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1 **Birnessite polytype systematics and identification by powder X-ray**
2 **diffraction**

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4 **Revision 1**

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18 **ABSTRACT**

19

20 The polytypes of birnessite with a periodic stacking along the \mathbf{c}^* axis of one-, two-,
21 and three-layers are derived in terms of an anion close-packing formalism. Birnessite layers
22 may be stacked so as to build two types of interlayers: P-type in which basal O atoms from
23 adjacent layers coincide in projection along the \mathbf{c}^* axis, thus forming interlayer prisms; and,
24 O-type in which these O atoms form interlayer octahedra. The polytypes can be categorized
25 into three groups that depend on the type of interlayers: polytypes consisting of homogeneous
26 interlayers of O- or P-type, and polytypes in which both interlayer types alternate. Ideal
27 birnessite layers can be described by a hexagonal unit-cell ($a_h = b_h \approx 2.85 \text{ \AA}$ and $\gamma = 120^\circ$) or
28 by an orthogonal C-centered cell ($a = \sqrt{3} b$, $b_h \approx 2.85 \text{ \AA}$ and $\gamma = 90^\circ$); and, hexagonal
29 birnessite polytypes ($1H$, $2H_1$, $2H_2$, $3R_1$, $3R_2$, $3H_1$, and $3H_2$) have orthogonal analogues ($1O$,
30 $2O_1$, $2O_2$, $1M_1$, $1M_2$, $3O_1$, and $3O_2$).

31 X-ray diffraction (XRD) patterns from different polytypes having the same layer
32 symmetry and the same number of layers per unit cell exhibit hkl reflections at identical 2θ
33 positions. XRD patterns corresponding to such polytypes differ only by their hkl intensity
34 distributions, thus leading to possible ambiguities in polytype identification. In addition, the
35 characteristics of the birnessite XRD patterns depends not only on the layer stacking but also
36 on the presence of vacant layer sites, and on the type, location and local environment of
37 interlayer cations.

38 Several structure models are described for birnessite consisting of orthogonal vacancy-
39 free or of hexagonal vacancy-bearing layers. These models differ by their stacking modes and
40 by their interlayer structures, which contain mono-, di-, or tri-valent cations. Calculated XRD
41 patterns for these models show that the hkl intensity distributions are determined by the
42 polytype, with limited influence of the interlayer structure. Actual structures of

43 phyllomanganates can thus be approximated by idealized models for polytype identification
44 purpose. General rules for this identification are formulated. Finally, the occurrence of the
45 different polytypes among natural and synthetic birnessite described in the literature is
46 considered with special attention given to poorly understood structural and crystal-chemical
47 features.

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72**INTRODUCTION**

Birnessite is a hydrous layered manganese oxide (phylломanganate). Its layers consist of edge-sharing MnO₆ octahedra and these layers are separated from each other by hydrated interlayer cations. These cations compensate for a layer charge deficit arising either from the presence of vacant layer sites or from the coexistence of heterovalent Mn cations in the octahedral layer. Birnessite interlayers incorporate a single sheet of interlayer H₂O molecules, and exhibit a minimum periodicity along the **c*** axis of ~7 Å (Giovanoli et al. 1970a, 1970b; Burns and Burns 1977; Chukhrov et al. 1978; Post and Veblen 1990). In the following the term “birnessite” will be used to describe all natural and synthetic materials with such a layer structure, whatever the origin of the layer charge, and the actual configuration and chemical composition of the interlayers.

Over the last few decades, birnessite has attracted a wide interest for several reasons. First, it is ubiquitous in geological environments in spite of the low abundance of Mn. It is for example a major component of Mn nodules, which cover huge areas of the ocean floor and the bottom of some lakes. It is also present in soils, sediments, and Mn-rich ore deposits (Burns and Burns 1977, 1978; Chukhrov et al. 1978, 1985; Drits et al. 1985; Golden et al. 1986; Cornell and Giovanoli 1988; Manceau et al. 2000c). It was recently shown that bacteria play a major role in the formation of birnessite in most of these environments (Tebo and He 1999; Tebo et al. 2004; and references therein). Second, this mineral plays an essential role in different ion-exchange and redox processes because of its unique surface charge, and adsorption and redox properties (Manceau and Charlet 1992; Manceau et al. 1992a, 1992b; Paterson et al. 1994; Stone et al. 1994; Tu et al. 1994; Le Goff et al. 1996; Silvester et al. 1997). In particular, birnessite plays a pivotal role in the fate of heavy metals and other pollutants in contaminated water systems and soils (Chao and Theobald 1976; Manceau et al.

73 1997, 1999, 2000a, 2000b). Despite its low concentration, birnessite controls the distribution
74 of some trace elements such as radionuclides, Pt-group elements, and rare earth elements
75 (Manceau et al. 1999). In addition, birnessite has also attracted special attention because of its
76 potential use as materials for batteries and other industrial applications (Kim et al. 1999).

77 Third, birnessite can be synthesized under a variety of physico-chemical conditions
78 and from 0 to 1000°C. Synthetic birnessite is used to mimic naturally occurring redox and
79 adsorption processes, being considered as analogous to natural varieties. Birnessite can be
80 synthesized by the oxidation of Mn^{2+} in a highly alkaline medium (Giovanoli et al. 1970a,
81 1970b; Cornell and Giovanoli 1988; Kim et al. 2000), leading, for example, to the topotactic
82 transformation of $Mn(OH)_2$ when subjected to the action of different oxidizers. Other
83 methods using MnO_4^- as starting reagent (Herbstein et al. 1971; Ching et al. 1995, 1997a,
84 1997b; Chen et al. 1996a, 1996b; Ching and Suib 1997; Kim et al. 1999) include mild
85 hydrothermal syntheses (Feng et al. 1995; Chen et al. 1996a, 1996b), sol-gel processes (Bach
86 et al. 1990, 1993; Le Goff et al. 1994; Ching et al. 1995, 1997a; Cho et al. 1999), interactions
87 of $KMnO_4$ with hydrochloric acid, and ion-exchange of the hydrogen form of birnessite to the
88 Na- or K-forms (Tsuji et al. 1992; Leroux et al. 1995), and thermal decomposition of $KMnO_4$
89 at high temperature (Kim et al. 1999).

90 These different methods lead to the crystallization of birnessite having different layer
91 stackings and different interlayer structures, which depend on the chemical nature of
92 interlayer cations, their amounts, distribution, and coordination geometry. In addition
93 birnessite is, as a rule, fine-grained and contains stacking faults and/or consists of
94 interstratified layer types corresponding to different birnessite polytypes (Drits et al. 1997a,
95 2002; Silvester et al. 1997; Manceau et al. 2000c, 2002; Lanson et al. 2002a, 2002b). As a
96 result, strikingly different X-ray diffraction patterns are obtained from birnessite crystallized
97 under different physico-chemical conditions. As a consequence, there has been a lot of

98 confusion, even in the recent literature, as to the structure of these layer manganates (e.g.,
99 Chen et al. 1996b; Kim et al. 1999; Yang and Wang 2001). One difficulty in the interpretation
100 of the birnessite XRD patterns is that until recently even unit-cell parameters reported in the
101 literature were not determined unambiguously. Therefore, determination of birnessite
102 structure was sometimes limited to a general description of the XRD patterns without any
103 indexing or accurate determination of the unit-cell parameters (Feng et al. 1997a, 1997b;
104 Aronson et al. 1999; Ma et al. 1999; Yang and Wang 2001). In some cases indexing of *hkl*
105 reflections was carried out without proper justification (e.g., Le Goff et al. 1994, 1996; Ching
106 et al. 1995; Aronson et al. 1999). Significant progress was achieved recently in the structural
107 characterization of birnessite (Post and Veblen 1990; Kuma et al. 1994; Drits et al. 1997a,
108 1998, 2002; Manceau et al. 1997, 2000c, 2002; Silvester et al. 1997; Lanson et al. 2000,
109 2002a, 2002b) and specifically in the determination of their unit-cell parameters (Chen et al.
110 1996a, 1996b; Kim et al. 1999; Lanson et al. 2000, 2002a, 2002b). However, no systematic
111 description of reliable criteria for the identification of birnessite polytypes is available, to our
112 knowledge, in existing literature.

113 As for layer silicates (Bailey 1988) the optimal way to establish such criteria is to
114 deduce theoretically all birnessite polytypes taking into account the main crystal chemical
115 features of their layers and interlayers, to calculate the corresponding XRD patterns and to
116 formulate diffraction criteria for their identification. This paper is devoted to such a
117 systematic approach and describes how birnessite polytypes having the same unit-cell
118 parameters can be identified.

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BIRNESSITE POLYTYPE DIVERSITY

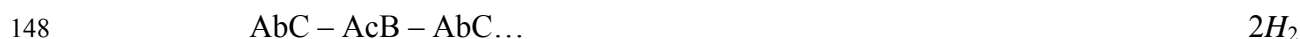
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122 **Polytype diversity in terms of close-packing formalism**

123 The two-dimensional periodicity of birnessite layers can be described either by a
 124 hexagonal unit-cell, with $a_h = b_h \approx 2.85 \text{ \AA}$ and $\gamma = 120^\circ$, or by an equivalent orthogonal C-
 125 centered cell, with $a = \sqrt{3} b$, $b_h \approx 2.85 \text{ \AA}$ and $\gamma = 90^\circ$. The orthogonal C-centered cell will be
 126 used systematically throughout the current manuscript. The birnessite layer consists of two
 127 closely packed anion sheets “sandwiching” Mn cations. The anion close-packing formalism
 128 can thus be used to describe the mutual arrangement of birnessite layers. As a first step all
 129 possible periodic stackings of birnessite layers with periodicity along the *c* axis of 1, 2, and 3
 130 layers will be considered. Non-equivalent crystallographic sites of the layer oxygen atoms
 131 (O_{layer}) will be hereafter described with capital letters A, B, and C, whereas positions of the
 132 Mn cations will be described with corresponding a, b and c letters (Fig. 1). It is systematically
 133 assumed that the lower surface of the first birnessite layer is an oxygen sheet in which O_{layer}
 134 occupy A sites, that Mn cations fill octahedral b positions, and that the upper surface is
 135 formed by O_{layer} in C sites. Such a layer can be symbolically represented as AbC. In the
 136 simulation of idealized polytypes, it is assumed that the O_{layer} in the lower sheet of the next
 137 birnessite layer in a stack can occupy A, B or C positions. If these O_{layer} are located in C sites,
 138 O_{layer} from adjacent layers define interlayer prisms. This type of interlayer will be referred to
 139 as a P-type interlayer and denoted with an equal sign (=). If they are located in A or B sites,
 140 O_{layer} from adjacent layers define interlayer octahedra. These interlayers are referred to as O-
 141 type and denoted with a dash sign (–) to distinguish them from the P-type interlayers. Using
 142 the above notions, a one-layer polytype having O-type interlayer (Fig. 1a) can be represented
 143 as:



145 Systematic consideration of possible two-layer polytypes leads to two independent
 146 hexagonal polytypes having homogeneous interlayers (Figs. 1b-c):



149 With this notation the first digit indicates the number of layers per unit-cell, the letter
 150 corresponds to the layer symmetry (H , R , and M standing for hexagonal, rhombohedral, and
 151 monoclinic, respectively), and the final numerical subscript determines the polytype. In $2H_1$
 152 and $2H_2$ polytypes adjacent layers are rotated with respect to each other by 180° around the
 153 axis parallel to the \mathbf{c} axis and passing either through Mn atoms of adjacent layers ($2H_1$) or
 154 through the “lower” O_{layer} (A sites – $2H_2$). In $1H$ and $2H_1$ the Mn_{layer} octahedral sites overlap
 155 in projection on the \mathbf{ab} plane, whereas these sites are distributed more homogeneously in $2H_2$.

156 Analysis of three-layer polytypes leads to two independent modifications with
 157 rhombohedral symmetry ($3R$). These two polytypes differ from each other by their interlayer
 158 structures (Figs. 2a-b):



161 Two additional three-layer polytypes having O-type interlayers and hexagonal
 162 symmetry may also be derived (Figs. 2c-d):



165 In terms of the C-centered orthogonal unit cell successive layers in $3R_1$ and $3R_2$
 166 polytypes are shifted by $-a/3$ and $+a/3$, respectively. As in $2H_2$ polytype successive layers in
 167 $3H_1$ and $3H_2$ polytypes are not related by the same interlayer displacement. In addition, layers
 168 from different layer pairs are related to each other by different elements of symmetry in $3H_1$
 169 and $3H_2$ polytypes. For example, layers in the first layer pair of the $3H_1$ polytype are related
 170 by a 180° rotation along the \mathbf{c} axis passing through A sites, whereas they are superimposed in
 171 the second pair (Fig. 2c). In the latter layer pairs, Mn octahedral sites overlap in projection on

172 the **ab** plane, whereas in $3R_1$, $3R_2$ and $3H_2$ polytypes, layer Mn cations are distributed
 173 homogeneously among all possible sites (Figs. 2a, b, d).

174 Heterogeneity arising from the coexistence of O- and P-type interlayers in a given
 175 birnessite polytype is likely not energetically favorable. Polytypes with alternating O- and P-
 176 type interlayers were thus excluded from the current study. However, transformation from one
 177 polytype to the other likely often occurs through layer translations. Such displacements occur,
 178 for example, as a result of cation exchange or during hydration-dehydration processes.
 179 Therefore, among birnessite polytypes some unusual modifications can be formed from one-
 180 layer polytype by shifting the layers. For example, a two-layer structure $AbC - BcA = AbC$
 181 with both interlayer types can be obtained if successive layers are shifted alternately by $+a/3$
 182 and $-a/3$ along the **a** axis of the C-centered unit cell.

183 The above idealized birnessite polytypes are similar to those of oxides with general
 184 formula A_xMO_2 (Delmas et al. 1980). These authors deduced four polytypes, T1, P2, P3, and
 185 O3, which correspond to $1H_1$, $2H_2$, $3R_1$, and $3R_2$ modifications in the present nomenclature.
 186 Birnessite polytypes are also similar to those of natural and synthetic layer double hydroxides
 187 $(R_{1-x}^{2+}R_x^{3+})(OH)_2(CO_3,SO_4)_{x/2}$ (Drits 1987; Bookin and Drits 1993) and to those of other
 188 natural and synthetic layered compounds (Bailey 1980).

189

190 **Layer symmetry and polytype diversity**

191 Structural characterization of birnessite shows layers with either hexagonal or pseudo-
 192 hexagonal symmetry. Birnessite has an hexagonal layer symmetry when octahedral vacancies
 193 represent the major source of layer charge deficit (Giovanoli et al. 1970b; Chukhrov et al.
 194 1985; Silvester et al. 1997; Lanson et al. 2000; 2002b; Gaillot et al. 2003; 2005). By contrast,
 195 birnessite has an orthogonal layer symmetry when the main source of negative charge in
 196 vacancy-free layers is the presence of a high amount of Mn^{3+} cations (Post and Veblen 1990;

197 Drits et al. 1998; Lanson et al. 2002a; Gaillot et al. 2004). In the latter case the layers have a
 198 C-centered unit-cell with $a > b\sqrt{3}$ (Burns and Burns 1977; Chukhrov et al. 1985; Post and
 199 Veblen 1990; Gorshkov et al. 1992; Drits et al. 1997a, 1998; Lanson et al. 2000, 2002a,
 200 2002b; Gaillot et al. 2003, 2004, 2005). Orthogonal layer symmetry results from the distortion
 201 of Mn^{3+} -octahedra because of the Jahn-Teller effect (Drits et al. 1997a). In Mn^{3+} octahedra,
 202 two Mn^{3+} -O distances are indeed much longer than the other four. For example, in crednerite
 203 CuMnO_2 Mn^{3+} -octahedra contain two 2.26 Å and four 1.929 Å bond lengths with an average
 204 $\langle \text{Mn-O} \rangle$ distance of 2.04 Å (Töpfer et al. 1995). Similar distortions of Mn^{3+} -octahedra have
 205 been reported by Shannon et al. (1975) for α - MnOOH (2.041 Å – Glasser and Ingram 1968),
 206 γ - MnOOH (2.037 Å – Dachs 1963) and α - Mn_2O_3 (2.039-2.045 Å – Norrestam 1967). The
 207 random distribution of Mn^{4+} and Mn^{3+} cations combined with a random azimuthal orientation
 208 of the long Mn^{3+} -O bonds of the Mn^{3+} octahedra would lead to unfavorable steric strains,
 209 because of the distortion of Mn^{3+} -octahedra. An ordered distribution of Mn^{3+} -octahedra all
 210 having the same azimuthal orientation allows minimizing these strains. According to SAED
 211 results, in vacancy-free birnessite layers Mn^{3+} are distributed in rows parallel to the **b** axis and
 212 have their long Mn^{3+} -O bonds parallel to the **a** axis (Drits et al. 1997a, 1998; Lanson et al.
 213 2002a; Gaillot et al. 2004). Because of the systematic elongation of Mn^{3+} -octahedra along the
 214 **a** axis and because the four short Mn^{3+} -O distances (1.92-1.93 Å) are similar to Mn^{4+} -O bond
 215 lengths (1.912 Å for λ - MnO_2), *b* parameters are similar (2.83-2.85 Å) in most natural and
 216 synthetic birnessite samples regardless of the average valency of the Mn_{layer} (Chukhrov et al.
 217 1985; Post and Veblen 1990; Chen et al. 1996b; Ching et al. 1997a; Drits et al. 1997a, 1998;
 218 Kim et al. 1999; Lanson et al. 2000, 2002a, 2002b; Gaillot et al. 2003, 2004, 2005).

219 The transition from birnessite having layers with hexagonal symmetry to that having
 220 pseudo-hexagonal symmetry leads to a modification of symbol notation for the corresponding
 221 polytypes. Specifically, hexagonal one-, two-, and three-layer polytypes ($1H$, $2H_1$, $2H_2$, $3H_1$

222 and $3H_2$) are changed to the corresponding orthogonal ones ($1O$, $2O_1$, $2O_2$, $3O_1$ and $3O_2$)
 223 whereas $3R_1$ and $3R_2$ are changed to $1M_1$ and $1M_2$ monoclinic modifications having $-a/3$ and
 224 $+a/3$ displacements of adjacent layers along the **a** axis (Table 1). In $1M_1$ and $1M_2$ birnessite
 225 adjacent layers may be shifted along the **a** axis by values different from $\pm 0.333a$ (Post and
 226 Veblen 1990; Lanson et al. 2002b).

227

228 **Cation composition, interlayer structure, and polytype diversity**

229 The arrangement of adjacent layers in different polytypes, the presence or absence of
 230 vacant layer octahedral sites, the nature of interlayer cations, and their local environments are
 231 interrelated structural characteristics. Therefore, it is reasonable to define possible interlayer
 232 structures for each particular layer stacking and specifically to propose optimum positions for
 233 interlayer cations as a function of their ionic radius and valency (Table 2). This approach also
 234 relies on existing birnessite structure models (Chukhrov et al. 1978, 1985; Post and Veblen
 235 1990; Drits et al. 1997a, 1998, 2002; Kim et al. 1999; Lanson et al. 2000, 2002a, 2002b;
 236 Manceau et al. 2002; Gaillot et al. 2003, 2005). To symbolize positions for interlayer water
 237 molecules ($H_2O_{\text{interlayer}}$) and cations the capital letters A', B', and C', and corresponding lower
 238 case a', b', and c' will be used, respectively.

239 **Polytypes with hexagonal layer symmetry.** The presence of layer vacancies allows
 240 interlayer cations to share one face with vacant octahedra so as to provide local charge
 241 compensation to undersaturated O_{layer} . If birnessite interlayers contain relatively small di- or
 242 tri-valent cations, such as $Mn^{2+,3+}$, $Co^{2+,3+}$, Cu^{2+} , Ca^{2+} , and Mg^{2+} , then they are commonly
 243 octahedrally coordinated by O_{layer} bound to layer vacancies and $H_2O_{\text{interlayer}}$. Depending on the
 244 layer stacking mode the presence of octahedrally coordinated interlayer cations located above
 245 and/or below layer vacancies can give rise to three types of bonding between $H_2O_{\text{interlayer}}$ and
 246 the nearest O_{layer} from the adjacent layer. In the first [model 1a (polytype 1H)] strong H-bonds

247 link these species as they form empty prisms with short $\text{H}_2\text{O}_{\text{interlayer}}\text{-O}_{\text{layer}}$ distances along the
248 prism edges (2.70-2.75 Å – Fig. 3a). In the second [model 2a (polytype $3R_1$), model 3a
249 (polytype $3R_2$), and model 4a (polytype $2H_1$)] O_{layer} and $\text{H}_2\text{O}_{\text{interlayer}}$ are linked by weak H-
250 bonds as they form empty octahedra with long $\text{H}_2\text{O}_{\text{interlayer}}\text{-O}_{\text{layer}}$ distances (3.0-3.15 Å – Fig.
251 3b). In the third interlayer type [model 5a (polytype $2H_2$), model 6a [polytype $3H_1$], and
252 model 7a (polytype $3H_2$)] empty prisms and empty octahedra formed by O_{layer} and $\text{H}_2\text{O}_{\text{interlayer}}$
253 coexist within a given interlayer, with prisms located on one side of the interlayer and
254 octahedra on the opposite one (Fig. 3c).

255 The presence of tetrahedrally coordinated interlayer cations located above and/or
256 below the vacant layer octahedra in model 3b (polytype $3R_2$) is associated with the formation
257 of strong H-bonds between $\text{H}_2\text{O}_{\text{interlayer}}$ coordinating the interlayer cations and nearest O_{layer}
258 from the adjacent layer. Both species are superimposed in projection on the **ab** plane and thus
259 located close to each other (Fig. 3d). The coexistence of both octahedrally and tetrahedrally
260 coordinated interlayer cations in model 5c (polytype $2H_2$) leads to the formation of empty
261 prisms between the $\text{H}_2\text{O}_{\text{interlayer}}$ and O_{layer} (strong H-bonds) on one side of the interlayer and to
262 short $\text{H}_2\text{O}_{\text{interlayer}}\text{-O}_{\text{layer}}$ distances on the other side (not shown).

263 On the other hand, if birnessite interlayers contain large mono- or di-valent cations,
264 such as K^+ , Ba^{2+} , Sr^{2+} , Cs^+ , then they will be located in the interlayer mid-plane either in
265 octahedra defined by O_{layer} from adjacent layers [model 5b (polytype $2H_2$), and model 6b
266 (polytype $3H_1$)] or in interlayer prisms [model 2b (polytype $3R_1$)]. In the latter case, interlayer
267 prisms share one face with a layer octahedron and three edges with occupied octahedra of the
268 adjacent layer. Local charge compensation is achieved when interlayer cations are distributed
269 so that prisms share a face with vacant layer octahedra. Random distribution of interlayer
270 cations leads to electrostatic repulsion with Mn_{layer} despite the presence of layer vacancies.
271 Table 2 lists birnessite polytypes consisting of hexagonal vacancy-bearing layers that differ

272 from each other by stacking modes and interlayer structures, which are reasonable from a
273 crystal chemical point of view.

274 **Polytypes with orthogonal layer symmetry.** The interlayer cations for vacancy-free
275 layers should have six-fold coordination by O_{layer} and $H_2O_{\text{interlayer}}$, and distributed so as to
276 avoid direct interaction with Mn_{layer} . The $1O$, $2O_2$, $3O_1$, and $3O_2$ polytypes are thus not
277 suitable to host large mono- or divalent cations as they cannot avoid such interactions. In
278 contrast, the $1M_2$ and $2O_1$ polytypes can host these cations in the interlayer mid-plane, with
279 octahedral [model 3e (polytype $1M_2$)], or prismatic [model 4c (polytype $2O_1$), and model 4e
280 (polytype $2O_1$)] coordinations.

281 Model 2c (polytype $1M_1$) represents a special case as interlayer cations cannot be
282 located in a' or b' sites because of the interaction with Mn_{layer} . However, smaller interlayer
283 cations, such as Na^+ , can be located, together with $H_2O_{\text{interlayer}}$, in the interlayer mid-plane
284 above and/or below O_{layer} of adjacent layers as was described for Na-rich synthetic birnessite,
285 hereafter referred to as NaBi (Lanson et al. 2002b). Similarly, in Na^+ -saturated $2O_1$ polytype
286 the interlayer cations are likely located above and/or below O_{layer} from adjacent layers (model
287 4e).

288 Relatively small di- and tri-valent interlayer cations may be located above and/or
289 below empty layer tetrahedra (tridentate cavities) sharing three edges with layer Mn octahedra
290 (^VITE sites). The $H_2O_{\text{interlayer}}$ provides octahedral coordination to these cations and may form
291 either empty prisms [model 3d (polytype $1M_2$) – Fig. 4a] or empty octahedra [model 1b,
292 (polytype $1O$), and model 4d (polytype $2O_1$) – Fig. 4b], with O_{layer} from the adjacent layer.
293 Empty prisms and empty octahedra coexist within a given interlayer [model 5d (polytype
294 $2O_2$)] if interlayer cations are octahedrally coordinated. If interlayer cations have both
295 octahedral and tetrahedral coordination then $H_2O_{\text{interlayer}}$ and O_{layer} in model 5e (polytype $2O_2$)
296 form empty prisms and strong H-bonds on either side of a given interlayer.

297 Vacancy-free birnessite layers can have hexagonal symmetry if the long $\text{Mn}^{3+}\text{-O}$
298 bonds of the layer Mn^{3+} -octahedra are randomly oriented with respect to the **a** axis by $n60^\circ$
299 (Gaillot et al. 2005, 2006a). Interlayer cations in such birnessite layers should be distributed
300 so as to avoid direct interaction with the nearest Mn_{layer} . In this case, suitable interlayer
301 structures are those described for vacancy-free orthogonal layers (Table 2).

302

303

CALCULATION OF XRD PATTERNS

304

305 The XRD patterns calculated for polytypes with the same layer symmetry and
306 periodicity along the **c*** axis have the same d-spacings, but differ by their *hkl* intensity
307 distributions. Characterization of layer silicates has shown that structures can be
308 approximated by models for polytype identification purpose. The influence of the actual layer
309 structure on the *hkl* intensity distributions is indeed a second-order effect compared to the
310 differences between polytypes (Bailey 1980). Structure models were thus proposed for each
311 birnessite variety and corresponding powder XRD patterns were calculated. All calculations
312 were performed using the program developed by Plançon (2002) on the basis of the formalism
313 described by Drits and Tchoubar (1990). No orientation function was considered, and no
314 random stacking faults were introduced for the calculations.

315

316 Initial structure models

317 In all structure models, Mn_{layer} and O_{layer} occupy special sites in the orthogonal C-
318 centered unit-cell: (0, 0, 0), (0.333, 0, z) and (-0.333, 0, -z), respectively, where z-coordinates
319 (in projection on the **c*** axis) were equal to 1.00\AA (Post and Veblen 1990; Drits et al. 1998;
320 Lanson et al. 2000, 2002a, 2002b; Gaillot et al. 2003, 2005). According to the close-packing
321 notation interlayer cations and $\text{H}_2\text{O}_{\text{interlayer}}$ also occupy special sites. In the initial structure

322 models, the z-coordinates of the interlayer cations (Me) and $\text{H}_2\text{O}_{\text{interlayer}}$ are the sole variable
 323 parameters. The initial z-coordinates of Me and H_2O molecules can be estimated from typical
 324 Me-O and Me- H_2O bond lengths for four- and six-fold coordinated Me and from elementary
 325 geometrical relationships between these bond lengths and corresponding z-coordinates. For
 326 example, if an interlayer cation is octahedrally coordinated above and/or below a vacant layer
 327 octahedron, then the following equations are deduced from the hexagonal symmetry of the
 328 layer (Lanson et al. 2002b):

$$329 \quad z(\text{Me}) = z(\text{O}_{\text{layer}}) + \sqrt{\frac{d^2(\text{Me}-\text{O}) - b^2}{3}} = z(\text{O}_{\text{layer}}) + \Delta z$$

$$330 \quad \text{and} \quad z(\text{H}_2\text{O}) = z(\text{O}_{\text{layer}}) + 2\Delta z$$

331 In the present work, Me-O and Me- H_2O interatomic distances were determined from
 332 the effective ionic radii given by Shannon (1976). Where applicable the interlayer atomic
 333 positions were adapted from published structural determination of synthetic Na-birnessite
 334 (Lanson et al. 2002a), Ca-birnessite (Drits et al. 1998), H-birnessite (Lanson et al. 2000), and
 335 K-birnessites (Gaillot et al. 2003, 2005). In the various structure models K, Ca, Mn, Na,
 336 and/or Mg were used as interlayer cations. For the different structure models presented in
 337 Table 2, corresponding atomic positions and their occupancies are listed in Table 3.

338

339 **Calculated XRD patterns**

340 Powder XRD patterns calculated for the different polytypes are shown in Figures 5-8,
 341 whereas d-values and hkl indices of reflections observed on the various patterns are listed in
 342 Table 4. Indexing is performed assuming an orthogonal C-centered cell for both hexagonal
 343 and orthogonal birnessite. Reflections in the $36\text{-}64^\circ$ 2θ $\text{CuK}\alpha$ range have $20\ell, 11\ell$ indices (10ℓ
 344 and 01ℓ when using a hexagonal unit-cell), whereas they have $31\ell, 02\ell$ indices (11ℓ when
 345 using a hexagonal unit-cell) over the $64\text{-}75^\circ$ 2θ $\text{CuK}\alpha$ range. The XRD patterns shown in

346 Figure 5 correspond to structure models in which interlayer Mn cations are located above
347 and/or below layer sites and are octahedrally coordinated by O_{layer} and $H_2O_{\text{interlayer}}$ (^{VI}TC sites
348 – Table 3). The calculated XRD patterns (Figure 5) can be used to identify vacancy-bearing
349 birnessite having one-, two- and three-layer periodicity along the c axis and different layer
350 stacking. However, analysis of the XRD patterns calculated for a given birnessite polytype
351 having different interlayer structures shows that for a given birnessite polytype the intensity
352 of hkl reflections also depends on the chemical nature of interlayer cations, their distribution
353 and local environment. For example, interlayer spaces of $3R_2$ polytype (models 4a and 4b)
354 may be occupied by Zn cations having octahedral and/or tetrahedral coordination (Manceau et
355 al. 2000c; Lanson et al. 2000, 2002a) and located in TC sites or TE sites. The replacement of
356 tetrahedrally for octahedrally coordinated Zn cations leads to a significant decrease of
357 204/114, 208/118 and 20.10/11.10 peak intensity (104, 018 and 10.10 assuming a hexagonal
358 cell), with respect to the strongest $20\ell/11\ell$ reflections (Figs. 6a-b). Location of Zn cations in
359 ^{IV}TE sites [model 3c (polytype $3R_2$) – Fig. 6c] strongly increases the 204/114 and 207/117
360 reflection intensities, with respect to 201/111. Important redistribution of intensities is
361 observed also for the $2O_1$ and $1M_2$ polytypes when interlayers are occupied either by large K^+
362 (models 4c and 3e) or by smaller Ca^{2+} (models 4d and 3d). The transition from model 3e to
363 model 3d significantly increases 201, 110, 112, 203 and 11-2 and decreases the 111 and 113
364 intensities (Figs. 7a-b). Similarly, the transition from model 4c to 4d is accompanied by
365 redistribution of the 112 and 114 maxima: strong 112 and moderate 114 peaks for model 4c
366 are replaced by strong 114 and moderate 112 ones for model 4d (Figs. 7c-d).

367 In contrast, the relative intensity of strong, moderate and weak reflections change very
368 little for the $3R_1$ polytype when interlayers are occupied by either K^+ , Ca^{2+} , or Mn^{3+} . The only
369 significant change in the MnBi XRD pattern compared to KBi is a strong increase of 201/111
370 intensity (Figs. 8a-b). For the $2H_1$ polytype, a strong increase of 200 and 203 intensities and a

371 limited increase of the 206 one is visible on the XRD pattern calculated for MnBi model
 372 compared to KBi (models 4a and 4b – Figs. 8c-d)

373 The calculated XRD patterns show the limited influence of the interlayer structure on
 374 the hkl intensity distribution for a given birnessite polytype. The intensity distribution is
 375 primarily determined by the polytype (Figs. 6-8). As a consequence, identification of
 376 birnessite polytypes having either hexagonal or C-centered orthogonal ($a > b\sqrt{3}$) unit cells may
 377 be performed without *a priori* details of their layer and interlayer structures.

378

379 DISCUSSION

380

381 Criteria for determination of birnessite polytypes

382 Birnessite polytypes having the same periodicity along the c axis, but with different
 383 layer symmetry, differ from each other by the number of hkl reflections. For example, the
 384 hexagonal birnessite exhibits a single series of $20\ell/11\ell$ reflections, whereas 20ℓ and 11ℓ series
 385 of reflections are individualized for birnessite with an orthogonal layer symmetry. In addition,
 386 XRD patterns of hexagonal birnessite usually contains a diagnostic 310/020 reflection (110
 387 when using the hexagonal cell) with $d = (1.42 \pm 0.01) \text{ \AA}$ whereas for the orthogonal birnessite
 388 this reflection is split with $d(310) > d(020) = (1.42 \pm 0.01) \text{ \AA}$.

389 Birnessites with similar periodicity and layer symmetry can be differentiated by the
 390 intensity distribution of hkl reflections. Figures 9a-b show that hkl reflections with $\ell = 2n$ are
 391 more intense for $2H_1$ polytype compared to those of $2H_2$ polytype. In contrast, $20\ell/11\ell$
 392 reflections (10ℓ and 01ℓ when using the hexagonal cell) with $\ell = 2n + 1$ are significantly
 393 stronger for $2H_2$ polytype. Similarly, 11ℓ and 20ℓ reflections with $\ell = 2n$ are stronger than
 394 those with $\ell = 2n + 1$ for the $2O_1$ polytype (Fig. 9c). XRD patterns from $3R_1$ and $3R_2$ polytypes

395 also differ from each other by their intensity distributions among hkl reflections. The $20\ell/11\ell$
 396 reflections with $\ell = 3n - 1$ (01ℓ with $\ell = 3n - 1$ ones if using the hexagonal cell) are intense
 397 for $3R_1$ polytype but not for $3R_2$, whereas $20\ell/11\ell$ reflections with $\ell = 3n + 1$ (10ℓ with $\ell =$
 398 $3n + 1$ ones if using the hexagonal cell) are intense for $3R_2$ polytype and weak for $3R_1$ (Figs.
 399 10a-b). $3H_1$ and $3H_2$ polytypes differ from $3R_1$ and $3R_2$ by the presence of $20\ell/11\ell$ reflections
 400 with $\ell = 3n$ (Figs 10c-d). Similarly, intensity of $20\ell/11\ell$ reflections with $\ell = 3n$ (10ℓ with
 401 $\ell = 3n$ if using the hexagonal cell) is significantly lower for $3H_2$ than for $3H_1$ (Figs. 10c-d).
 402 The intensity distribution among hkl reflections described above for $3R_1$, $3R_2$, $3H_1$ and $3H_2$
 403 polytypes remain valid for the equivalent birnessite polytypes with orthogonal layer
 404 symmetry ($1M_1$, $1M_2$, $3O_1$, $3O_2$).

405 Special attention should be paid to identify one- ($1H$ and $1O$) and two-layer ($2H_1$
 406 and $2O_1$) polytypes having the same layer symmetry. The presence of a weak $203/113$
 407 reflection is the sole distinguishing feature allowing identification of the two-layer polytypes
 408 (Figs. 5a-b). Note that the difference between XRD patterns corresponding to these two
 409 polytypes is further reduced when $1H$ layer pairs are present in the $2H_1$ polytype (that is when
 410 $AbC - AbC$ pairs are present in crystals dominated by $AbC = CbA = AbC\dots$ sequences) as
 411 the intensity of the $203/113$ reflection is significantly decreased by the presence of such $1H$
 412 layer pairs in a mixed-layered structure (not shown).

413

414 **Stacking faults**

415 The above described method can be used not only for the identification of birnessite
 416 polytypes and also to determine the nature of stacking faults which are typically present in
 417 natural and synthetic birnessites. Well-defined and random stacking faults significantly alter
 418 XRD patterns from defective layer structures (for definition of well-defined and random

419 stacking faults see Drits and Tchoubar, 1990). Well-defined stacking faults correspond to the
420 interstratification of layer pairs having the same thickness but different internal structure and
421 interlayer displacements within a periodic polytype. As the result of such interstratification,
422 hkl reflections are shifted, and their positions become irrational.

423 Drits and McCarty (1996) have shown that Méring's rules, initially proposed for basal
424 reflections (Méring 1949), can be generalized to account for the behavior of hkl reflections
425 from defective layer structures. According to these generalized rules, hkl reflections observed
426 from a defective layer structure are located between neighboring hkl reflections of periodic
427 phases whose fragments (layer pairs in the present case) are interstratified. The actual position
428 of hkl reflections corresponding to the defective layer structure depends on the relative
429 proportion of the structure fragments and on relative intensities of the "involved" hkl
430 reflections of the periodic phases.

431 For example, Lanson et al. (2002b – Fig. 3) showed that reflections of Zn-sorbed
432 birnessite are located between hkl reflections calculated for $3R_2$ and $1H$ polytypes and
433 hypothesized that the main $3R_2$ polytype contained some $1H$ layer pairs (i.e. AbC – AbC pairs
434 are present in crystals dominated by AbC – BcA – CaB – AbC ... sequences). As a result,
435 positions of hkl reflections of the main $3R_2$ polytype should indeed be shifted from their ideal
436 position towards those of the defect-free $1H$ polytype. Accordingly, the best agreement
437 between experimental and calculated XRD patterns was obtained for a defective $3R_2$ polytype
438 containing 12% of $1H$ layer pairs (Lanson et al. 2002b). A similar approach may be applied to
439 mixtures containing periodic and defective birnessites. For example, Figure 11 shows the best
440 possible agreement between an experimental XRD pattern and that calculated for a mixture of
441 four birnessites: a periodic $2H_1$ polytype and three defective ones ($2O_1/2H_1$, $2H_1/3R_1$, and
442 $3R_1/2H_1$). In the three mixed-layered structures, layer pairs of the $2H_1$ polytype are randomly

443 interstratified with those of the $2O_1$ and $3R_1$ polytypes in proportions 1:1, 7:3, and 1:9,
444 respectively. Note on Figure 11 that each of these mixed-layered structures gives a diagnostic
445 contribution to the calculated XRD pattern (Gaillot et al. 2004).

446 In our experience, one of the most effective way to study defective birnessite is to
447 combine the above rules for polytype identification and interstratification to build up starting
448 models for XRD pattern calculation (Manceau et al. 1997; Drits et al. 1998; Lanson et al.
449 2000, 2002a, 2002b; Gaillot et al. 2003, 2004, 2005). Defective birnessite may contain layer
450 pairs which were not reported so far for natural and synthetic periodic birnessite. Therefore,
451 all theoretically possible birnessite polytypes should be considered to determine the nature of
452 stacking faults XRD by comparing experimental and calculated XRD patterns.

453

454 **Birnessite polytypes reported for natural and synthetic birnessites**

455 **1H Polytype.** The first detailed structural study of natural birnessite was performed by
456 Chuckhrov et al. (1985) on monomineralic birnessite micronodules dredged from the oceanic
457 floor. The sample has a one-layer hexagonal unit-cell and its structure corresponds to the *1H*
458 polytype (model 1a) in which interlayer Mn^{3+} and Mg^{2+} cations are octahedrally coordinated
459 above and/or below vacant layer octahedra. Ca^{2+} and Na^+ cations were also present in the
460 interlayer. This structure model was further supported by X-ray absorption spectroscopy data
461 (Manceau et al. 1992a, 1992b). Analysis of published experimental XRD patterns shows that
462 *1H* birnessite dominates in Mn-nodules from ocean and lake floors (Burns and Burns 1977;
463 Drits et al. 1985). This *1H* polytype occurs also in soil birnessite (Glover 1977).

464 Birnessite resulting from the equilibration at low pH of NaBi (obtained according to
465 the Giovanoli protocol – Giovanoli et al. 1970b) was studied by Silvester et al. (1997), Drits
466 et al. (1997a) and in more details by Lanson et al. (2000). This proton-rich birnessite,
467 hereafter referred to as HBi, has a one-layer hexagonal unit cell and a structure similar to

468 model 1a. HBi can thus be considered a synthetic analogue of natural 1*H* birnessite. As
 469 natural 1*H* birnessite, HBi layers contain a significant amount of vacant layer octahedra
 470 capped by Mn²⁺ and Mn³⁺. The negative layer charge of HBi is compensated for by protons
 471 and interlayer Mn cations, and the distribution of layer vacancies is inherited from the ordered
 472 Mn³⁺ distribution in NaBi. The H₂O_{interlayer} provides octahedral coordination to Mn_{interlayer} and
 473 forms empty prisms, and strong H-bonds, with O_{layer} of the adjacent layer. Manceau et al.
 474 (1997) and Lanson et al. (2002b) showed that equilibration of NaBi in the presence of
 475 aqueous heavy metals (Co, Cd and Pb) leads also to the formation of the 1*H* polytype (model
 476 1a). When Zn²⁺ is present, the resulting Zn-sorbed synthetic birnessite (ZnBi) has a 3*R*₂
 477 polytype, in which models 3a and 3b coexist. Interlayer Zn²⁺ cations are systematically
 478 located above and/or below vacant layer sites but can have both octahedral and tetrahedral
 479 coordinations. As a result, H₂O_{interlayer} providing octahedral (model 3a) and tetrahedral (model
 480 3b) coordination of Zn form weak and strong H-bonds, respectively, with O_{layer} of the
 481 adjacent layer.

482 **1*M*₁ Polytype.** Na-rich birnessite synthesized at high pH (Giovanoli et al. 1970a) was
 483 first described by Post and Veblen (1990) as a one-layer monoclinic polytype (1*M*₁ polytype,
 484 model 2c). To refine the structure they used *C2/m* space group and the Rietveld technique.
 485 However, their results were not precise enough to draw definitive conclusions on the origin of
 486 the layer charge. Lanson et al. (2002a) showed that NaBi has a one-layer triclinic unit-cell
 487 (*C* $\bar{1}$ space group) and consists of vacancy-free layers, the layer negative charge arising from
 488 the Mn³⁺-for-Mn⁴⁺ substitution within octahedral layers. The orthogonal layer symmetry
 489 results from the Jahn-Teller distortion of Mn³⁺-octahedra which all have their long Mn³⁺-O_{layer}
 490 bond oriented along the **a** axis. Structural sites of interlayer Na and H₂O, and their
 491 occupancies, have also been determined. The triclinic character of NaBi originates from a
 492 small layer displacement along the **b** axis.

493 NaBi varieties with different monovalent and divalent cations that were exchanged for
494 Na^+ were studied by Post and Veblen (1990), Kuma et al. (1994) and Bartoli (1997). XRD
495 patterns of these different birnessites can be indexed with a one-layer monoclinic unit-cell
496 whose parameters depend on the interlayer cation. However, essential details of these
497 birnessites remain poorly understood. For example, Mg^{2+} cations in Mg-exchanged birnessite
498 (MgBi) are supposedly located almost above or below octahedral sites (Post and Veblen
499 1990). Such a location is possible for interlayer Mg^{2+} cations only if the underlying octahedral
500 sites are vacant, NaBi layers being vacancy-free.

501 Similarly, Bartoli (1997) reported in K-exchanged birnessite the location of K^+ cations
502 in either a' or b' sites, whereas the presence of K^+ cations in these sites would lead to their
503 direct interaction with Mn_{layer} from adjacent layers, as can be seen from symbolic notations
504 (Model 2c – Table 2). Post and Veblen (1990) reported K^+ positions in KBi that are shifted
505 from the center of the interlayer prism toward its edges.

506 Ca^{2+} -for- Na^+ exchange in NaBi dramatically modifies the initial one-layer triclinic
507 structure of NaBi (model 2c) leading to a four-layer polytype in which layer pairs having
508 orthogonal stacking are shifted alternately by $\pm b/2$ along the **b** axis (Drits et al. 1998).
509 Gorshkov et al. (1992) described an occurrence of natural Ca-bearing birnessite, which was
510 analogous to the synthetic Ca-exchanged variety of NaBi.

511 **$3R_1$ Polytype.** Chen et al. (1996b) synthesized K-rich birnessite (KBi) with a $3R_1$ unit-
512 cell (model 2b). The KBi layers contain only Mn^{4+} and vacancies. From the refinement of
513 integrated intensities they concluded that both K^+ and $\text{H}_2\text{O}_{\text{interlayer}}$ were not located in the
514 prism's centers (a' and b' sites) as in the idealized model 2b but rather in the center of the
515 prism's faces. Gaillot et al. (2005) further refined this structure and showed that interlayer
516 prisms contain three possible K sites, each shifted from the faces of the prism toward its
517 center. Similar positions of interlayer cations were found for Cs^+ , Ba^{2+} and Sr^{2+} -exchanged

518 KBi (Gaillot et al. 2006b). The Ca^{2+} -for- K^+ exchange in KBi modifies the initial layer
519 stacking from the $3R_1$ polytype (model 2b) to the $1H$ one (model 1a). The driving force for the
520 KBi-to-CaBi transformation is likely the possibility of forming strong H-bonds between
521 $\text{H}_2\text{O}_{\text{interlayer}}$ providing octahedral coordination of Ca cations and O_{layer} of the adjacent layer
522 (model 1a). Using mild hydrothermal conditions, Chen et al. (1996a) and Gaillot et al. (2005)
523 synthesized directly Na-rich birnessite (NaBi_h) having a $3R_1$ unit-cell. According to these
524 authors, these NaBi_h layers consist of Mn^{4+} cations and vacant octahedra but positions of
525 interlayer Na^+ were not determined.

526 **$2H_1$ Polytype.** Kim et al. (1999) synthesized K-rich birnessite (KBi) from the
527 decomposition of KMnO_4 at temperatures ranging from 200-1000°C. Using the Rietveld
528 technique, these authors showed that KBi obtained at 800°C has two-layer hexagonal
529 symmetry because of the regular alternation of octahedral layers rotated with respect to each
530 other by 180° around the axis passing through layer Mn cations (polytype $2H_1$, model 4b).
531 Gaillot et al. (2003) has shown that the actual structure of KBi obtained at 800°C differs from
532 the model of Kim et al. (1999) by several important details. First, KBi interlayers have
533 heterogeneous cation composition with the coexistence of both K^+ and Mn^{3+} cations; second,
534 because of the layer-to-interlayer migration of Mn^{3+} cations KBi layers contain only Mn^{4+}
535 cations and vacant octahedra. Finally, interlayer K^+ is not located in the prism's center. Rather
536 K^+ is distributed over three possible sites, each of which being shifted from the center of the
537 prism towards its faces. Thus, the idealized KBi structure corresponds to the coexistence of
538 models 4a and 4b ($2H_1$ polytype).

539 **$2O_1$ Polytype.** KBi synthesized from the thermal decomposition of KMnO_4 at 1000°C
540 has vacancy-free layers and orthogonal layer symmetry (polytype $2O_1$, model 5c – Gaillot et
541 al. 2005, 2006a).

542 **Ambiguously determined polytypes.** Kim et al. (2000) used the Rietveld technique
543 to determine structures of synthetic K-Li-rich birnessites (Li-K-Bi) obtained from the thermal
544 decomposition of a Mn-KNO₃-LiOH mixture at 800°C and 1050°C. They concluded that the
545 800°C Li-K-Bi has a three layer periodicity and hexagonal symmetry of layers whereas the
546 1050°C Li-K-Bi has an orthogonal layer symmetry and two-layer periodicity due to an
547 ordered rotation of layers by 180°. However, the description of these structures was rather
548 confusing because of technical errors. In particular, symbolic notations for the structures do
549 not correspond to the proposed structure models. For example, the 1050°C Li-K-Bi is
550 described as AaB a' BbA b' instead of the actual notation given for model 4b (AcB a' BcA).
551 In addition, unit-cell parameters given for the 1000°C Li-K-Bi are not consistent with the
552 proposed space group. Similarly, interatomic Mn-O distances differ significantly from those
553 expected when heterovalent Mn_{layer} cations coexist within the octahedral layers. These authors
554 also describe the structure of the Li-K-Bi sample synthesized at 800°C as AcB a' CbA c' BaC
555 b' (model 3d, polytype 3R₂), with octahedrally coordinated interlayer K⁺ cations. However,
556 atomic coordinates reported for this sample (Table 1 – Kim et al. 2000) correspond to
557 polytype 3R₁ (model 2b) with interlayer K⁺ having prismatic coordination. This latter
558 structure model is consistent with the experimental XRD pattern reported for this sample
559 (Figure 4 – Kim et al. 2000) which is similar to those obtained by Chen et al. (1996a) and
560 Gaillot et al. (2005) from 3R₁ polytypes (model 2b) synthesized under mild hydrothermal
561 conditions. All these experimental patterns are similar to the one displayed on Figure 8a.

562 **Turbostratic samples.** Finally, one has to note that among different natural
563 environments, and especially in soils, turbostratic birnessite is extremely common. For
564 example, turbostratic birnessite has been reported as resulting from the bacterial oxidation of
565 Mn²⁺ by different strains (Mandernack et al. 1995; Villalobos et al. 2003; Jurgensen et al.
566 2004; Bargar et al. 2005; Webb et al. 2005) and from abiotic processes (Mandernack et al.

567 1995). However, so far there is little unambiguous information derived from XRD data on the
568 structural and crystal chemical of these varieties. Most often the structural characterization of
569 disordered birnessite is limited to the description of $00l$ peak positions as a function of
570 relative humidity to assess the lamellar character of these “poorly crystalline birnessites”. The
571 position of hkl reflections has also been used to hypothesize the actual layer symmetry (and
572 thus the origin of the layer charge of these varieties) however without much experimental
573 support (Villalobos et al. 2003; Jurgensen et al. 2004; Webb et al. 2005).

574 However, as described, birnessite having different layer symmetry may be
575 unambiguously distinguished from each other from the shape of their hk bands (Fig. 12). A
576 shoulder, resulting from the individualization of 20 and 11 reflections, is indeed visible on the
577 low-angle side of main maximum of the 20,11 band for orthogonal modifications (at ~ 2.55 Å
578 and 2.45 Å, respectively – Fig. 12b), whereas this shoulder is logically absent for hexagonal
579 modifications (Fig. 12a). Similarly, the 31,02 band of the orthogonal modifications contains
580 two distinct maxima (~ 1.474 Å and 1.422 Å – Fig. 12b) which are merged for the hexagonal
581 modifications (peak at ~ 1.422 Å – Fig. 12a). The features described for the orthogonal
582 modifications are like those reported for the Mn oxides resulting from the oxidation of Mn^{2+}
583 by *Bacillus sp.* strain SG-1 (Fig. 3 in Webb et al. 2005) indicating the presence of a high
584 proportion of Mn^{3+} within the octahedral layers of this birnessite. The presence of Mn^{3+} -rich
585 rows in vacancy-free layers, as in NaBi, is also supported by the splitting of the 8 Å⁻¹ feature
586 in the EXAFS spectra (Fig. 5 in Webb et al. 2005) which has been described as characteristic
587 of the presence of Mn^{3+} -rich rows in the octahedral Mn layer leading to its orthogonal
588 symmetry (Fig. 9 in Gaillot et al. 2003; Fig. 6 in Marcus et al. 2004; Fig. 5 in Manceau et al.
589 2004; Manceau et al. 2005). To our knowledge, XRD patterns of all other turbostratic
590 varieties reported so far in the literature correspond to hexagonal modifications.

591 In addition Villalobos et al. (2006) demonstrated the high sensitivity of XRD profiles
592 to the layer and interlayer structure of turbostratic phyllomanganates. In their study,
593 Villalobos et al. (2006) observed contrasting experimental modulations of the 20,11 and 31,02
594 bands, and successfully reproduced them assuming a turbostratic stacking. In this case, the
595 position and profile of the bands depend essentially on the amount and atomic coordinates of
596 both layer and interlayer species, and these authors were able to determine the amount of
597 vacant layer sites, as well as the amount and coordinates of both “heavy” ($\text{Mn}^{3+,2+}$) and “light”
598 (Na^+ , K^+ , $\text{H}_2\text{O}_{\text{interlayer}}$) interlayer species. Such calculations also provided them with an
599 estimate of the lateral extension of the octahedral layers (Drits and Tchoubar 1990; Jurgensen
600 et al. 2004; Villalobos et al. 2006). The influence of the layer and interlayer structure on
601 calculated profiles for 20,11 and 31,02 bands is illustrated in Figure 13. As compared to the
602 structure model shown in Figure 12a (Model 1a), decreasing both the proportion of interlayer
603 Mn and layer vacancies from 0.167 to 0.075 broadens the lineshape of the 20,11 and
604 smoothes out the scattering dip at $\sim 45^\circ 2\theta \text{ CuK}\alpha$, thus rendering the calculated hump at ~ 50 -
605 $55^\circ 2\theta \text{ CuK}\alpha$ less pronounced (Fig. 12b). Moving interlayer Mn from the $^{\text{VI}}\text{TC}$ position
606 dramatically modifies the 20,11 lineshape, as observed when the 0.167 interlayer Mn atoms
607 are located above and/or below the tridentate cavities ($^{\text{VI}}\text{TE}$ sites – Fig. 13c). The sensitivity
608 of the 20,11 profile to the position of “light” interlayer species is illustrated next by assuming
609 either the presence of Na^+ above and/or below O_{layer} [(0.333, 0.0, 0.5) – Fig. 13d] or that of K^+
610 above/below the tridentate cavities [Position (-0.222, 0, 0.5) and equivalent positions – Fig.
611 13e], H_2O molecules sitting in both cases above and/or below O_{layer} . In the second case, the
612 20,11 band is broadened and the “hump” observed at $\sim 50^\circ 2\theta \text{ CuK}\alpha$ in Figure 13d is both
613 shifted towards higher angles and smoothed out. Similar modulations can however result
614 from the partial ordering of the layer stacking (e.g., Ben Brahim et al. 1983, 1984; Drits and
615 Tchoubar 1990; Viani et al. 2002). Special attention should thus be paid to the structural

616 interpretation of these modulations, and, in this respect, verifying the structural XRD model
617 with independent data from another structural technique, such as EXAFS spectroscopy, is
618 always warranted.

619

620

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621

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627

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885

FIGURE CAPTIONS

886

887 **FIGURE 1.** Idealized structure model of birnessite polytypes. **a)** $1H$ polytype. Top: projection
 888 along the **b** axis. Open and solid symbols indicate atoms at $y = 0$ and $y = \pm 1/2$,
 889 respectively. Large circles represent O_{layer} atoms and small circles represent Mn_{layer} ,
 890 atoms. Dashed lines outline specific positions of the close-packing formalism.
 891 Irregular dashed lines outline the interlayer octahedra defined by O_{layer} from adjacent
 892 layers. Bottom: projection on the **ab** plane. The upper surface of the lower layer is
 893 shown as light shaded triangles whereas the lower surface of the upper layer is
 894 shown as dark shaded triangles. Mn_{layer} of the upper layer are shown as small open
 895 circles. **b)** $2H_1$ polytype. Top: projection along the **b** axis. Irregular dashed lines
 896 outline the interlayer prisms defined by O_{layer} from adjacent layers. Bottom:
 897 projection on the **ab** plane. Mn_{layer} of the lower layer are shown as small solid circles.
 898 Other symbols as in Figure 1a. **c)** $2H_2$ polytype. Top: projection along the **b** axis.
 899 Irregular dashed lines outline the interlayer octahedra defined by O_{layer} from adjacent
 900 layers. Bottom: projection on the **ab** plane. Symbols and notations as in Figure 1a.

901 **FIGURE 2.** Idealized structure model of birnessite polytypes in projection along the **b** axis. **a)**
 902 $3R_1$ polytype. Symbols and notations as in Figure 1. Irregular dashed lines outline the
 903 interlayer prisms defined by O_{layer} from adjacent layers. **b)** $3R_2$ polytype. Symbols
 904 and notations as in Figure 1. Irregular dashed lines outline the interlayer octahedra
 905 defined by O_{layer} from adjacent layers. **c)** $3H_1$ polytype. Symbols and notations as in
 906 Figure 1. Irregular dashed lines as in Figure 2b. **d)** $3H_2$ polytype. Symbols and
 907 notations as in Figure 1. Irregular dashed lines as in Figure 2b.

908 **FIGURE 3.** Idealized interlayer structure model in projection along the **b** axis for birnessite
 909 polytypes with layer vacancies (hexagonal layer symmetry). **a)** $1H$ polytype with

910 octahedrally coordinated cations above/below vacant layer sites (^{VI}TC position –
 911 Model 1a). Symbols and notations as in Figure 1. Irregular dashed lines outline the
 912 interlayer prisms defined by $H_2O_{interlayer}$ coordinating the interlayer cations and O_{layer}
 913 from adjacent layers (H-bonds). **b)** $3R_1$, $3R_2$ and $2H_1$ polytypes with octahedrally
 914 coordinated cations above/below vacant layer sites (^{VI}TC position – Models 2a, 3a
 915 and 4a, respectively). Symbols and notations as in Figure 1. Irregular dashed lines
 916 outline the interlayer octahedra defined by $H_2O_{interlayer}$ coordinating the interlayer
 917 cations and O_{layer} from adjacent layers (weak H-bonds). **c)** $2H_2$, $3H_1$ and $3H_2$
 918 polytypes with octahedrally coordinated cations above/below vacant layer sites (^{VI}TC
 919 position – Models 5a, 6a and 7a, respectively). Irregular dashed lines outline the
 920 interlayer prisms (left) and octahedra defined by $H_2O_{interlayer}$ coordinating the
 921 interlayer cations and O_{layer} from adjacent layers (strong and weak H-bonds,
 922 respectively). **d)** $3R_2$ polytype with tetrahedrally coordinated cations above/below
 923 vacant layer sites (^{IV}TC position – Model 3b). Irregular dashed line outlines the
 924 strong H-bond between $H_2O_{interlayer}$ coordinating the interlayer cation and O_{layer} from
 925 adjacent layers.

926 **FIGURE 4.** Idealized interlayer structure model in projection along the **b** axis for birnessite
 927 polytypes with vacancy-free layers (orthogonal layer symmetry). **a)** $1M_2$ polytype
 928 with octahedrally coordinated cations above/below empty layer tetrahedra (tridentate
 929 cavities) sharing three edges with layer Mn octahedra (^{VI}TE position – Model 3d).
 930 Symbols and notations as in Figure 1. Irregular dashed lines outline the interlayer
 931 prisms defined by $H_2O_{interlayer}$ coordinating the interlayer cations and O_{layer} from
 932 adjacent layers (H-bonds). **b)** $1O$ and $2O_1$ polytypes with octahedrally coordinated
 933 cations above/below empty layer tetrahedra (tridentate cavities) sharing three edges
 934 with layer Mn octahedra (^{VI}TE position – Models 1b and 4d, respectively). Symbols

935 and notations as in Figure 1. Irregular dashed lines outline the interlayer octahedra
 936 defined by $\text{H}_2\text{O}_{\text{interlayer}}$ coordinating the interlayer cations and O_{layer} from adjacent
 937 layers (weak H-bonds).

938 **FIGURE 5.** XRD patterns calculated for idealized structure models of birnessite polytypes. **a)**
 939 $1H$ polytype with $\text{Mn}^{3+,2+}$ in $^{\text{VI}}\text{TC}$ position (Model 1a). **b)** $3R_1$ polytype with $\text{Mn}^{3+,2+}$
 940 in $^{\text{VI}}\text{TC}$ position (Model 2a). **c)** $3R_2$ polytype with Zn^{2+} in $^{\text{VI}}\text{TC}$ position (Model 3a).
 941 **d)** $2H_1$ polytype with $\text{Mn}^{3+,2+}$ in $^{\text{VI}}\text{TC}$ position (Model 4a). **e)** $2H_2$ polytype with
 942 $\text{Mn}^{3+,2+}$ in $^{\text{VI}}\text{TC}$ position (Model 5a). **f)** $3H_1$ polytype with $\text{Mn}^{3+,2+}$ in $^{\text{VI}}\text{TC}$ position
 943 (Model 6a). **g)** $3H_2$ polytype with $\text{Mn}^{3+,2+}$ in $^{\text{VI}}\text{TC}$ position (Model 7a).

944 XRD patterns were calculated using the idealized structure models described in
 945 Table 3. a and b unit-cell parameters for the polytypes having a hexagonal layer
 946 symmetry are 4.936 and 2.850 Å, respectively, whereas they are 5.180 and 2.850 Å,
 947 respectively, for the polytypes having a orthogonal layer symmetry. In all cases the
 948 minimum periodicity along the \mathbf{c}^* axis is 7.10 Å. All calculations were performed
 949 assuming a periodic stacking mode devoid of random stacking faults. The radius of
 950 the coherent scattering domains in the \mathbf{ab} plane was set to 150 Å for all calculations,
 951 whereas the mean extent of the coherent scattering domains perpendicular to the
 952 layer plane is 7 layers (maximum extent: 35 layers). The distribution of coherent
 953 scattering domain size along the \mathbf{c}^* axis was assumed to be lognormal (Drits et al.
 954 1997b). The values of Debye-Waller thermal factor (B) were 0.5, 1.0 and 1.5 for
 955 Mn_{layer} , O_{layer} and $\text{H}_2\text{O}_{\text{interlayer}}$, respectively. B factors for $\text{Me}_{\text{interlayer}}$ were either 1.0
 956 (metal cations Zn^{2+} , $\text{Mn}^{3+,2+}$, ...) or 2.0 (alkali and alkali-earth cations: K^+ , Ca^{2+} , ...).

957 **FIGURE 6.** XRD patterns calculated for idealized structure models of birnessite $3R_2$ polytype.
 958 **a)** With Zn^{2+} in $^{\text{IV}}\text{TC}$ position (Model 3b). **b)** With Zn^{2+} in $^{\text{VI}}\text{TC}$ position (Model 3a).
 959 **c)** With Zn^{2+} in $^{\text{IV}}\text{TE}$ position (Model 3c).

960 **FIGURE 7.** XRD patterns calculated for idealized structure models of birnessite polytypes. **a)**
 961 $1M_2$ polytype with K^+ in the interlayer mid-plane (Model 3e). **b)** $1M_2$ polytype with
 962 Ca^{2+} in ^{VI}TE sites (Model 3d). **c)** $2O_1$ polytype with K^+ in the interlayer mid-plane
 963 (Model 4c). **d)** $2O_1$ polytype with Ca^{2+} in ^{VI}TE sites (Model 4d).

964 **FIGURE 8.** XRD patterns calculated for idealized structure models of birnessite polytypes. **a)**
 965 $3R_1$ polytype with K^+ in the interlayer mid-plane (Model 2b). **b)** $3R_1$ polytype with
 966 $Mn^{3+,2+}$ in ^{VI}TC position (Model 2a). **c)** $2H_1$ polytype with K^+ in the interlayer mid-
 967 plane (Model 4b). **d)** $2H_1$ polytype with $Mn^{3+,2+}$ in ^{VI}TC position (Model 4a).

968 **FIGURE 9.** XRD patterns calculated for idealized structure models of birnessite polytypes. **a)**
 969 $2H_2$ polytype with $Mn^{3+,2+}$ in ^{VI}TC position (Model 5a). **b)** $2H_1$ polytype with $Mn^{3+,2+}$
 970 in ^{VI}TC position (Model 4a). **c)** $2O_1$ polytype with K^+ in the interlayer mid-plane
 971 (Model 4c).

972 **FIGURE 10.** XRD patterns calculated for idealized structure models of birnessite polytypes. **a)**
 973 $3R_1$ polytype with K^+ in the interlayer mid-plane (Model 2b). **b)** $3R_2$ polytype with
 974 Zn^{2+} in ^{VI}TC position (Model 3a). **c)** $3H_1$ polytype with $Mn^{3+,2+}$ in ^{VI}TC position
 975 (Model 6a). **d)** $3H_2$ polytype with $Mn^{3+,2+}$ in ^{VI}TC position (Model 7a).

976 **FIGURE 11.** Comparison between experimental and calculated XRD patterns for a K-rich
 977 birnessite sample synthesized at $700^\circ C$ from the thermal decomposition of $KMnO_4$
 978 (Gaillot et al. 2004). Experimental data are shown as crosses, whereas calculated
 979 profiles are shown as solid lines. Arrows outline the misfits between experimental
 980 and calculated patterns. Only $20l$ and $11l$ reflections are calculated. Atomic
 981 coordinates and other structural parameters used for the calculations as described by
 982 (Gaillot et al. 2004). (a) Optimum model and difference plot. The optimum model
 983 includes contributions from a defect-free $2H$ polytype and from $2O/2H$, $2H/3R$, and
 984 $3R/2H$ mixed-layered structures (relative proportions 7:29:41:23). (b) Calculation

985 made replacing the optimum $2O/2H$ contribution ($2O:2H$ ratio 50:50) by a defect-
 986 free $2H$ contribution. (c) Calculation made by subtracting the $2H/3R$ contribution
 987 ($2H:3R$ ratio 70:30) from the optimum model. (d) Calculation made by subtracting
 988 the $3R/2H$ contribution ($3R:2H$ ratio 90:10) from the optimum model. Adapted from
 989 (Gaillot et al. 2004).

990 **FIGURE 12.** XRD patterns calculated for idealized structure models of turbostratic birnessite.

991 **a)** Birnessite with $Mn^{3+,2+}$ in ^{VI}TC position (Model 1a). **b)** Birnessite with $0.67 Na^+$
 992 and $H_2O_{interlayer}$ in the interlayer mid-plane above below O_{layer} (Model 2c).

993 Calculations were performed assuming a turbostratic stacking (100% random
 994 stacking faults). The radius of the coherent scattering domains in the **ab** plane was
 995 set to 75 \AA . All other parameters for XRD pattern calculations as described for
 996 Figure 5.

997 **FIGURE 13.** XRD patterns calculated for idealized structure models of turbostratic birnessite

998 having hexagonal layer symmetry. **a)** Birnessite with 0.833 vacant layer sites capped
 999 by $Mn^{3+,2+}$ in ^{VI}TC position (Model 1a). **b)** Birnessite with 0.925 vacant layer sites
 1000 capped by $Mn^{3+,2+}$ in ^{VI}TC position. **c)** Birnessite with 0.833 vacant layer sites
 1001 capped by $Mn^{3+,2+}$ in ^{VI}TE position (similar to Model 3d with interlayer $Mn^{3+,2+}$
 1002 cations). **d)** Birnessite with 0.925 vacant layer sites and interlayer Na^+ (0.30 per
 1003 octahedron) and H_2O molecules (0.90 per octahedron) in c' position ($+1/3, 0, 1/2$). **e)**
 1004 Birnessite with 0.925 vacant layer sites and interlayer K^+ (0.30 per octahedron) in
 1005 and H_2O molecules (0.90 per octahedron) in a' ($-0.222, 0, 1/2$) and c' ($+1/3, 0, 1/2$)
 1006 positions, respectively.

1007 Calculations were performed as described for Figure 12.

1008

Table 1. List of possible periodic layer stacking modes in birnessite consisting of hexagonal (vacancy-bearing) or orthogonal (vacancy-free) layers

Layer stacking	Hexagonal layers	Orthogonal layers
AbC – AbC ...	1 <i>H</i>	1 <i>O</i>
AbC = CbA = AbC ...	2 <i>H</i> ₁	2 <i>O</i> ₁
AbC – AcB – AbC ...	2 <i>H</i> ₂	2 <i>O</i> ₂
AbC = CaB = BcA = AbC ...	3 <i>R</i> ₁	1 <i>M</i> ₁
AbC – BcA – CaB – AbC ...	3 <i>R</i> ₂	1 <i>M</i> ₂
AbC – AcB – AcB – AbC ...	3 <i>H</i> ₁	3 <i>O</i> ₁
AbC – AcB – CaB – AbC ...	3 <i>H</i> ₂	3 <i>O</i> ₂

Table 2. Symbolic notations of birnessite consisting of hexagonal (vacancy-bearing) and orthogonal (vacancy-free) layers and differing from each other by stacking modes and interlayer structures.

Hexagonal layer symmetry				Layers with orthogonal symmetry			
Polyt.	Model	XRD (fig.)	Notation	Polyt.	Model	XRD (fig.)	Notation
1H	1a	5a	AbC _{b'A'} C ^{b'} AbC...	1O	1b		AbC _{a'B'} B ^{c'} AbC...
3R ₁	2a	5b, 8b	AbC _{b'A'} B ^{a'} CaB _{a'C'} A ^{c'} BcA _{c'B'} C ^{b'} AbC...	1M ₁	2c		AbC c' CaB b' BcA a' AbC...
3R ₁	2b	8a, 10a	AbC b'/a' CaB a'/c' BcA c'/b' AbC...		2d		AbC _{a'A'} B ^{b'} CaB _{c'C'} A ^{a'} BcA _{b'B'} C ^{c'} AbC...
3R ₂	3a	6b, 10b	AbC _{b'A'} A ^{c'} BcA _{c'B'} B ^{a'} CaB _{a'C'} C ^{b'} AbC...	1M ₂	3d	7b	AbC _{a'B'} C ^{a'} BcA _{b'C'} A ^{b'} CaB _{c'A'} B ^{c'} AbC...
3R ₂	3b	5c, 6a	AbC _{b'B'} C ^{c'} BcA _{c'C'} A ^{a'} CaB _{a'A'} B ^{b'} AbC...	1M ₂	3e	7a	AbC a' BcA b' CaB c' AbC...
3R ₂	3c	6c	AbC _{a'A'} A ^{a'} BcA _{b'B'} B ^{b'} CaB _{c'C'} C ^{c'} AbC...				
2H ₁	4a	5d, 8d, 9b	AbC _{b'A'} A ^{b'} CbA _{b'C'} C ^{b'} AbC...	2O ₁	4c	7c, 9c	AbC a' CbA c' AbC...
2H ₁	4b	8c	AbC a'/C' CbA c'/A' AbC...	2O ₁	4d	7d	AbC _{a'B'} B ^{a'} CbA _{c'B'} B ^{c'} AbC...
		5e, 9a		2O ₁	4e		AbC c' CbA a' AbC...
2H ₂	5a		AbC _{b'A'} B ^{c'} AcB _{c'A'} C ^{b'} AbC...	2O ₂	5d		AbC _{a'B'} C ^{b'} AcB _{a'C'} B ^{c'} AbC...

$2H_2$	5b		$AbC\ b'\ AcB\ c'\ AbC\dots$	$2O_2$	5e		$AbC_{a'A'}\ ^{C'b'}\ AcB_{a'A'}\ ^{B'c'}\ AbC\dots$
$2H_2$	5c		$AbC_{b'A'}\ ^{C'c'}\ AcB_{c'A'}\ ^{B'b'}\ AbC\dots$				
$3H_1$	6a	5f, 10c	$AbC_{b'A'}\ ^{B'c'}\ AcB_{c'A'}\ ^{B'c'}\ AcB_{c'A'}\ ^{C'b'}\ AbC\dots$				
$3H_1$	6b	5g, 10d	$AbC\ b'\ AcB\ c'\ AcB\ c'\ AbC\dots$				
$3H_2$	7a		$AbC_{b'A'}\ ^{B'c'}\ AcB_{c'A'}\ ^{B'a'}\ CaB_{a'C'}\ ^{C'b'}\ AbC\dots$				

Table 3. Atomic positions and site occupancies for the idealized structure models described in

Table 2.

Model		1a	2a	2b
Polytype		1H	3R ₁	3R ₁
XRD pattern	Fig.	5a	5b, 8b	8a
Mn _{layer}	x ^a	0	0	0
	y ^a	0	0	0
	ζ ^b	0	0	0
O _{layer}	occ	0.833	0.833	0.925
	x ^a	+/-0.333	+/-0.333	+/-0.333
	y ^a	0	0	0
Cat. Inter.	ζ ^b	+/-1.00	+/-1.00	+/-1.00
	Occ	1 x 2	1 x 2	1 x 2
	Type	Mn	Mn	K
H ₂ O	x ^a	0.000	0.000	0
	y ^a	0	0	0
	ζ ^b	+/-2.15	+/-2.15	+/-3.55
	Occ	0.0833 x2	0.0833 x2	0.15 x2
	x ^a	-/+0.333	-/+0.333	+/-0.333
Interlayer shift	y ^a	0	0	0
	ζ ^b	+/-3.35	+/-3.35	+/-3.55
	Occ	0.250 x2	0.250 x2	0.300 x2
Interlayer shift		0.0	-0.333a	-0.333a

Notes: ^ax and y atomic positions are expressed in fraction of ideal C-centered unit-cell *a* and *b* parameters, respectively. x positions are given in projection normal to the **ab** plane. ^bPosition ζ along *c* is expressed in Å to emphasize the thickness of layer and interlayer polyhedra. Occupancy (occ) is given as the sum of all equivalent sites.

Table 3. (continued).

Model		3a	3b	3c	3d	3e
Polytype		$3R_2$	$3R_2$	$3R_2$	$1M_2$	$1M_2$
XRD pattern	Fig.	8b, 10b	5c, 6a	6c	7b	7a
Mn _{layer}	x ^a	0	0	0	0	0
	y ^a	0	0	0	0	0
	ζ ^b	0	0	0	0	0
O _{layer}	Occ	0.833	0.833	0.833	0.833	1.000
	x ^a	+/-0.333	+/-0.333	+/-0.333	+/-0.333	+/-0.333
	y ^a	0	0	0	0	0
Cat. Inter.	ζ ^b	+/-1.00	+/-1.00	+/-1.00	+/-1.00	+/-1.00
	Occ	2	2	2	2	2
	Type	Zn	Zn	Zn	Ca	K
H ₂ O ^c	x ^a	0.000	0.000	-/+0.333	-/+0.333	-/+0.333
	y ^a	0	0	0	0	0
	ζ ^b	+/-2.20	+/-1.77	+/-1.77	+/-2.30	+/-3.55
Int. shift	Occ	0.0833 x2	0.0833 x2	0.0833 x2	0.0833 x2	0.150 x2
	x ^a	-/+0.333	0	-/+0.333	0	-/+0.333
	y ^a	0	0	0	0	0
Int. shift	ζ ^b	+/-3.55	+/-3.70	+/-3.70	+/-3.70	+/-3.55
	Occ	0.250 x2	0.0833 x2	0.0833 x2	0.250 x2	0.300 x2
Int. shift		+0.333a	+0.333a	+0.333a	+0.333a	+0.333a

Table 3. (continued).

Model		4a	4b	4c	4d	5a
Polytype		$2H_1$	$2H_1$	$2O_1$	$2O_1$	$2H_2$
XRD pattern	Fig.	5d, 8d, 9b, 10d	8c	7c	7d	5e, 9a
Mn _{layer}	x ^a	0	0	0	0	0
	y ^a	0	0	0	0	0
	ζ ^b	0	0	0	0	0
	Occ	0.833	0.925	1.000	1.000	0.833
O _{layer}	x ^a	+/-0.333	+/-0.333	+/-0.333	+/-0.333	+/-0.333
	y ^a	0	0	0	0	0
	ζ ^b	+/-1.00	+/-1.00	+/-1.00	+/-1.00	+/-1.00
	Occ	2	2	2	2	2
Cat. Inter.	Type	Mn	K	K	Ca	Mn
	x ^a	0.000	-0.222 0.111/0.111	-0.222 0.111/0.111	+/-0.333	0
	y ^a	0	0 +/-0.333	0 +/-0.333	0	0
	ζ ^b	+/-2.15	3.55	3.55	+/-2.30	+/-2.15
H ₂ O ^c	Occ	0.0833 x2	0.100 x3	0.100 x3	0.0833 x2	0.0833 x2
	x ^a	+/-0.333	0.333	0.333	0	+/-0.333
	y ^a	0	0	0	0	0
	ζ ^b	+/-3.35	+3.55	+3.55	+/-3.70	+/-3.35
	Occ	0.250 x2	0.600	0.600	0.250 x2	0.250 x2
Mn _{layer}	x ^a	0	0	0	0	0.333
	y ^a	0	0	0	0	0
	ζ ^b	7.10	7.10	7.10	7.10	7.10
	Occ	0.833	0.925	1.000	1.000	0.833
O _{layer}	x ^a	+/-0.333	+/-0.333	+/-0.333	+/-0.333	-0.333/0.000
	y ^a	0	0	0	0	0
	ζ ^b	6.10/8.10	6.10/8.10	6.10/8.10	6.10/8.10	6.10/8.10
	Occ	2	2	2	2	2
Cat. Inter.	Type	Mn	K	K	Ca	Mn
	x ^a	0.000	0.222 -0.111/-0.111	0.222 -0.111/-0.111	+/-0.333	0.333
	y ^a	0	0 +/-0.333	0 +/-0.333	0	0
	ζ ^b	4.95/9.25	10.65	10.65	4.80/9.40	4.95/9.25
H ₂ O ^c	Occ	0.0833 x2	0.100 x3	0.100 x3	0.0833 x2	0.0833 x2
	x ^a	+/-0.333	-0.333	-0.333	0	0.000/-0.333
	y ^a	0	0	0	0	0
	ζ ^b	3.75/10.45	10.65	10.65	3.40/10.80	3.75/10.45
	Occ	0.250 x2	0.600	0.600	0.250 x2	0.250 x2
Int. shift		0	0	0	0	0

Table 3. (continued).

Model		6a	7a
Polytype		$3H_1$	$3H_2$
XRD pattern	Fig.	5f, 10c	5g
Mn _{layer}	x ^a	0	0
	y ^a	0	0
	ζ ^b	0	0
	occ	0.833	0.833
O _{layer}	x ^a	+/-0.333	+/-0.333
	y ^a	0	0
	ζ ^b	+/-1.00	+/-1.00
	occ	2	2
Cat. Inter.	Type	Mn	Mn
	x ^a	0	0
	y ^a	0	0
	ζ ^b	+/-2.15	+/-2.15
	occ	0.0833 x2	0.0833 x2
H ₂ O ^c	x ^a	-/+0.333	-/+0.333
	y ^a	0	0
	ζ ^b	+/-3.35	+/-3.35
	occ	0.250 x2	0.250 x2
Mn _{layer}	x ^a	0.333	0.333
	y ^a	0	0
	ζ ^b	7.10	7.10
	occ	0.833	0.833
O _{layer}	x ^a	-0.333/0.000	-0.333/0.000
	y ^a	0	0
	ζ ^b	6.10/8.10	6.10/8.10
	occ	2	2
Cat. Inter.	Type	Mn	Mn
	x ^a	0.333	0.333
	y ^a	0	0
	ζ ^b	4.95/9.25	4.95/9.25
H ₂ O ^c	occ	0.0833 x2	0.0833 x2
	x ^a	0.000/-0.333	0.000/-0.333
	y ^a	0	0
	ζ ^b	3.75/10.45	3.75/10.45
Mn _{layer}	occ	0.250 x2	0.250 x2
	x ^a	0.333	-0.333
	y ^a	0	0
	ζ ^b	14.20	14.20
O _{layer}	occ	0.833	0.833
	x ^a	-0.333/0.000	0.333/0.000
	y ^a	0	0
	ζ ^b	13.20/15.20	13.20/15.20
Cat. Inter.	occ	2	2
	Type	Mn	Mn
	x ^a	0.333	-0.333
	y ^a	0	0
H ₂ O ^c	ζ ^b	12.05/16.35	12.05/16.35
	occ	0.0833 x2	0.0833 x2
	x ^a	0.000/-0.333	0.000/0.333
	y ^a	0	0
Int. shift	ζ ^b	10.85/17.55	10.85/17.55
	occ	0.250 x2	0.250 x2
		0	0

Table 4A. Calculated $d(hkl)$ values for birnessite polytypes consisting of vacancy-bearing layers having a hexagonal layer symmetry (See Table 1).

Polytype	1H	2H	3R/3H
$d(hkl)$	hkl	hkl	hkl
2.468	200,110	200,110	200,110
2.452	-	-	201,111
2.432	-	201,111	-
2.404	-	-	202,112
2.331	201,111	202,112	203,113
2.239	-	-	204,114
2.188	-	203,113	-
2.136	-	-	205,115
2.026	202,112	204,114	206,116
1.917	-	-	207,117
1.863	-	205,115	-
1.810	-	-	208,118
1.708	203,113	206,116	209,119
1.613	-	-	20.10,11.10
1.567	-	207,117	-
1.523	-	-	20.11,11.11
1.441	204,114	208,118	20.12,11.12
1.425	020,310	020,310	020,310
1.422	-	-	021,311
1.418	-	021,311	-
1.412	-	-	022,312
1.397	021,311	022,312	023,313
1.376	-	-	024,314
1.365	-	-	20.13,11.13
1.364	-	023,313	-
1.351	-	-	025,315
1.329	-	209,119	-
1.322	022,312	024,314	026,316
1.295	-	-	20.14, 11.14
1.290	-	-	027,317
1.274	-	025,315	-
1.256	-	-	028,318
1.231	-	20.10,11.10	20.15,11.15
1.221	023,313	026,316	029,319

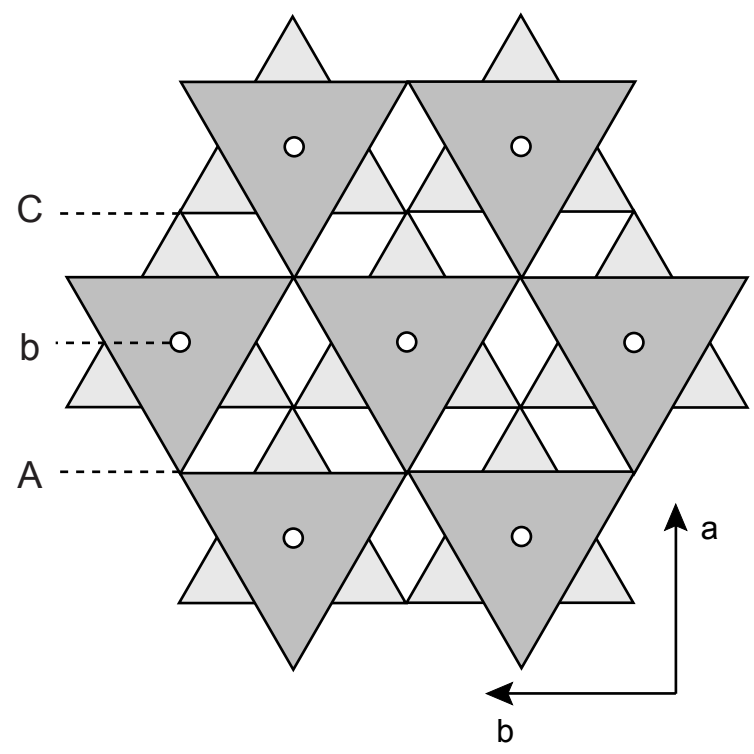
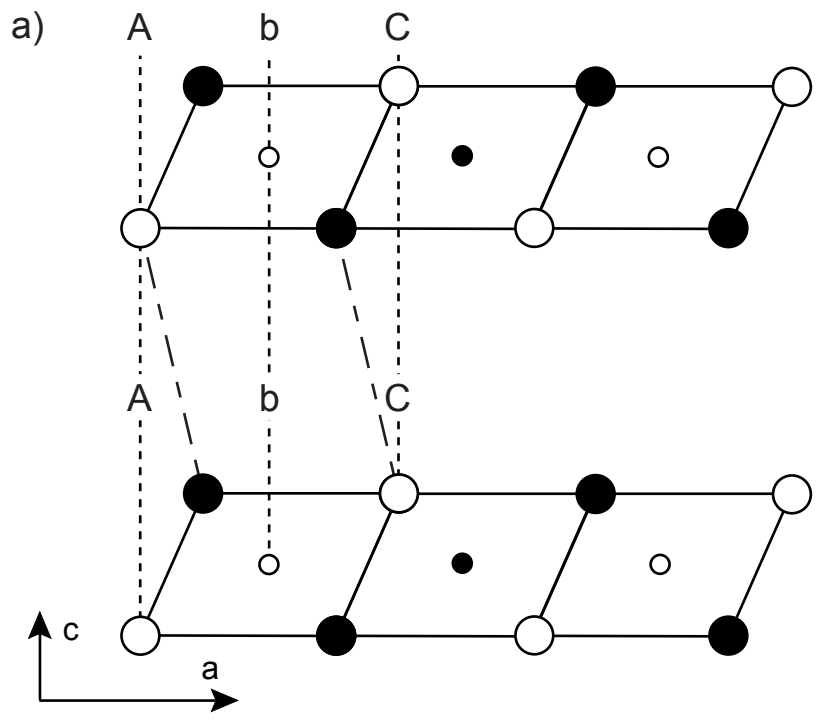
Notes: a and b unit-cell parameters are 4.936, and 2.850 Å, respectively. The minimum periodicity along the c^* axis is 7.10 Å for all polytypes.

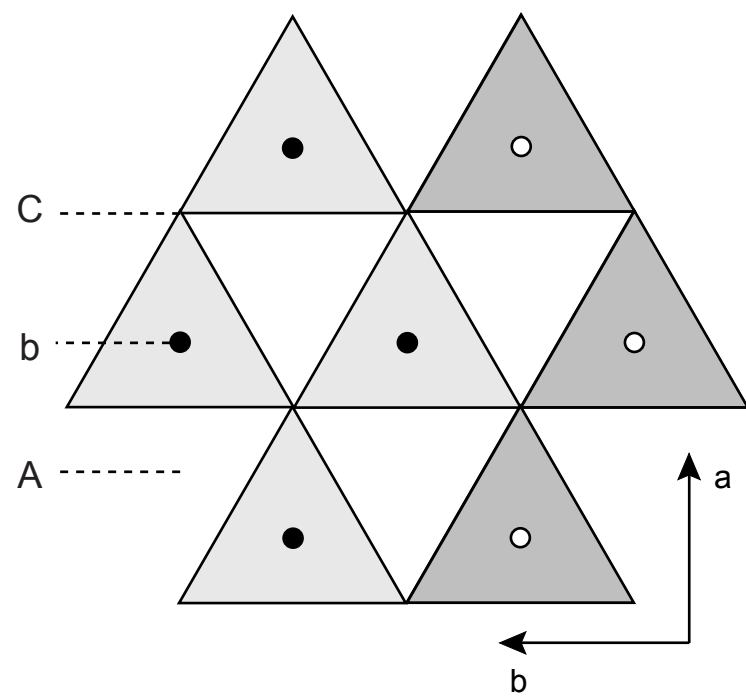
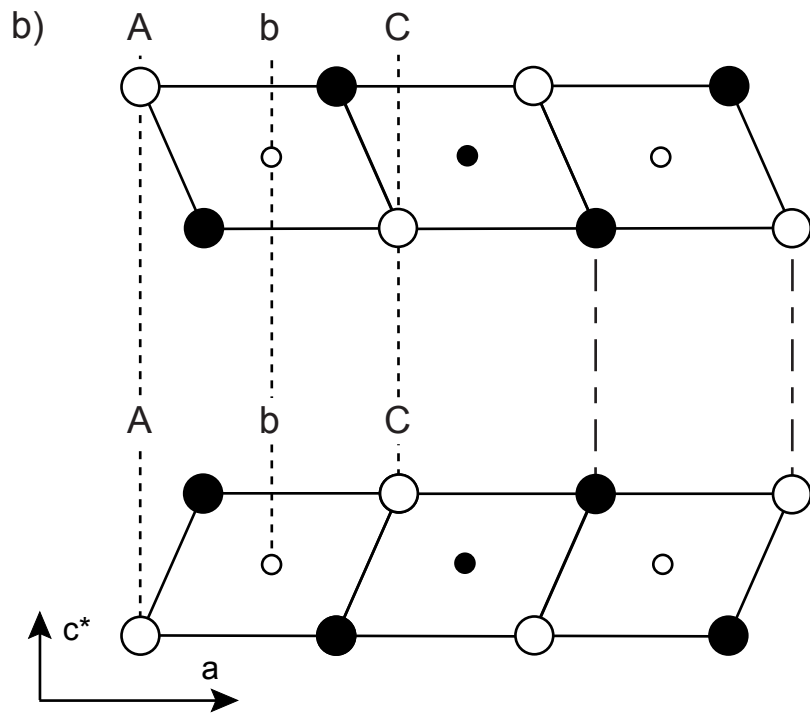
Table 4B. Calculated $d(hkl)$ values for birnessite polytypes consisting of vacancy-free layers having an orthogonal layer symmetry (See Table 1)

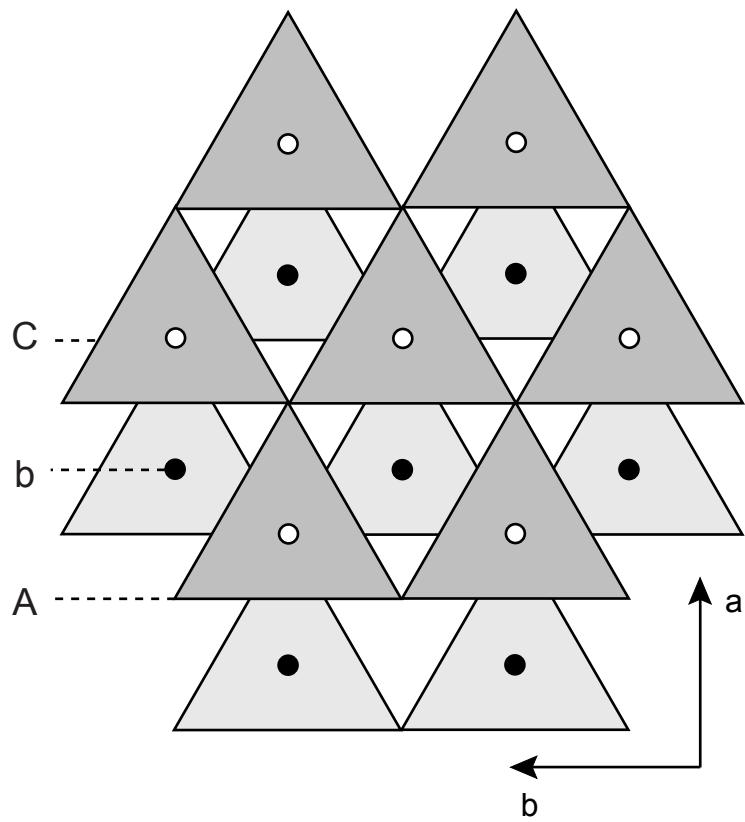
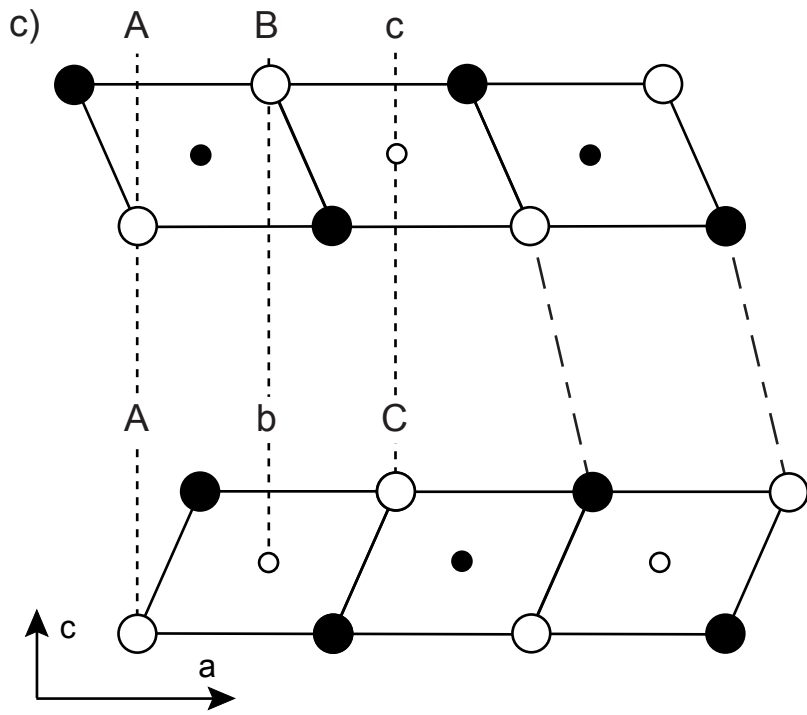
Polytype	$1O$	$1M_1$	$1M_2$	$2O_1/2O_2$
$d(hkl)$	Hkl	hkl	Hkl	hkl
2.590	200			200
2.571		20-1	201	
2.548				201/20-1
2.517		200	200	
2.497	110			110
2.480		110	110	
2.459				111/11-1
2.433	201/20-1			202/20-2
2.431		11-1	111	
2.356	111/11-1			112/11-2
2.329		20-2	202	
2.272				203/20-3
2.261		111	11-1	
2.214		201	20-1	
2.209				113/11-3
2.154		11-2	112	
2.092	202/20-2			204/20-4
2.042	112/11-2			114/11-4
1.972		20-3	203	
1.930		112	11-2	
1.914				205/20-5
1.875				115/11-5
1.857		202	20-2	
1.821		11-3	113	
1.747	203/20-3			206/20-6
1.718	113/11-3			116/11-6
1.645		20-4	204	
1.621		113	11-3	
1.597				207/20-7
1.574				117/11-7
1.551		203	20-3	
1.530		11-4	114	
1.477	310	31-1	311	310
1.469				311/31-1
1.464	204/20-4			208/20-8
1.447	114/11-4			118/11-8
1.446	311/31-1	310/31-2	310/312	312/31-2
1.425	020	020	020	020
1.418				021/02-1
1.410				313/31-3
1.397	021/02-1	021/02-1	021/02-1	022/02-2
1.384		20-5	205	
1.370		114	11-4	
1.365				023/02-3
1.364	312/31-2	311	31-1	314/31-4
1.363		31-3	313	
1.347				209/20-9
1.334				119/11-9
1.322	022/02-2	022/02-2	022/02-2	024/02-4
1.312		204	20-4	
1.310				315/31-5
1.299		11-5	115	
1.274				025/02-5
1.253	313/31-3	312/31-4	314/31-2	316/31-6
1.245	205/20-5			20.10/20.-10
1.234	115/11-5			11.10/11.-10

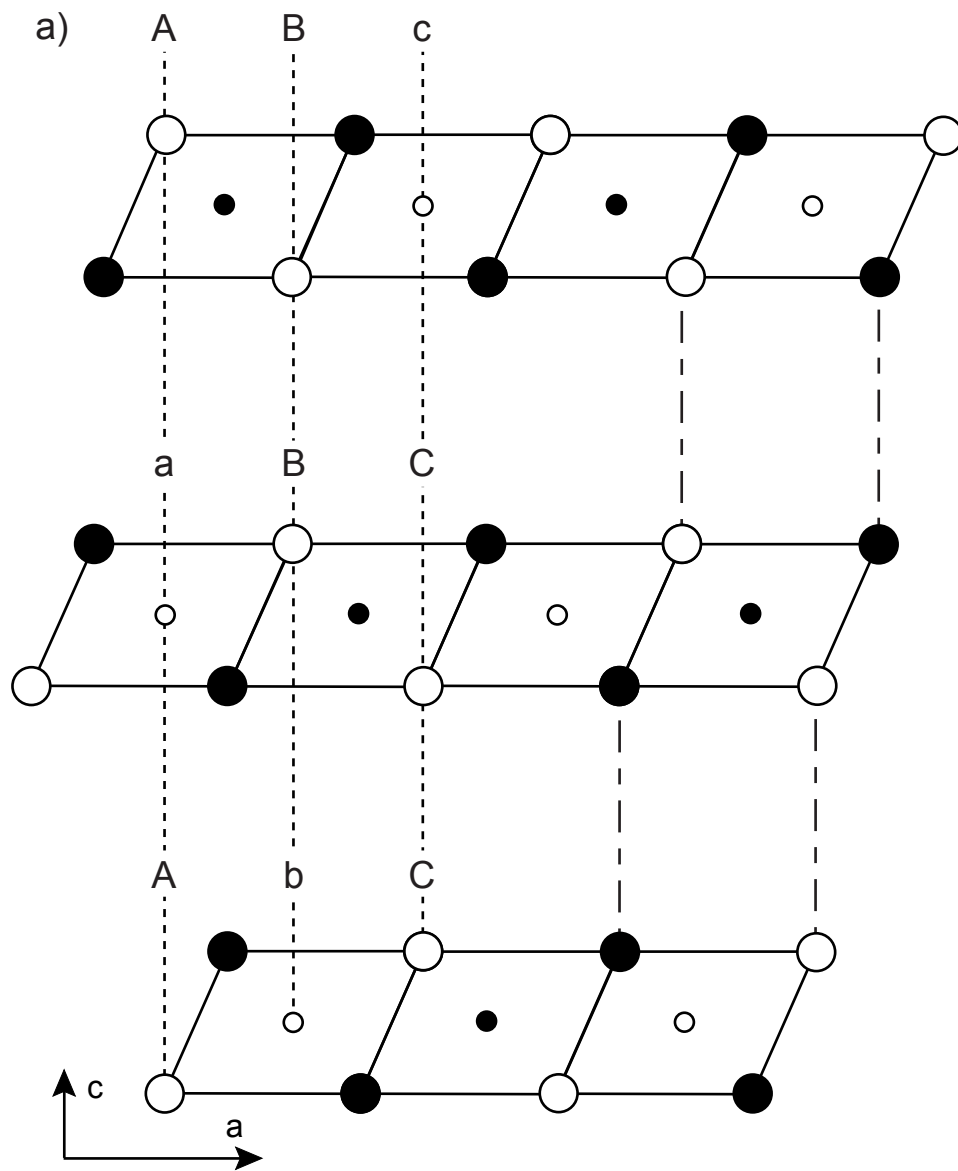
1.221	023/02-3	023/02-3	023/02-3	026/02-6
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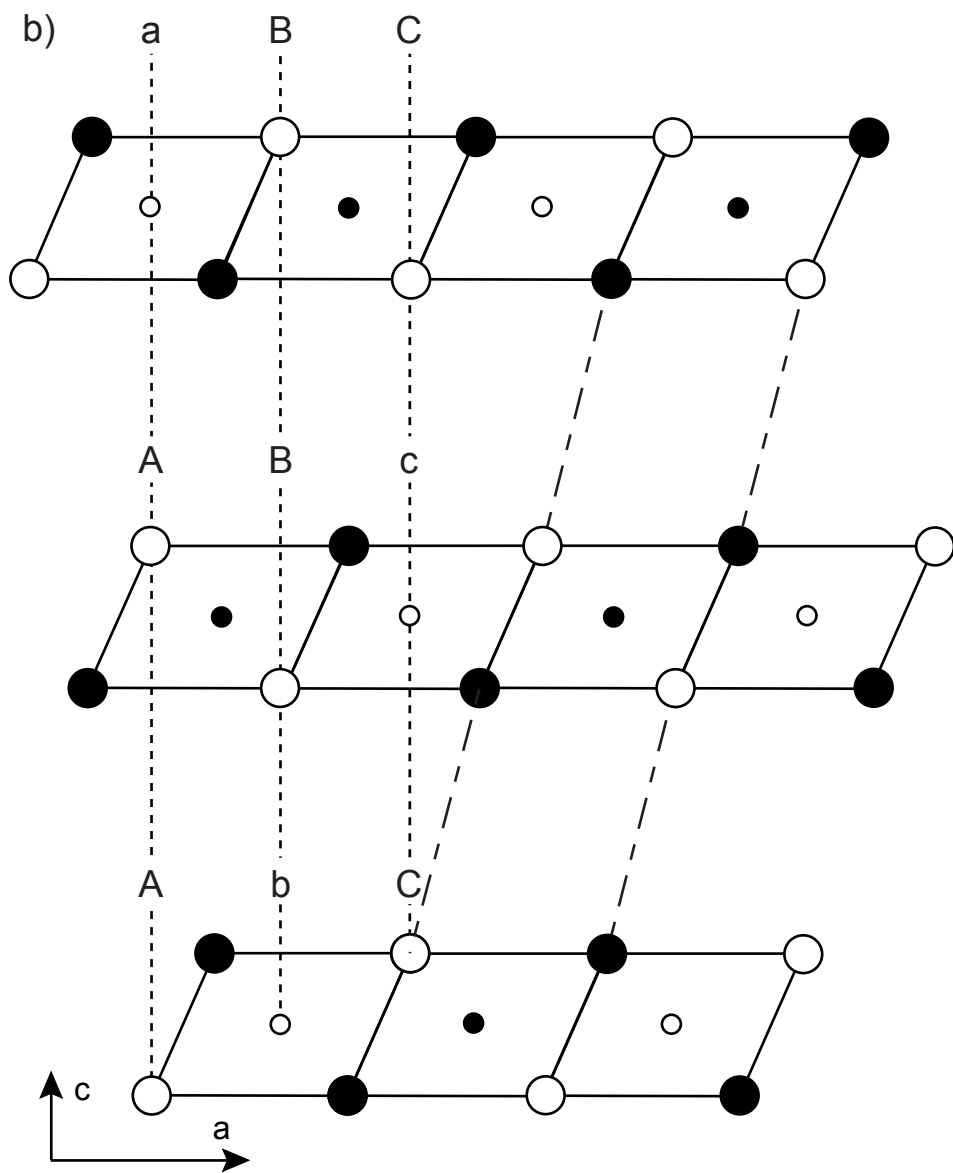
Notes: a and b unit-cell parameters are 5.180 and 2.850 Å, respectively. The minimum periodicity along the \mathbf{c}^* axis is 7.10 Å for all polytypes. The β angle is 103.65 and 76.35° for $1M_1$ and $1M_2$ polytypes, respectively.

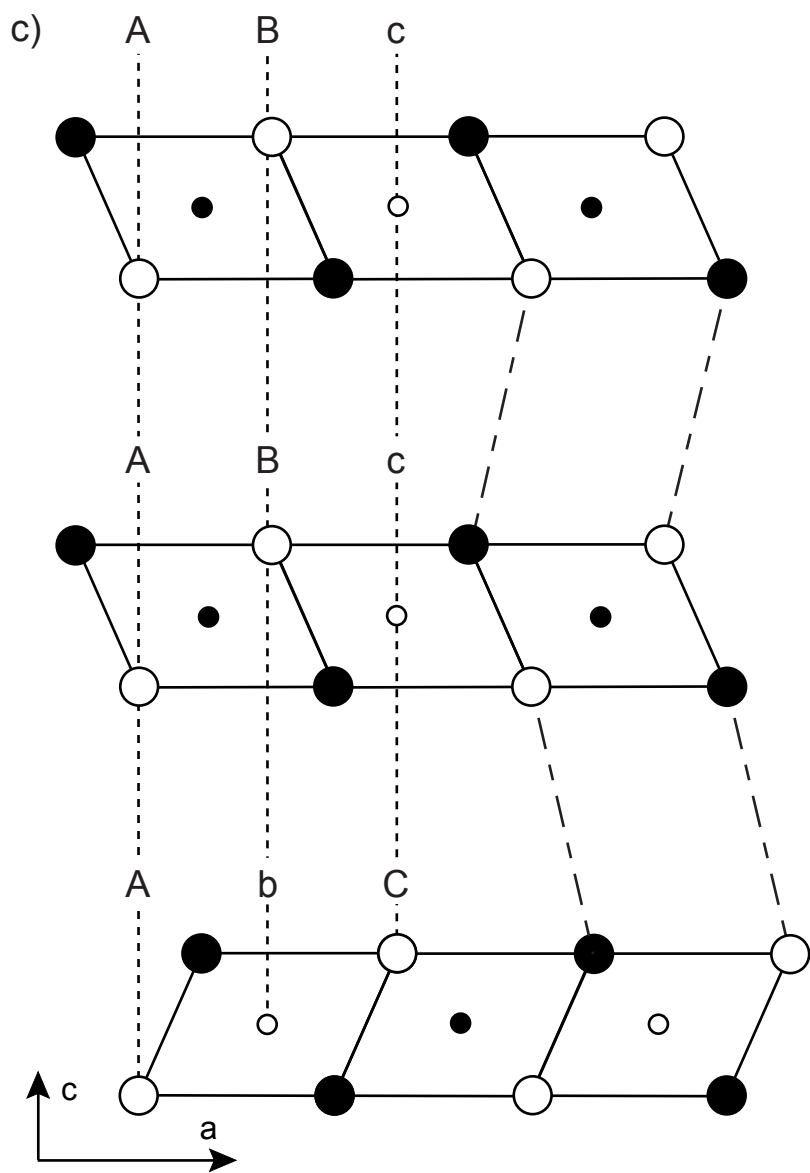


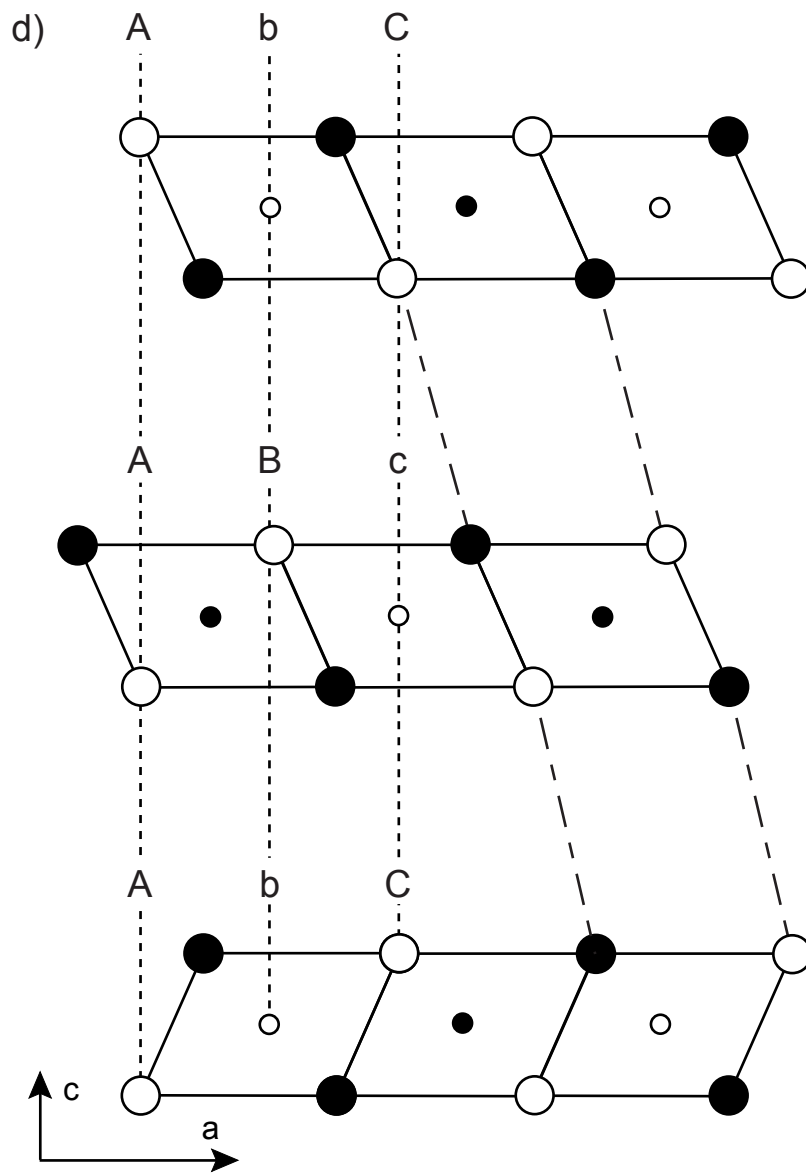




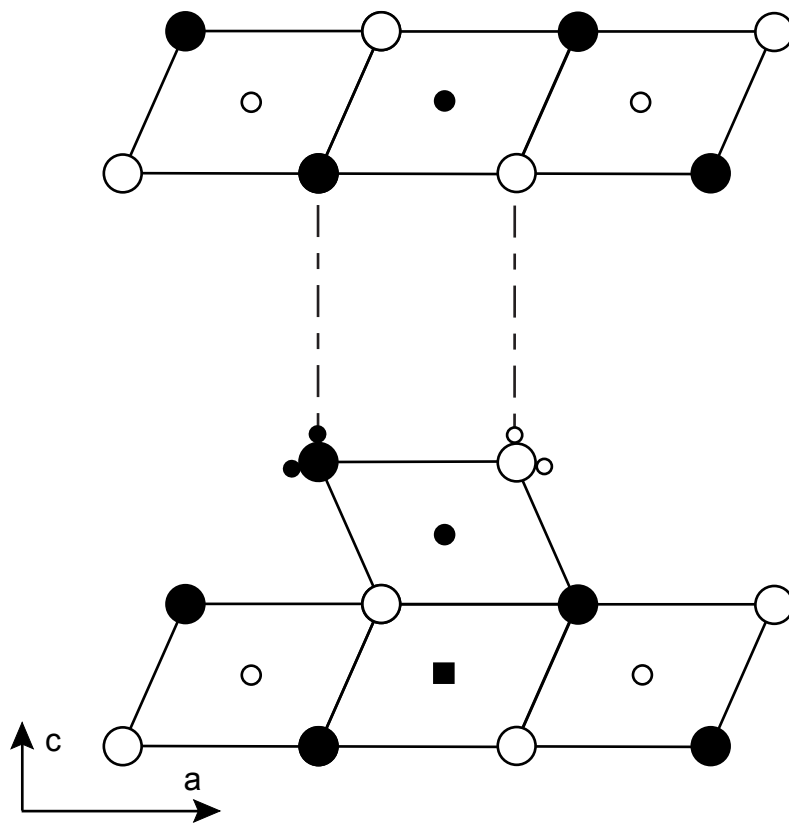




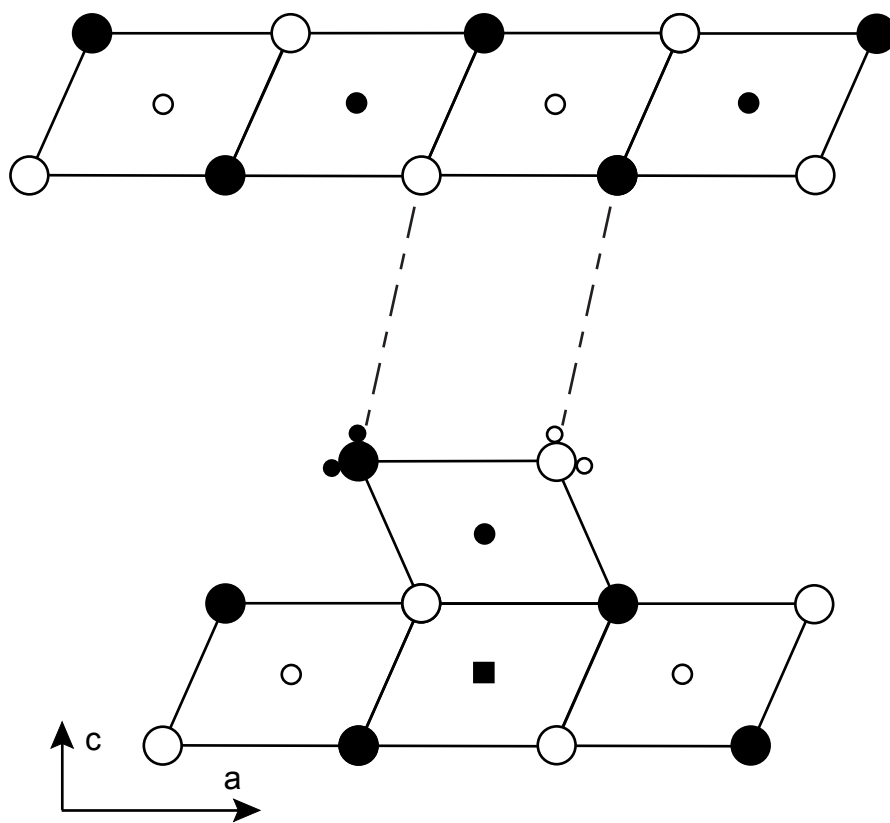




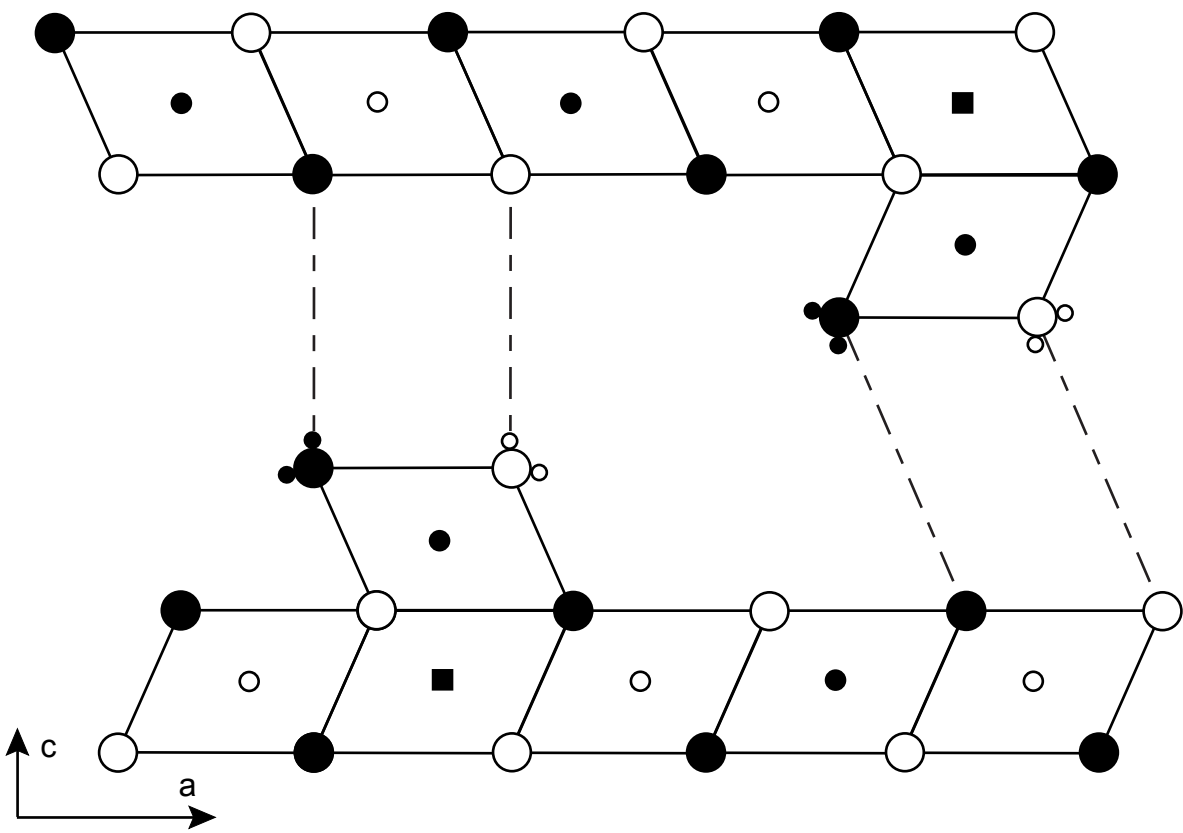
a)



b)



c)



d)

