2 Å). This

231 increased basal distance is consistent with the weak bonding between adjacent layers  
232 supported by the small CSD sizes.

233

## 234 **Discussion**

### 235 *Composition of the interlayer*

236 Except for Na, all atomic positions are consistent with those previously determined for metal-  
237 sorbed birnessite-like compounds, either well or poorly crystallised (Manceau *et al.*, 1997,  
238 2002; Lanson *et al.*, 2002b, 2008; Villalobos *et al.*, 2006). The Na<sup>+</sup> position [(-0.525, 0, 1/2)  
239 and equivalent positions] however provides this cation with an environment similar to that  
240 commonly reported in Na-bearing disordered birnessite (Villalobos *et al.*, 2006; Lanson *et al.*,  
241 2008) with  $d(\text{Na}-\text{O}_{\text{layer}}) \sim 2.66 \text{ \AA}$ . Na<sup>+</sup> coordination consists essentially of adjacent O<sub>layer</sub>  
242 atoms and interlayer H<sub>2</sub>O molecules, however failing to fully compensate the charge of this  
243 cation (Table 4). The nanocrystalline character of  $\delta$ -MnO<sub>2</sub>, and specifically the prevalence of  
244 monolayers, may account for the compensation of the remaining charge, as H<sub>2</sub>O molecules  
245 hydrating the crystals may actually contribute to charge compensation. For crystals composed  
246 of more than one layer, O<sub>layer</sub> from adjacent layers could also contribute to compensate the  
247 charge of interlayer Na, but sample turbostratism precludes the calculation of this bond  
248 valence.

249       The sensitivity of XRD patterns calculated for turbostratic birnessite to small variations  
250 of the site coordinates or occupancies has been discussed previously (Villalobos *et al.*, 2006;  
251 Drits *et al.*, 2007; Lanson *et al.*, 2008), and is not discussed further here to assess model  
252 robustness. The proposed structure model implies the replacement of interlayer Mn and Na  
253 cations by interlayer Ni (Table 3) with increasing Ni/Mn content. If based on XRD data only,  
254 this model could appear questionable as XRD is sensitive only to the distribution of electronic  
255 density but does not provide element-specific information. One could thus argue that XRD

256 simulation demonstrates essentially an increase of the electronic density above/below vacant  
257 layer sites with increasing Ni/Mn content, especially for the pH 7 series. This modification of  
258 the electron density distribution could possibly result from a limited adsorption of Ni  
259 assuming a constant number of interlayer Mn. Various constraints allow rejection of this  
260 alternative structure model. First, the two elements do not have the same  $z$ -coordinates, thus  
261 allowing their differentiation in the interlayer. Second, the mean oxidation degree of Mn  
262 increases with increasing Ni loading, showing that the number of  $\text{Mn}^{3+}$ , which is dominantly  
263 present as an interlayer species, decreases with increasing Ni/Mn content. In addition, a  $\text{Ni}^{2+}$ -  
264 for- $\text{Na}^+$  exchange would lead to a strong excess of charge in  $\delta$ - $\text{MnO}_2$  structure, whereas the  
265  $\text{Ni}^{2+}$ -for- $\text{Mn}^{3+}$  exchange avoids this effect despite the increased number of interlayer cations  
266 above/below vacant layer sites. Finally, the evolution of the Ni/Mn ratio requires increasing  
267 the Ni content in the XRD simulations. EXAFS showed that Ni was not present as a  
268 precipitate (Manceau *et al.*, 2007b), that would most likely have been detected also by XRD.  
269 The hypothesis of Ni sorption on the edges of  $\delta$ - $\text{MnO}_2$  crystals at a octahedral layer site (E  
270 site – Fig. 2) may also be rejected as it would lead to a significant increase of the CSD size of  
271 these crystals within the  $a$ - $b$  plane. The sorption of 2 Ni octahedra on the edges of  $\delta$ - $\text{MnO}_2$   
272 crystals would increase indeed the CSD size by 20-25% (from 54 to 66 Å in diameter), which  
273 would be easily detected by XRD owing to the high sensitivity of calculated patterns to this  
274 parameter (Villalobos *et al.*, 2006). For sample NidBi105-4, such an increase of the CSD size  
275 would lead to  $R_{\text{wp}}$  and GoF values of 7.04% and 6.62, respectively, about two times the value  
276 of the optimal model (5.00%, and 3.33, respectively – Fig. 3). Such sorption would impact  
277 also the EXAFS signal, inconsistent with the data since edge-sharing Ni-Mn pairs are  
278 excluded at high Ni/Mn (Manceau *et al.*, 2007b).

279 The local environment of Ni can be constrained further from Ni-EXAFS results  
280 obtained on the same samples by Manceau *et al.* (2007b). According to these results, Ni sorbs

281 predominantly as  $^{TC}Ni$  and  $^{DC}Ni$  complex at pH 4-7 and Ni/Mn ratios  $> 1\%$ . The XRD and  
282 EXAFS models are therefore consistent as the  $^{TC}Ni$  and  $^{DC}Ni$  sites are equivalent for XRD,  
283 the investigated solids being too disordered to allow the discrimination of small differences in  
284 atomic coordinates. Despite the partial sorption of Ni at DC sites, that is on particle edges  
285 (Manceau *et al.*, 2007b), no increase of the CSD is observed. This observation is possibly due  
286 to the multiplicity of Ni sorption sites (E, TC, DC) and to the possibility for Ni atoms to sorb  
287 on the two DC sites apart the same edge octahedron. Our results also agree with those  
288 reported by Peacock and Sherman (2007b) in their study of Ni sorption on synthetic  
289 hexagonal birnessite, a well crystallised phyllosilicate in which one sixth of the layer sites  
290 are vacant and capped by interlayer  $Mn^{3+}$  (Drits *et al.*, 1997; Silvester *et al.*, 1997; Lanson *et*  
291 *al.*, 2000). At pH 7, Peacock and Sherman (2007b) observed that  $\sim 90\%$  of total Ni occupy TC  
292 sites. The apparent absence of  $^{DC}Ni$  in their study is likely related to the larger lateral  
293 dimension of birnessite layers relative to  $\delta-MnO_2$  as the proportion of border sites, and thus  
294 surface reactivity of phyllosilicates in general, tremendously decreases when layer size  
295 increases (Tournassat *et al.*, 2002; Villalobos *et al.*, 2005; Webb *et al.*, 2005).

296 Sorption of metal cations in TE site has been seldom described (Lanson *et al.*, 2002b,  
297 2008). Here, it may be favoured by the combined effects of the high density of interlayer  
298 cations in TC position and the probable presence of some layer  $Mn^{3+}$  cations (Table 1). The  
299 occupancy of the two TC positions apart the same vacancy induces electrostatic repulsion,  
300 especially when  $Ni^{2+}$  is facing a  $Mn^{3+}$  cation, that can be minimised by moving one cation in  
301 TE position. In addition, the combined presence of  $Mn^{3+}$  cations and of vacant sites in the  
302 octahedral layers results in the strong undersaturation of some  $O_{layer}$  atoms that is best  
303 compensated for by the presence of interlayer cations in both TC and TE sites (Lanson *et al.*,  
304 2002b).

305

306 *Ni sorption mechanism*

307 Although similar structure models were obtained for the two  $\delta$ -MnO<sub>2</sub> series, the mechanism  
308 of Ni sorption likely differs at the two pHs, as attested macroscopically by the twofold  
309 increase in the evolution of the Mn mean oxidation degree with Ni loading at pH 7 (Fig. 7).  
310 Chemical data and XRD simulations suggest that at pH 4 Ni<sup>2+</sup> replaces preferentially Na<sup>+</sup> and  
311 H<sup>+</sup>, Mn<sup>3+</sup> being strongly bound to the octahedral layers, whereas Ni<sup>2+</sup> more readily exchanges  
312 for Mn<sup>3+</sup> at pH 7. This contrasting behaviour could result from the higher number of Mn<sup>3+</sup>  
313 cations in the octahedral layers at low pH. As discussed above, the coexistence in octahedral  
314 layers of vacant layer sites and Mn<sup>3+</sup> cations induces a strong undersaturation of O<sub>layer</sub> atoms,  
315 and therefore favours the binding of high-charge interlayer cations such as Mn<sup>3+</sup>.

316

317 *Comparison to structure models previously reported for  $\delta$ -MnO<sub>2</sub>*

318 For a long time, the structure of  $\delta$ -MnO<sub>2</sub> has been controversial. This compound, now known  
319 to be analogous to vernadite and turbostratic birnessite, was first reported by McMurdie  
320 (1944), and described as poorly crystalline cryptomelane (McMurdie and Golovato, 1948). In  
321 contrast, Feitknecht and Marti (1945) suggested a lamellar structure similar to pyrochroïte.  
322 The structural analogy between  $\delta$ -MnO<sub>2</sub> and birnessite was suggested by Giovanoli (1969,  
323 1980), and a structure model was proposed recently by Villalobos *et al.* (2006) using XRD  
324 and EXAFS spectroscopy. Despite the availability of structure models, and the demonstrated  
325 potential for structure characterization (Drits *et al.*, 2007),  $\delta$ -MnO<sub>2</sub> is however commonly  
326 referred to as “amorphous manganese oxide” or as “hydrous manganese oxide – HMO” (Xu  
327 and Yang, 2003; Boonfueng *et al.*, 2005; Huang *et al.*, 2007) without precision on important  
328 structural parameters such as the origin of the layer charge (vacant layer sites vs Mn<sup>3+</sup> in the  
329 layers).

330 The structure model proposed here differs in three points from the model proposed by  
331 Villalobos *et al.* (2006), for another sample synthesized following the same protocol.  
332 Previously, the structure was considered to contain only  $\text{Mn}^{4+}$ , because the average oxidation  
333 degree obtained by the oxalate and iodine titration methods was  $4.02 \pm 0.02$  (see Villalobos *et*  
334 *al.*, 2003, for details). Here, a value of  $3.80 \pm 0.03$  has been measured at pH 7 and low Ni  
335 content (NidBi2-7), suggesting the presence of  $\text{Mn}^{3+}$  or  $\text{Mn}^{2+}$ . The presence of  $\text{Mn}^{3+}$  both  
336 within the octahedral layer and as interlayer species at TC and TE sites is supported by  
337 chemical, bond valence, and XRD results which consistently show that  $\text{Mn}^{2+}$  occurs only as a  
338 minor interlayer species if present at all. In particular, the presence of  $\text{Mn}^{2+}$  at TC or TE sites  
339 is not consistent with the coordination of interlayer Mn cations determined from XRD  
340 modelling requiring the mean Mn-O bond length to be  $\sim 0.15 \text{ \AA}$  longer than in the proposed  
341 structure model (Table 2). Although  $\delta\text{-MnO}_2$  was equilibrated at pH 8 in the previous study,  
342 the 0.2 difference in Mn mean oxidation state is likely experimental because the oxalate and  
343 iodine methods used previously are less accurate than the Mohr salt / sodium pyrophosphate  
344 method used here (Gaillot, 2002). This hypothesis was verified by re-measuring the original  
345  $\delta\text{-MnO}_2$  sample (pH 8) studied by Villalobos *et al.* (2006) with the second titration method. A  
346 new value of  $3.88 \pm 0.03$  was obtained, consistent with the  $3.80 \pm 0.03$  value measured for  
347 NidBi2-7 taking into account the decrease in mean oxidation degree of manganese with  
348 decreasing pH observed here and for soil manganese oxides (Negra *et al.*, 2005). Note also  
349 that the new model yielded a better fit to XRD data ( $R_{\text{wp}} = 6.2\% - \text{GoF} \sim 4.6$ ) than the  
350 previous model ( $R_{\text{wp}} = 10.7\% - \text{GoF} \sim 9.4$ ). The second difference, which derives directly  
351 from the lower mean oxidation degree of Mn, is the presence of  $\text{Mn}^{3+}$  in the interlayer.  
352 Multivalent cations in TC and TE sites are more efficient at compensating the charge deficit  
353 of most undersaturated  $\text{O}_{\text{layer}}$  atoms than  $\text{Na}^+$  and  $\text{H}^+$  only, as in the previous model. The  
354 presence of multivalent cations at TC positions is also consistent with other structural studies



355 on  $\delta$ -MnO<sub>2</sub> and vernadite (Manceau *et al.*, 2007b; Peacock and Sherman, 2007b; Lanson *et*  
356 *al.*, 2008). Third, the new model has 18% vacant layer sites, compared to 6% for the  $\delta$ -MnO<sub>2</sub>  
357 sample studied previously. However, the new value does not reflect the actual number of  
358 vacant sites in the layer when CSDs are small in the *a-b* plane (Webb *et al.*, 2005). Here, with  
359 a CSD size of  $\sim 55$  Å, compared to  $\sim 120$  Å previously, a large fraction of Ni atoms is sorbed  
360 on border sites as <sup>DC</sup>Ni complex when Ni/Mn > 1% (Fig. 2 – Manceau *et al.*, 2007b). This  
361 complex increases the apparent number of layer vacancies seen by XRD because it has 2-3  
362 nearest Mn neighbours instead of 6 for <sup>TC</sup>Ni on basal planes. Thus, the  $\delta$ -MnO<sub>2</sub> crystals  
363 studied here have fewer layer vacancies than determined by XRD, because some of them are  
364 actually border sites. The distinction between interlayer and border sites becomes flimsy when  
365 crystals are vanishingly small.

366

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368

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374

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538



539 **Figure captions**

540

541 FIG. 1. XRD patterns of Ni-sorbed  $\delta$ -MnO<sub>2</sub>. **(a)** pH 4. **(b)** pH 7. The grey bar indicates a  
542 5 $\times$  scale factor for the high-angle region except for samples NidBi56-7 and NidBi177-7  
543 (1.67 $\times$  scale factor). For each pH series, the sample with the lowest Ni/Mn ratio is  
544 systematically shown as a light grey line to emphasize the modification of XRD traces with  
545 Ni content (arrows).

546

547 FIG. 2. Schematic representation of layer and interlayer sites reported in the literature for  
548 metal cations (including Mn) in  $\delta$ -MnO<sub>2</sub>. TC, DC and TE labels refer respectively to triple-  
549 corner sharing, double-corner sharing and triple-edge sharing sites. E label refers to layer  
550 sites.

551

552 FIG. 3. Simulations of the 11,20, 31,02 and 22,40 X-ray scattering bands (C-centred  
553 layer cell) for Ni-sorbed  $\delta$ -MnO<sub>2</sub> samples. Black crosses are experimental data, solid grey  
554 overplots are calculated profiles, and solid lines at the bottom are difference plots. Structural  
555 parameters used for the simulations are listed in Tables 2, and 3.

556

557 FIG. 4. Structure model of Ni-sorbed  $\delta$ -MnO<sub>2</sub>. **(a)** Projection on the  $a$ - $b$  plane. **(b)**  
558 Projection on the  $b$ - $c^*$  plane. Shaded octahedra represent layer Mn and its coordination  
559 sphere. Bonds between interlayer species and coordinating oxygens are shown in ball-and-  
560 stick. The coordinates of the different species along the  $c^*$  axis are given in Å.

561

562 FIG. 5. Simulations of the 31,02 X-ray scattering band (C-centred layer cell) for sample  
563 NidBi105-4. Gray crosses are experimental data, and lines are calculated profiles. The

564 optimum fit to the data (solid line) was obtained with  $b = 2.835 \text{ \AA}$  and  $a = \sqrt{3} \times b$  (Table 2).  
565 Varying  $b$  by  $\pm 0.01 \text{ \AA}$  with  $a = \sqrt{3} \times b$  significantly decreases the fit quality. The inset shows  
566 the evolution of  $R_{\text{wp}}$  with  $b$ .

567

568 FIG. 6. Simulations of the 001 and 002 diffraction lines for Ni-sorbed  $\delta$ - $\text{MnO}_2$ . Patterns  
569 as in Figure 4. Structural parameters used for the simulations are listed in Tables 2 and 3.

570

571 FIG. 7. Average oxidation degree of Mn as a function of Ni/Mn ratio for Ni-sorbed  $\delta$ -  
572  $\text{MnO}_2$  samples (circles: pH 4, triangles: pH 7).

TABLE 1. Chemical composition of Ni-sorbed  $\delta$ -MnO<sub>2</sub> expressed as atomic ratios.

Sample	Na/Mn (%)	Ni/Mn (%)	Mn Ox.	Layer Mn <sup>3+</sup>
NidBi2-4	18.39 ±0.30	0.23 ±0.23	3.74 ±0.03	0.09
NidBi11-4	16.99 ±0.27	1.07 ±0.23	3.73 ±0.03	N.D.
NidBi50-4	10.90 ±0.05	4.97 ±0.04	3.75 ±0.02	0.08
NidBi105-4	5.57 ±0.15	10.57 ±0.15	3.77 ±0.02	0.07
NidBi2-7	26.53 ±0.19	0.25 ±0.14	3.80 ±0.03	0.04
NidBi11-7	26.80 ±0.40	1.07 ±0.24	3.80 ±0.03	N.D.
NidBi56-7	20.87 ±0.22	5.66 ±0.15	3.85 ±0.02	0.01
NidBi177-7	7.61 ±0.22	17.78 ±0.21	3.94 ±0.01	0.00

*Note:* Mn Ox. stands for “oxidation degree”. Layer Mn<sup>3+</sup> is calculated from the average oxidation degree of Mn and from the number of interlayer Mn atoms (Table 3), which are considered to be trivalent. Uncertainties on the mean values are calculated as the mean of standard errors (Webster, 2001). Sample names as in Manceau *et al.* (2007b)

TABLE 2. Crystal data for Ni-sorbed  $\delta$ -MnO<sub>2</sub>.

	NidBi2-4	NidBi50-4	NidBi105-4	NidBi2-7	NidBi56-7	NidBi177-7
$a$ (Å)	4.916	4.912	4.910	4.917	4.919	4.917
$b$ (Å)	2.838	2.836	2.835	2.839	2.840	2.839
$d(001)$ (Å)	7.3	7.3	7.3	7.3	7.3	7.3
Average CSD along $c$ (Å)	11.0	10.2	9.5	12.4	15.3	11.0
CSD in the $a$ - $b$ plane (Å) <sup>a</sup>	56	54	54	54	54	50
$R_{wp}$ (%) <sup>b</sup>	5.72-6.32	4.12-5.17	4.97-5.00	8.74-6.15	5.22-5.82	5.21-6.06
GoF (%) <sup>b</sup>	6.49-4.53	3.57-3.32	5.41-3.33	15.40-4.45	8.42-6.52	5.41-4.17

<sup>a</sup> Diameter of the disk-like coherent scattering domains. <sup>b</sup> First and second values are calculated over the low- and high-angle regions, respectively.

TABLE 3. Structural parameters of Ni-sorbed  $\delta$ -MnO<sub>2</sub> derived from XRD.

Atom	$x^a$	$y$	$z$	$\zeta^b$	Occ. <sup>c</sup> NidBi2-4	Occ. <sup>c</sup> NidBi50-4	Occ. <sup>c</sup> NidBi105-4	Occ. <sup>c</sup> NidBi2-7	Occ. <sup>c</sup> NidBi56-7	Occ. <sup>c</sup> NidBi177-7
Mn <sub>layer</sub> (Mn1)	0.000	0.000	0.000	0.000	0.82	0.82	0.82	0.82	0.815	0.84
O <sub>Mn1</sub> (O1)	0.333	0.000	0.139	1.015	2.00	2.00	2.00	2.00	2.00	2.00
<sup>TC</sup> Mn (Mn2)	0.000	0.000	0.299	2.183	0.14	0.16	0.16	0.10	0.085	0.07
H <sub>2</sub> O <sub>Mn2</sub> (O2)	-0.333	0.000	0.472	3.446	0.42	0.48	0.48	0.30	0.255	0.21
<sup>TE</sup> Mn (Mn3)	-0.333	0.000	0.299	2.183	0.03	0.00	0.00	0.05	0.04	0.00
H <sub>2</sub> O <sub>Mn3</sub> (O3)	0.000	0.000	0.472	3.446	0.09	0.00	0.00	0.15	0.12	0.00
<sup>TC</sup> Ni (Ni1)	0.000	0.000	0.306	2.234	0.00	0.04	0.07	0.00	0.05	0.13
H <sub>2</sub> O <sub>Ni1</sub> (O4)	-0.333	0.000	0.486	3.548	0.00	0.12	0.21	0.00	0.15	0.39
<sup>TE</sup> Ni (Ni2)	-0.333	0.000	0.315	2.300	0.00	0.02	0.02	0.00	0.00	0.02
H <sub>2</sub> O <sub>Ni2</sub> (O5)	0.000	0.000	0.486	3.548	0.00	0.06	0.06	0.00	0.00	0.06
Na <sub>interlayer</sub> (Na) <sup>d</sup>	-0.525	0.000	0.500	3.650	0.18	0.06	0.06	0.24	0.18	0.06
H <sub>2</sub> O <sub>Na+</sub> (O6) <sup>e</sup>	0.200	0.000	0.500	3.650	0.54	0.18	0.18	0.72	0.54	0.18

<sup>a</sup> Atomic coordinates  $x$ ,  $y$ ,  $z$  are expressed as fractions of the  $a$ ,  $b$  and  $d(001)$  parameters, respectively. Positions are given in the  $(x, 0, z)$  form. Equivalent positions are  $(x + \frac{1}{2}, \frac{1}{2}, z)$ , because the unit cell is C-centred. Additional equivalent positions are  $(-x, 0, -z)$ . <sup>b</sup> Coordinates along the  $c^*$  axis,  $\zeta$ , are expressed in Å to emphasize the thickness of layer and interlayer polyhedra. <sup>c</sup> Occupancies are given per half

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formula unit as the sum of the occupancies for all equivalent positions. <sup>d</sup> Additional symmetry operations:  $(-x/2 - 1/2, 3x/2 + 1/2, z)$ , and  $(-x/2 - 1/2, -3x/2 - 1/2, z)$ . <sup>e</sup> Additional symmetry operations:  $(-x/2, 3x/2, z)$ , and  $(-x/2, -3x/2, z)$ .

Unrefined Debye-Waller thermal factors (B) are equal to 0.5 for Mn<sub>layer</sub>, 1.0 for O<sub>layer</sub>, interlayer Mn and Ni, 1.5 for H<sub>2</sub>O molecules bound to interlayer Mn and Ni, and 2.0 for other interlayer species (alkali cations and H<sub>2</sub>O molecules).

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TABLE 4. Bond valences calculated<sup>a</sup> for Ni-sorbed  $\delta$ -MnO<sub>2</sub>

	O1 <sup>b</sup>	O1 <sup>c</sup>	O1 <sup>d</sup>	O1 <sup>e</sup>	O2/O3	O4/O5	O6	$\Sigma$	Formal valence
Mn1	0.625 $\times 6 \rightarrow$ $\times 3 \downarrow$	0.625 $\times 2 \downarrow$	0.625 $\times 2 \downarrow$	0.625 $\times 2 \downarrow$				3.75	4
Mn2, Mn3		0.509 $\times 3 \rightarrow$			0.433 $\times 3 \rightarrow$			2.8	3
Ni1, Ni2			0.298-0.352 <sup>f</sup> $\times 3 \rightarrow$			0.300-0.317 <sup>f</sup> $\times 3 \rightarrow$		1.9	2
Na <sup>+</sup>				0.091 0.012 $\times 2 \rightarrow$			0.261, 0.053, 0.045 <sup>g</sup>	0.5	1
H <sup>+</sup>				0.105 <sup>h</sup>	0.815 $\times 2 \downarrow$	0.815 $\times 2 \downarrow$	0.815 $\times 2 \downarrow$		
$\Sigma$	1.9	1.8	1.5-1.6 <sup>f</sup>	1.3-1.4 <sup>i</sup>	2.1	1.9	1.7-1.9 <sup>g</sup>		

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<sup>a</sup> Bond valences in valence unit (v.u.) were calculated using the Valence for Dos program (v. 2.0 - [http://www.ccp14.ac.uk/solution/bond\\_valence/index.html](http://www.ccp14.ac.uk/solution/bond_valence/index.html) – Brown, 1996) and the parameters from Brese and O' Keeffe (1991). <sup>b</sup> O1 coordinated to 3 Mn<sup>4+</sup> in Mn1 (Table 3). <sup>c</sup> O1 coordinated to 2 Mn<sup>4+</sup> in Mn1 and 1 Mn<sup>3+</sup> in Mn2 or Mn3 (Table 3). <sup>d</sup> O1 coordinated to 2 Mn<sup>4+</sup> in Mn1 and 1 Ni<sup>2+</sup> in Ni1 or Ni2 (Table 3). <sup>e</sup> O1 coordinated to 2 Mn<sup>4+</sup> in Mn1 (Table 3). <sup>f</sup> Depending on whether Ni is located in Ni1 or in Ni2. <sup>g</sup> Na<sup>+</sup> is coordinated to 3 H<sub>2</sub>O molecules at 2.30, 2.89, and 2.95 Å. <sup>h</sup> O6-H-O1 H-bond. <sup>i</sup> Depending on whether this O1 receives additional valence from Na<sup>+</sup> or from H<sup>+</sup> through H-bond.

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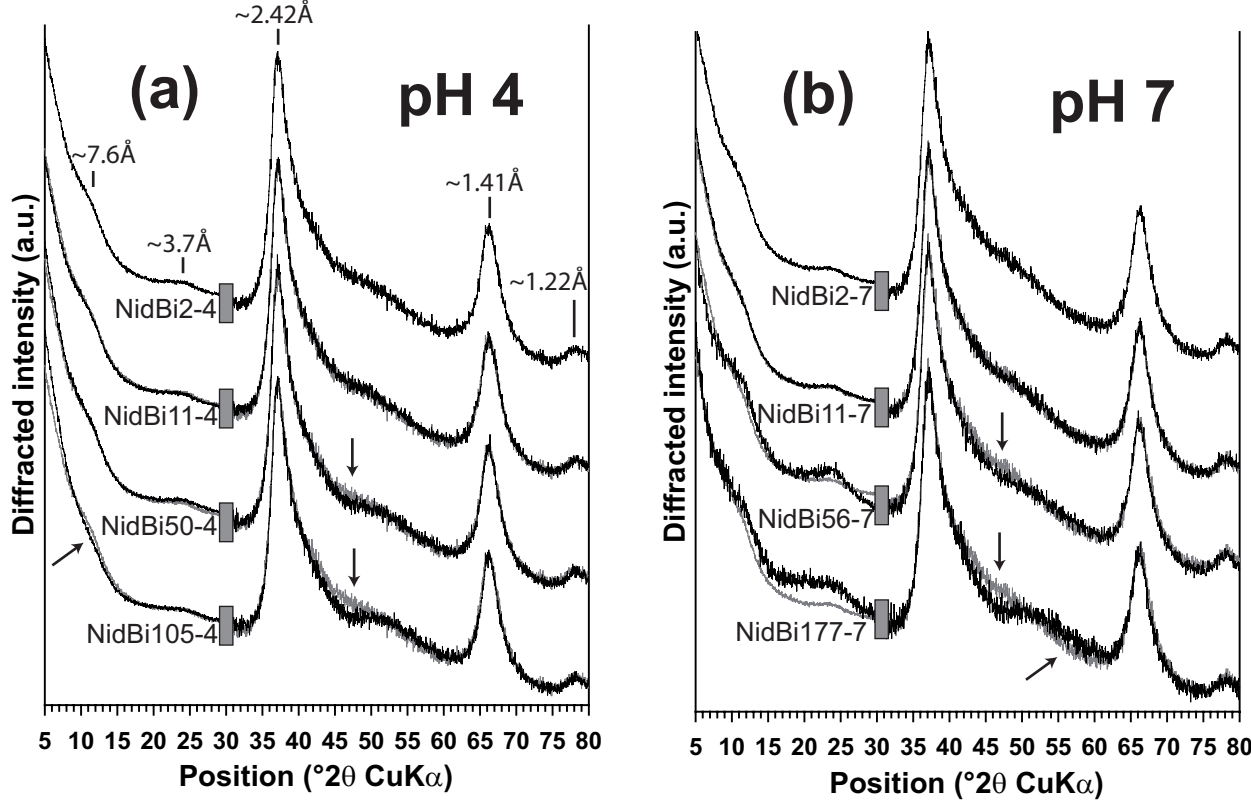


Figure 1

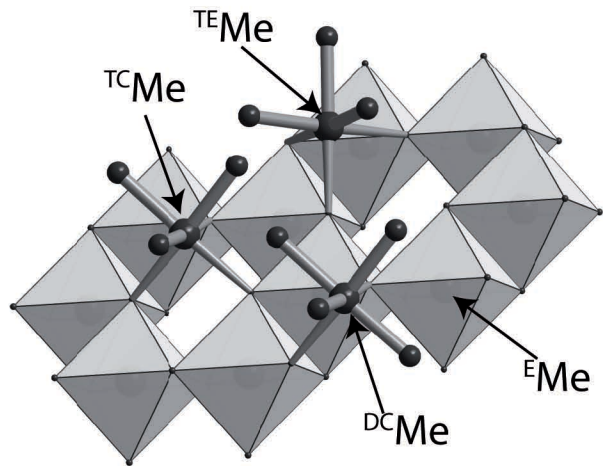


Figure 2

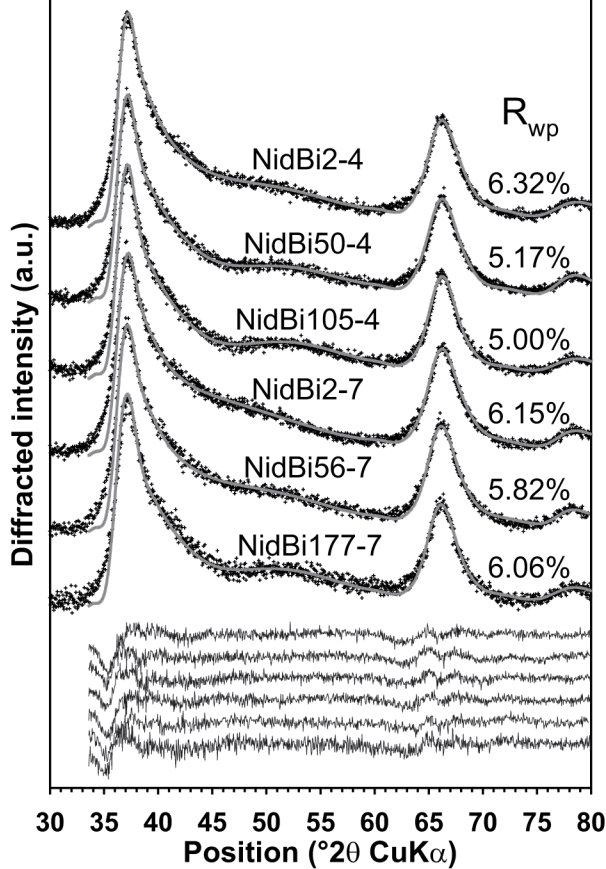


Figure 3

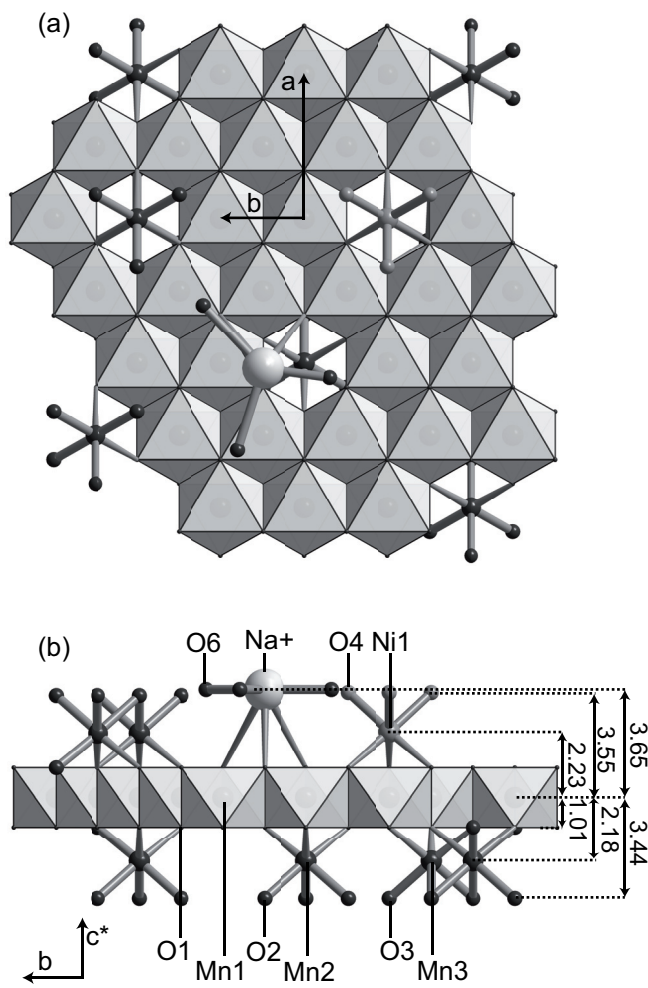


Figure 4

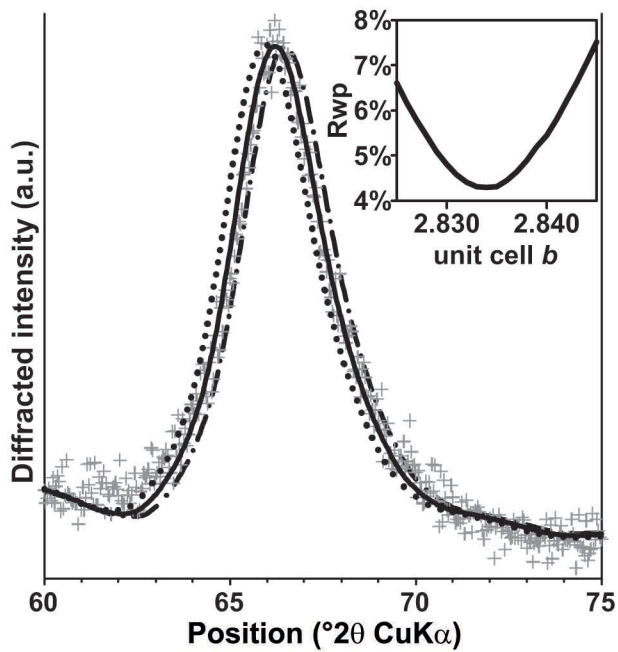


Figure 5

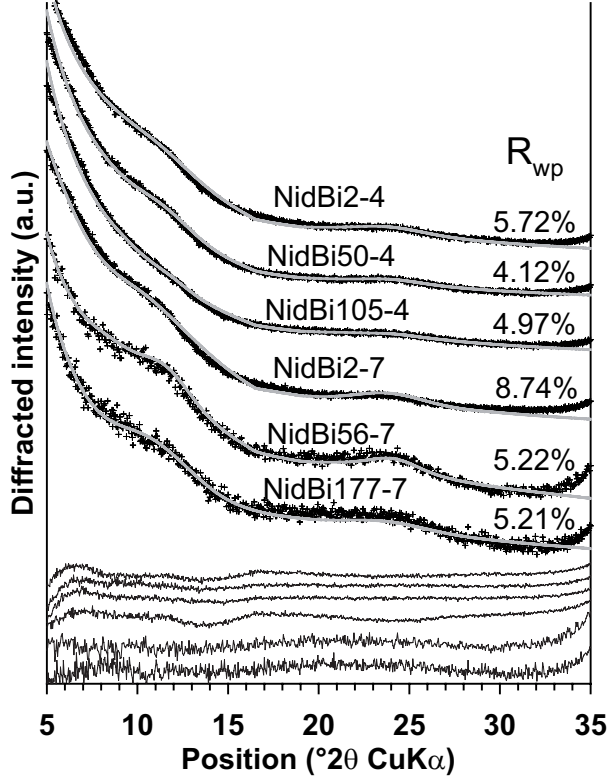


Figure 6

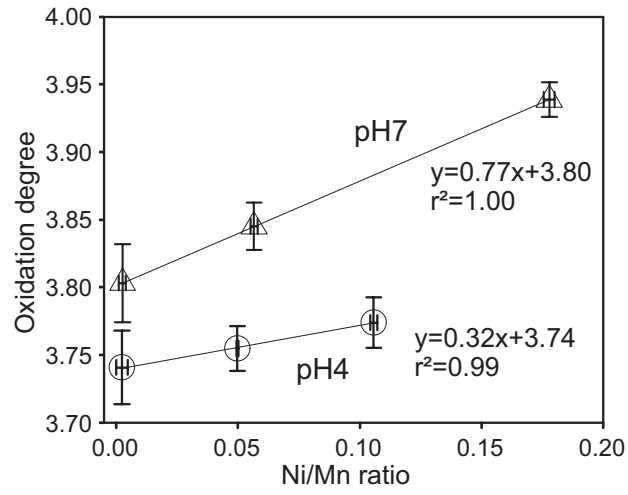


Figure 7