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

2

3 Sylvain Grangeon*, Bruno Lanson, Martine Lanson, and Alain Manceau

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5 ¹Mineralogy & Environments Group, LGCA, Maison des Géosciences, BP53, Université

6 Joseph Fourier – CNRS, 38041 Grenoble Cedex 9, France

7

8 * E-mail: Sylvain.Grangeon@obs.ujf-grenoble.fr

9

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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 (δ -
20 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 δ - MnO_2 nano-crystals are essentially monolayers with coherent scattering domain sizes of
23 ~ 10 Å perpendicular to the layer and of ~ 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 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 δ - MnO_2 .

34

35 **Introduction**

36

37 The phylломanganate vernadite, like its synthetic analog δ -MnO₂ (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 MnO₆ octahedra (Bricker, 1965; Giovanoli, 1980). In
40 the structure model presently available for δ -MnO₂ (Villalobos *et al.*, 2006), the nano-sized
41 layers contain only Mn⁴⁺ cations and vacant octahedral sites (6%), whose charge is
42 compensated for by interlayer Na⁺ (Na_{0.24}(H₂O)_{0.72}[Mn⁴⁺_{0.94}vac_{0.06}]O₂). 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 δ -MnO₂ 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 δ -MnO₂ crystals are proposed from the
71 integration of all results.

72

73 **Experimental methods**

74 *Synthesis of δ -MnO₂ and Ni sorption protocol*

75 The sample preparation was described previously (Manceau *et al.*, 2007b). Briefly,
76 suspensions of Na-rich δ -MnO₂ 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 5×10^{-4} mol/L
79 Ni(NO₃)₂ 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 NH_3OHCl (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 θ angular range
96 (17.6 Å – 1.20 Å) with a 0.04 °2 θ 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 θ $\text{CuK}\alpha$) and low-angle (5-30 °2 θ $\text{CuK}\alpha$) 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 α and β
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 ~ 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 δ -MnO₂ are typical of turbostratic birnessite-like crystals
131 (Fig. 1 – Drits *et al.*, 1997; Villalobos *et al.*, 2006). The peaks at ~ 7.6 Å and ~ 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 ~ 2.42 Å,

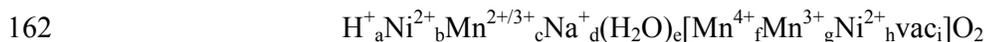
134 $\sim 1.41 \text{ \AA}$ and $\sim 1.22 \text{ \AA}$ are indexed as 11,20, 31,02 and 22,40 bands, respectively, using a C-
135 centred unit cell (Drits *et al.*, 1997, 2007; Webb *et al.*, 2005; Villalobos *et al.*, 2006; Lanson
136 *et al.*, 2008). For all samples, the d -spacings of the 11,20 and 31,02 bands are in a ratio
137 (~ 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 Mn^{4+} ,
175 Mn^{3+} , Ni^{2+} , and 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 Mn^{3+} cations between layer
178 and interlayer sites, the position of interlayer Na^+ and coordinated H_2O molecules, and the
179 coordinates of interlayer Mn, Ni, and associated H_2O 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 Mn³⁺ and/or Ni²⁺, depending on the Ni/Mn loading
196 and on the equilibration pH. Na⁺ and H⁺ 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⁺ and/or interlayer Mn, depending on the pH series. At pH 4, Ni preferentially replaces
199 Na⁺, the number of ^{TC}Mn remaining constant within error, whereas Ni replaces both Na⁺,
200 ^{TC}Mn, and ^{TE}Mn at pH 7.

201 Interlayer Mn³⁺ and Ni²⁺ 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 H₂O molecules. The first coordination sphere of Na⁺ is limited to ~3.0 Å, consistent
208 with theoretical studies (Delville, 1992). However, the sum of bond valence with H₂O
209 molecules (O6) and layer oxygen (O1) is not sufficient to fully compensate the Na⁺ charge
210 (Table 4), as discussed in the following section. The position of H₂O molecules coordinated to
211 interlayer Na⁺ allows for the formation of strong H-bonds with layer oxygen atoms (O_{layer}),
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, Mn³⁺ cations have to be included
214 in the octahedral layers, but the number of ^EMn³⁺ 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-MnO₂
218 (2.838 \AA – Villalobos *et al.*, 2006). The sensitivity to this parameter was assessed with sample
219 NidBi105-4 from the variation of R_{wp} 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*^{*} 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⁺ 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⁺ coordination consists essentially of adjacent O_{layer}
242 atoms and interlayer H₂O molecules, however failing to fully compensate the charge of this
243 cation (Table 4). The nanocrystalline character of δ -MnO₂, and specifically the prevalence of
244 monolayers, may account for the compensation of the remaining charge, as H₂O molecules
245 hydrating the crystals may actually contribute to charge compensation. For crystals composed
246 of more than one layer, O_{layer} 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 constrains 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 Mn^{3+} , which is dominantly
263 present as an interlayer species, decreases with increasing Ni/Mn content. In addition, a Ni^{2+} -
264 for- Na^+ exchange would lead to a strong excess of charge in $\delta\text{-MnO}_2$ structure, whereas the
265 Ni^{2+} -for- 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_{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 δ -MnO₂ 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 Ni²⁺ replaces preferentially Na⁺ and
311 H⁺, Mn³⁺ being strongly bound to the octahedral layers, whereas Ni²⁺ more readily exchanges
312 for Mn³⁺ at pH 7. This contrasting behaviour could result from the higher number of Mn³⁺
313 cations in the octahedral layers at low pH. As discussed above, the coexistence in octahedral
314 layers of vacant layer sites and Mn³⁺ cations induces a strong undersaturation of O_{layer} atoms,
315 and therefore favours the binding of high-charge interlayer cations such as Mn³⁺.

316

317 *Comparison to structure models previously reported for δ -MnO₂*

318 For a long time, the structure of δ -MnO₂ 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 δ -MnO₂ 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), δ -MnO₂ 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 Mn³⁺ 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 Mn^{4+} , because the average oxidation
333 degree obtained by the oxalate and iodine titration methods was 4.02 ± 0.02 (see Villalobos *et*
334 *al.*, 2003, for details). Here, a value of 3.80 ± 0.03 has been measured at pH 7 and low Ni
335 content (NidBi2-7), suggesting the presence of Mn^{3+} or Mn^{2+} . The presence of 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 Mn^{2+} occurs only as a
338 minor interlayer species if present at all. In particular, the presence of 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 ± 0.03 was obtained, consistent with the 3.80 ± 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 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 O_{layer} atoms than Na^+ and 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 δ -MnO₂ 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 δ -MnO₂
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 ~ 55 Å, compared to ~ 120 Å previously, a large fraction of Ni atoms is sorbed
360 on border sites as ^{DC}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 ^{TC}Ni on basal planes. Thus, the δ -MnO₂ 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 δ -MnO₂. **(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 δ -MnO₂. 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 δ -MnO₂ 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 δ -MnO₂. **(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_{wp} with b .

567

568 FIG. 6. Simulations of the 001 and 002 diffraction lines for Ni-sorbed δ - 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 δ -
572 MnO_2 samples (circles: pH 4, triangles: pH 7).

TABLE 1. Chemical composition of Ni-sorbed δ -MnO₂ expressed as atomic ratios.

| Sample | Na/Mn (%) | Ni/Mn (%) | Mn Ox. | Layer Mn ³⁺ |
|------------|-------------|-------------|------------|------------------------|
| 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 Mn³⁺ 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 δ -MnO₂.

| | 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) ^a | 56 | 54 | 54 | 54 | 54 | 50 |
| R_{wp} (%) ^b | 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 (%) ^b | 6.49-4.53 | 3.57-3.32 | 5.41-3.33 | 15.40-4.45 | 8.42-6.52 | 5.41-4.17 |

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

TABLE 3. Structural parameters of Ni-sorbed δ -MnO₂ derived from XRD.

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

^a 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 $(-x, 0, -z)$. ^b Coordinates along the c^* axis, ζ , are expressed in Å to emphasize the thickness of layer and interlayer polyhedra. ^c Occupancies are given per half

formula unit as the sum of the occupancies for all equivalent positions. ^d Additional symmetry operations: $(-x/2 - 1/2, 3x/2 + 1/2, z)$, and $(-x/2 - 1/2, -3x/2 - 1/2, z)$. ^e 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_{layer}, 1.0 for O_{layer}, interlayer Mn and Ni, 1.5 for H₂O molecules bound to interlayer Mn and Ni, and 2.0 for other interlayer species (alkali cations and H₂O molecules).

TABLE 4. Bond valences calculated^a for Ni-sorbed δ -MnO₂

| | O1 ^b | O1 ^c | O1 ^d | O1 ^e | O2/O3 | O4/O5 | O6 | Σ | 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 ^f $\times 3 \rightarrow$ | | | 0.300-0.317 ^f $\times 3 \rightarrow$ | | 1.9 | 2 |
| Na ⁺ | | | | 0.091 0.012 $\times 2 \rightarrow$ | | | 0.261, 0.053, 0.045 ^g | 0.5 | 1 |
| H ⁺ | | | | 0.105 ^h | 0.815 $\times 2 \downarrow$ | 0.815 $\times 2 \downarrow$ | 0.815 $\times 2 \downarrow$ | | |
| Σ | 1.9 | 1.8 | 1.5-1.6 ^f | 1.3-1.4 ⁱ | 2.1 | 1.9 | 1.7-1.9 ^g | | |

^a 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 – Brown, 1996) and the parameters from Brese and O' Keeffe (1991). ^b O1 coordinated to 3 Mn⁴⁺ in Mn1 (Table 3). ^c O1 coordinated to 2 Mn⁴⁺ in Mn1 and 1 Mn³⁺ in Mn2 or Mn3 (Table 3). ^d O1 coordinated to 2 Mn⁴⁺ in Mn1 and 1 Ni²⁺ in Ni1 or Ni2 (Table 3). ^e O1 coordinated to 2 Mn⁴⁺ in Mn1 (Table 3). ^f Depending on whether Ni is located in Ni1 or in Ni2. ^g Na⁺ is coordinated to 3 H₂O molecules at 2.30, 2.89, and 2.95 Å. ^h O6-H-O1 H-bond. ⁱ Depending on whether this O1 receives additional valence from Na⁺ or from H⁺ through H-bond.

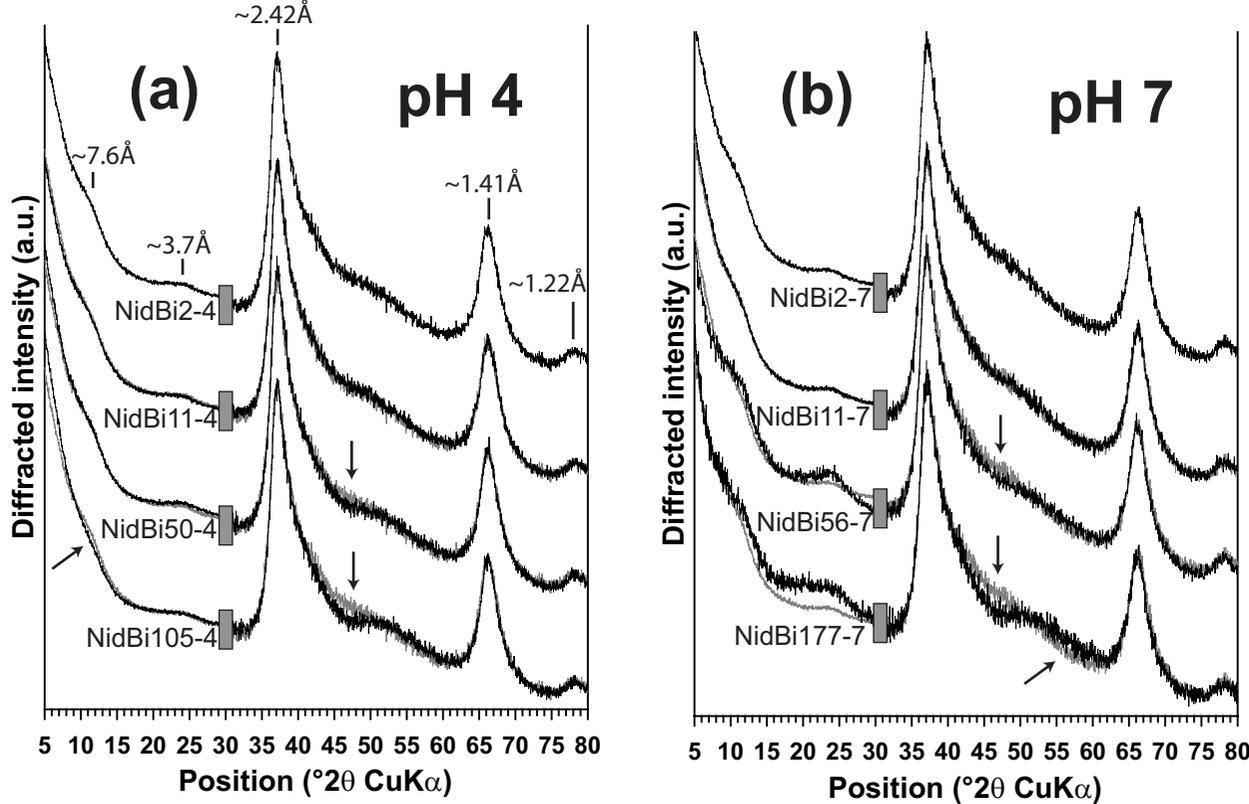


Figure 1

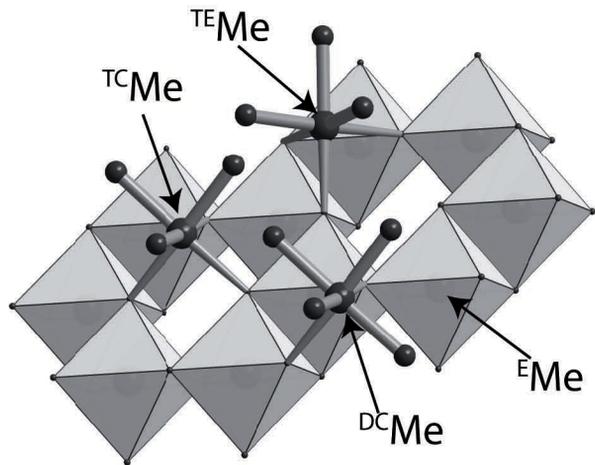


Figure 2

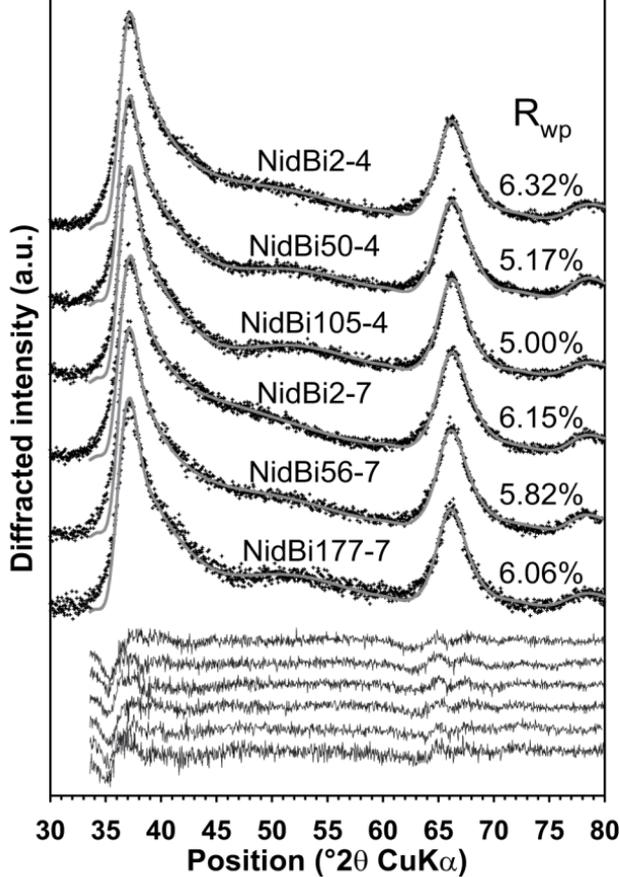


Figure 3

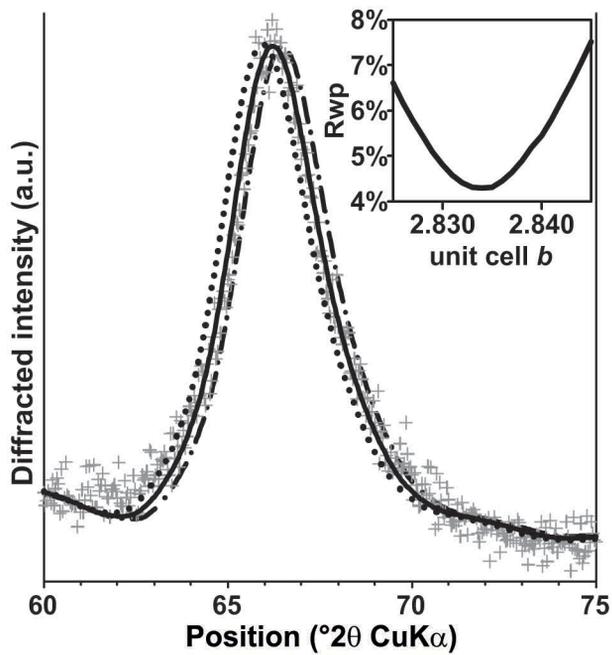


Figure 5

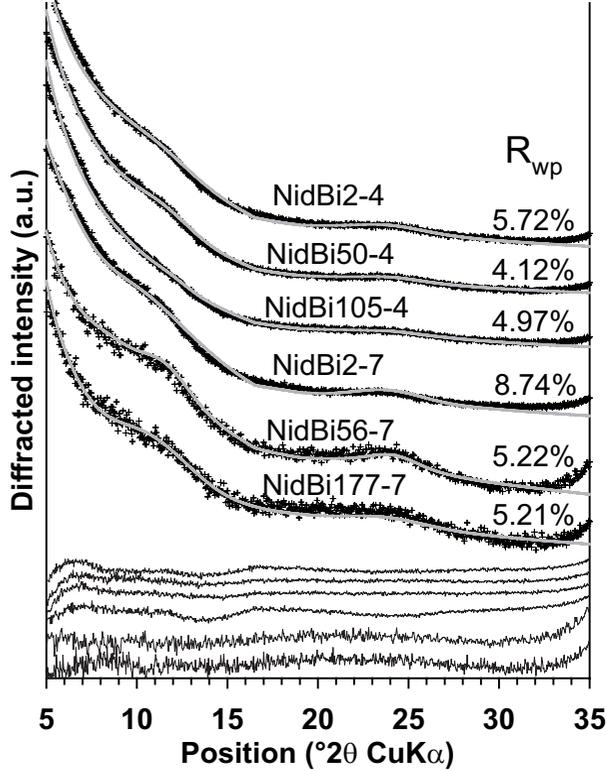


Figure 6

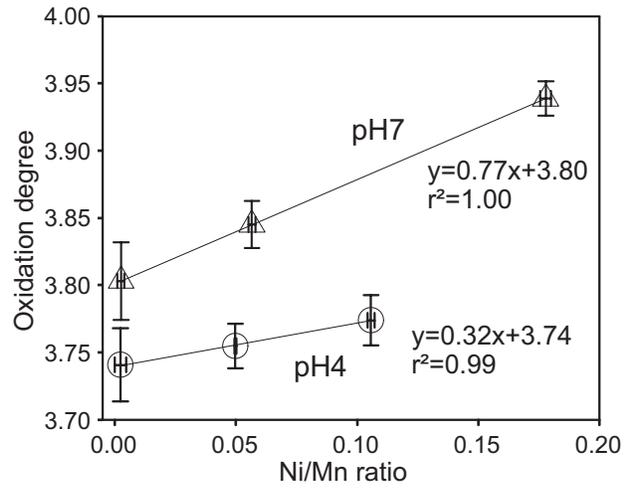


Figure 7