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The astrophyllite supergroup: nomenclature and classification

Elena Sokolova^{1,*}, Fernando Cámara², Frank C. Hawthorne¹ and Marco E. Ciriotti³

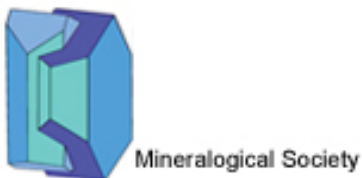
¹ Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

² Dipartimento di Scienze della Terra, Università degli Studi di Torino, via Valperga Caluso 35, I-10125 Torino, Italy

³ AMI – Associazione Micromineralogica Italiana, via San Pietro 55, I-10073 Devesi-Ciriè, Italy

* Corresponding author, e-mail: elena_sokolova@umanitoba.ca

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18 **Abstract**

19 Here we report a nomenclature and classification for the astrophyllite-supergroup minerals. The
20 HOH block is the main structural unit in all astrophyllite-supergroup structures; it consists of
21 three H–O–H sheets where the T_4O_{12} astrophyllite ribbons occur in the H sheets. In each
22 structure, HOH blocks alternate with **I** (Intermediate) blocks along [001]. The twelve minerals of
23 the astrophyllite supergroup are divided into three groups basing on (1) the type of self-linkage
24 of HOH blocks, i.e. (a) HOH blocks link directly where they share common vertices of D
25 octahedra, or (b) HOH blocks do not link directly; and (2) the dominant cation of the O sheet
26 (the C group: C_7 a.p.f.u.). In the astrophyllite group (HOH blocks connect via $D-X^P_D-D$ bridges,
27 Fe^{2+} is dominant at C_7), there are six minerals: astrophyllite, niobophyllite, zircophyllite,
28 tarbagataite, nalivkinite and bulgakite. In the kupletskite group (HOH blocks connect via $D-X^P_D-$
29 D bridges, Mn^{2+} is dominant at C_7), there are three minerals: kupletskite, niobokupletskite and
30 kupletskite-(Cs). In the devitoite group (HOH blocks do not connect via $D-X^P_D-D$ bridges), there
31 are three minerals: devitoite, sveinbergeite and lobanovite. The general formula for the
32 astrophyllite-supergroup minerals is of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn}W_{A2}$, where C
33 [cations at the $M(1-4)$ sites in the O sheet] = Fe^{2+} , Mn, Na, Mg, Zn, Fe^{3+} , Ca, Zr, Li; D (cations in
34 the H sheets) = $^{[6,5]}Ti$, Nb, Zr, Sn^{4+} , $^{[5]}Fe^{3+}$, Mg, Al; T = Si, minor Al; $A_{2p}B_rIW_{A2}$ (**I** block) where $p =$
35 1,2; $r = 1,2$; A = K, Cs, Ba, H_2O , Li, Rb, Pb^{2+} , Na, \square ; B = Na, Ca, Ba, H_2O , \square ; I represents the
36 composition of the central part of the **I** block, excluding peripheral layers of the form $A_{2p}B_rW_{A2}$,
37 e.g. $(PO_4)_2(CO_3)$ (devitoite); $X^O_D = O$; $X^O_A = OH, F$; $X^P_D = F, O, OH, H_2O, \square$, where $n = 0, 1, 2$
38 for $(X^P_D)_n$; $W_A = H_2O, \square$.

39

40 *Keywords:* astrophyllite supergroup, nomenclature, classification, ideal formula, astrophyllite,
41 kupletskite and devitoite groups

42

43 Introduction

44 The Nomenclature Voting proposal 15-B – “*Magnesioastrophyllite*” validated under the name
45 “*lobanovite*”, and *astrophyllite* supergroup classification – has been approved by the CNMNC-
46 IMA (in accord with Mills *et al.*, 2009) with the two conclusions: (1) “*Magnesioastrophyllite*” has
47 been validated under the name lobanovite, $K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$; (2) According
48 to the new classification scheme, the *astrophyllite* supergroup is now divided in three groups:
49 the *astrophyllite* group, the *kupletskite* group, and the *devitoite* group. Following the above
50 decision, the formal description of the lobanovite has been reported by Sokolova *et al.* (2015). In
51 this paper, we address the second part of the Voting proposal 15-B and report the nomenclature
52 and classification of the *astrophyllite* supergroup based on the work of Sokolova (2012).

53 Twelve minerals of the *astrophyllite* supergroup are listed in Table 1. The HOH block is
54 the main structural unit in all *astrophyllite*-supergroup structures; it consists of a central O sheet
55 between two adjacent H sheets where the T_4O_{12} *astrophyllite* ribbons occur in the H sheets. In
56 each structure, HOH blocks alternate with I (Intermediate) blocks along [001]. They are divided
57 into three groups based on (1) the type of self-linkage between HOH blocks, i.e. (a) HOH blocks
58 link directly where they share common vertices of D octahedra, or (b) HOH blocks do not link
59 directly; and (2) the dominant cation of the O sheet (the C group: C_7 a.p.f.u.). These three
60 groups are as follows:

61 *Astrophyllite* group: HOH blocks connect via $D-X^P_D-D$ bridges, Fe^{2+} is dominant at C_7 ;

62 *Kupletskite* group: HOH blocks connect via $D-X^P_D-D$ bridges, Mn^{2+} is dominant at C_7 ;

63 *Devitoite* group: HOH blocks do not connect via $D-X^P_D-D$ bridges.

64

65 Background

66 For many years, the *astrophyllite*-group minerals have been divided into two main subgroups on
67 the basis of the dominance of Fe^{2+} (*astrophyllite*; Weibye, 1848) or Mn^{2+} (*kupletskite*; Semenov,
68 1956) at the octahedrally coordinated sites in the O (Octahedral) sheet in the structure. The

69 general crystal chemistry of the astrophyllite-group minerals was considered by Belov (1963,
70 1976), Piilonen *et al.* (2003a,b) and Cámara *et al.* (2010). All references pertinent to work on the
71 general crystal chemistry of the astrophyllite-group minerals prior to 2012 are given in Sokolova
72 (2012). Sokolova (2012) developed a structural hierarchy for the astrophyllite group and showed
73 that (1) In the astrophyllite group, there are two topologically distinct types of structures based
74 on the type of self-linkage of HOH blocks: (1) HOH blocks link directly where they share
75 common vertices of D octahedra, HOH blocks connect via $D-X_D^P-D$ bridges, and (2) HOH
76 blocks do not link directly via polyhedra of the H sheets. For the description of atom
77 arrangements in the intermediate space between adjacent HOH blocks the astrophyllite-group
78 structures, Sokolova (2012) introduced the **I** (Intermediate) block [by analogy with the **I** block in
79 TS-block (Titanium Silicate) structures, Sokolova, 2006]. She considered nine minerals of the
80 astrophyllite group [astrophyllite, niobophyllite, zircophyllite, tarbagataite, nalivkinite, kupletskite,
81 niobokupletskite, kupletskite-(Cs) and lobanovite (Table 1)], suggested extending the
82 astrophyllite group to include devitoite and sveinbergeite (Table 1), and wrote the general
83 formula of these minerals in the form $A_{2p}B_rC_7D_2(T_4O_{12})_2I X_{D2}^O X_{A4}^O X_{Dn}^P$, where C and D are
84 cations of the O and H sheets, $C = [^{6}](Fe^{2+}, Mn, Fe^{3+}, Na, Mg \text{ or } Zn)$ at the $M(1-4)$ sites; $D =$
85 $[^{6,5}](Ti, Nb, Zr, Fe^{3+})$; $T = Si, \text{ minor Al}$; $A_{2p}B_rI$ is the composition of the **I** block where $p = 1,2$; $r =$
86 $1,2$; $A = K, Cs, Li, Ba, H_2O, \square$; $B = Na, Ca, Ba, H_2O, \square$; I represents the composition of the
87 central part of the **I** block, excluding peripheral layers of the form A_2B ; $X = X_{D2}^O X_{A4}^O X_{Dn}^P = O,$
88 $OH, F \text{ and } H_2O$; $n = 0, 1, 2$.

89

90 **New data**

91 Sokolova (2012) listed zircophyllite [described by Kapustin (1972) from Tuva, Russia; $Mn >$
92 Fe^{2+}] as a member of the kupletskite group. However Kapustin (1972) called zircophyllite a
93 *zirconium analogue of astrophyllite* and wrote its empirical formula as follows:

94 $(K_{1.70}Na_{0.71}Ca_{0.24}Mn_{0.35}Sr_{0.02})_{\Sigma 3}(Fe^{2+}_{3.57}Mn_{3.43})_{\Sigma 7}(Zr_{1.58}Nb_{0.25}Ti_{0.17})_{\Sigma 2}(Si_{7.76}Ti_{0.24})_{\Sigma 8}[O_{26.84}$

95 $(\text{OH})_{3.26}\text{F}_{0.90}]_{\Sigma 31}(\text{H}_2\text{O})_{0.9}$, where the composition of the O sheet is $\text{C}_7 = (\text{Fe}^{2+}_{3.57}\text{Mn}_{3.43})_{\Sigma 7}$, i.e. Fe^{2+}
96 $> \text{Mn}$. Following the original definition of zircophyllite, we place zircophyllite in the astrophyllite
97 group (in accord with the nomenclature voting proposal 15-B). Here (Tables 1–3), we report
98 some crystallographic data based on the structure refinement of zircophyllite from Mont Saint-
99 Hilaire, Québec, Canada (Sokolova *et al.*, in preparation).

100 Agakhanov *et al.* (2014, 2015) described a new astrophyllite-group mineral bulgakite,
101 $\text{Li}_2(\text{Ca},\text{Na})\text{Fe}^{2+}_7\text{Ti}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_4(\text{O},\text{F})(\text{H}_2\text{O})_2$, a Ca-analogue of nalivkinite, and revised the
102 crystal structure and chemical formula of nalivkinite: $\text{Li}_2\text{NaFe}^{2+}_7\text{Ti}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_4\text{F}(\text{H}_2\text{O})_2$
103 (Agakhanov *et al.*, 2008; Uvarova *et al.*, 2008) (Table 1). Refinement of the bulgakite and
104 nalivkinite structures resulted in the location of H_2O groups at the *W* site in the I block. An H_2O
105 group at the *W* site is a necessary ligand to complete the coordination of the cation at the *A*(2)
106 site, where *A*(2) and *A*(1) are subsites of the *A* site. Hence the number of H_2O groups at the *W*
107 site must equal the number of cations at the *A*(2) site. The presence of H_2O groups in the
108 bulgakite and nalivkinite structures was confirmed by infrared spectroscopy (Agakhanov *et al.*,
109 2014, 2015). Revision of the topology of the *A*(2) site in the astrophyllite-supergroup minerals
110 required revision of the general formula for the astrophyllite-type structures (Sokolova, 2012),
111 and Agakhanov *et al.* (2015) suggested writing the general formula as $\text{A}_{2p}\text{B}_r\text{C}_7\text{D}_2(\text{T}_4\text{O}_{12})_2\text{I}$
112 $\text{X}^{\text{O}}_{\text{D}_2}\text{X}^{\text{O}}_{\text{A}_4}\text{X}^{\text{P}}_{\text{D}_n}\text{W}_{\text{A}_2}$.

113

114 **The HOH block in the astrophyllite-supergroup structures**

115 *General topology*

116 The HOH block is the main structural unit in all astrophyllite-supergroup structures. In the crystal
117 structure of astrophyllite, the M octahedra (C-group atoms) share edges to form an O
118 (Octahedral) sheet (Fig. 1a). The characteristic feature of the astrophyllite structure is the T_4O_{12}
119 astrophyllite ribbon that extends along [100] (Fig. 1a). The astrophyllite ribbons share common
120 vertices with [6,5]-coordinated D polyhedra to form the H (Heteropolyhedral) sheet (Fig. 1a).

121 Two T_2O_7 groups oriented perpendicular to [100] constitute the minimal repeat of the
122 astrophyllite ribbon which defines the a cell parameter of ~ 5.4 Å (Fig. 1a, Table 1). The H and O
123 sheets are characterized by a minimal planar cell with $a \sim 5.4$, $b \sim 11.9$ Å, $\alpha \wedge \beta \sim 103^\circ$ (Table 1,
124 Fig. 1a). Two H sheets and a central O sheet form the HOH block (Fig. 1b). The linkage of O
125 and H sheets is identical in all astrophyllite-supergroup structures, except for lobanovite
126 (Sokolova, 2012).

127

128 *Cation sites*

129 In the O sheet of the crystal structure of astrophyllite, there are four M sites per minimal cell,
130 $2M(1) + 2M(2) + 2M(3) + 1M(4)$, which give a total of $M_7 (= C_7)$ a.p.f.u. (atoms per formula unit)
131 (Fig. 1a). In the astrophyllite-supergroup minerals, the dominant cations at the M sites are
132 mainly Fe^{2+} and Mn^{2+} (Table 2). Other dominant M cations are rare: Mg at the $M(4)$ site and Na
133 at the $M(1)$ site in lobanovite, and Zn at the $M(4)$ site in kupletskite-(Cs) and Zn-rich astrophyllite
134 (Piilonen *et al.*, 2006). In the H sheet, there are four T sites, mainly occupied by Si with minor Al
135 (Piilonen *et al.*, 2003a,b). There is one D site which gives D_2 a.p.f.u. The dominant cation at the
136 D site is mainly $^{[6,5]}Ti$; $^{[6]}Nb$ (niobophyllite and niobokupletskite), $^{[6]}Zr$ (zircophyllite) and $^{[5]}Fe^{3+}$
137 (devitoite) are less common (Table 2). In the minimal cell, there are one D site and one minimal
138 repeat of the astrophyllite ribbon (Fig. 1a), and the ideal composition of the H sheet is DT_4
139 a.p.f.u. The ideal cation composition of the HOH layer is C_7D_2 a.p.f.u., T atoms are considered
140 as part of the complex anion $(T_4O_{12})^{8-}_2$ in the anion part of the structure.

141

142 *Anion sites*

143 In the HOH block, O atoms which tetrahedrally coordinate T atoms in two H sheets sum to the
144 24 O a.p.f.u. The D polyhedra of two H sheets share two X^O_D anions with M octahedra of the O
145 sheet (for X^O , the O superscript defines anions of the O sheet) (Figs. 1a,b), the X^O_D site is
146 occupied by an O atom, giving $(X^O_D)_2 = O_2$ a.p.f.u. There are four anions p.f.u. at the X^O_A sites

147 which occur just under the interstitial A sites (Fig. 1a) and they are occupied by monovalent
148 anions, mainly OH groups and minor F, summing to ideally $(X^{\text{O}}_{\text{A}})_4 = (\text{OH})_4$ p.f.u. (Table 2). The
149 X^{P}_{D} site is occupied by an anion at the periphery of the HOH block ($P = \textit{peripheral}$) where the D
150 cation is [6]-coordinated (Figs. 1a,b). The X^{P}_{D} site is occupied by F, OH, O, H₂O and □, and in a
151 structure, $X^{\text{P}}_{\text{D}} = 0, 1$ or 2 p.f.u. (Table 2). The anion composition of the HOH block is
152 $(\text{T}_4\text{O}_{12})_2\text{X}^{\text{O}}_{\text{D}2}\text{X}^{\text{O}}_{\text{A}4}\text{X}^{\text{P}}_{\text{D}n}$, where $n = 0, 1, 2$. The number of X^{P}_{D} anions depends on the coordination
153 number of the D cation (see above) and the type of self-linkage between the HOH blocks (see
154 below).

155

156 *General formula of the HOH block*

157 The composition of the HOH block can be written as the sum of the cation and anion sites: C_7D_2
158 $+ (\text{T}_4\text{O}_{12})_2\text{X}^{\text{O}}_{\text{D}2}\text{X}^{\text{O}}_{\text{A}4}\text{X}^{\text{P}}_{\text{D}n} = \text{C}_7\text{D}_2(\text{T}_4\text{O}_{12})_2\text{X}^{\text{O}}_{\text{D}2}\text{X}^{\text{O}}_{\text{A}4}\text{X}^{\text{P}}_{\text{D}n}$, where C and D are cations of the O and H
159 sheets: C = ^[6](Fe²⁺, Mn, Na, Mg, Zn, Fe³⁺, Ca, Zr, Li); D = ^[6,5]Ti, Nb, Zr, Sn⁴⁺, ^[5]Fe³⁺, Mg, Al; T =
160 Si, minor Al; X are anions: X^{O}_{D} anions coordinate three M cations in the O sheet and a D cation
161 in the H sheet, i.e. O; X^{O}_{A} (monovalent anions) coordinate three M cations in the O sheet, i.e.
162 OH, F; and X^{P}_{D} are peripheral anions of the D cations, i.e. $X^{\text{P}}_{\text{D}} = \text{F, O, OH, H}_2\text{O, } \square$, where $n = 0,$
163 $1, 2$ for $(X^{\text{P}}_{\text{D}})_n$. For astrophyllite, the ideal composition of the HOH block is
164 $[\text{Fe}^{2+}_7\text{Ti}_2(\text{Si}_4\text{O}_{12})_2\text{O}_2(\text{OH})_4\text{F}]^{3-}$ (Table 1).

165

166 **Self-linkage of HOH blocks: the I (Intermediate) block**

167 Following Sokolova (2012), we divide all structures of the astrophyllite-supergroup minerals into
168 two types on the basis of the type of self-linkage between the HOH blocks: (1) HOH blocks link
169 directly where they share common vertices of D octahedra, and (2) HOH blocks do not link
170 directly.

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173 *Type 1: HOH blocks link directly*

174 HOH blocks link directly where they share common vertices of D octahedra, X_D^P anions, *i.e.*
175 HOH blocks connect via $D-X_D^P-D$ bridges (e.g. Ti–F–Ti in astrophyllite) (Fig. 2a). This type of
176 self-linkage of HOH blocks occurs in astrophyllite, niobophyllite, zircophyllite, tarbagataite,
177 nalivkinite, bulgakite, kupletskite, niobokupletskite and kupletskite-(Cs). These type-1 structures
178 belong to the *astrophyllite* structure type with space group $P\bar{1}$ (or space group *C2/c* in
179 kupletskite-2*M*, Table 1). In the space between two HOH blocks, cations at two interstitial sites,
180 *A* and *B*, constitute a layer of the form A_2B in the **I** (*Intermediate*) block ($m = 1$, where m denotes
181 number of cation layers in the **I** block). In astrophyllite, niobophyllite, kupletskite and
182 niobokupletskite, the dominant cations at the *A* and *B* sites are K and Na, respectively (Figs.
183 2a,b); other dominant cations are as follows: ^ACs [kupletskite-(Cs)] and ^BCa (tarbagataite)
184 (Tables 2, 3). In bulgakite and nalivkinite, the *A* site is split into two subsites, *A*(1) and *A*(2),
185 which are occupied mainly by K and Li, respectively, where $\text{Li} > \text{K}$ (Fig. 3a). Hence we write the
186 ideal composition of the *A* site as Li_2 a.p.f.u. (Tables 1-3). Li and K at the *A*(1) and *A*(2) sites
187 occur at short distances and must be locally mutually exclusive. Figure 3b gives a short-range
188 order model for $\text{Li} + \text{H}_2\text{O}$ and K in the structure of nalivkinite. The large K cation at the *A*(1) site
189 is coordinated by thirteen O atoms, and a smaller Li cation at the *A*(2) site is coordinated by five
190 O atoms and an H_2O group at the *W* site. The analogous arrangement of $\text{Na} + \text{H}_2\text{O}$ and K has
191 been reported for nafertisite, $\text{Na}_3\text{Fe}^{2+}_{10}\text{Ti}_2(\text{Si}_6\text{O}_{17})_2\text{O}_2(\text{OH})_6\text{F}(\text{H}_2\text{O})_2$ (Cámara *et al.*, 2014).

192 Based on the dominant cation of the O sheet, we divide the nine minerals listed above
193 into two groups (Tables 1–3):

194 **Astrophyllite group:** HOH blocks connect via $D-X_D^P-D$ bridges, Fe^{2+} is dominant at C_7 ;

195 **Kupletskite group:** HOH blocks connect via $D-X_D^P-D$ bridges, Mn^{2+} is dominant at C_7 ;

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199 *Type 2: HOH blocks do not link directly*

200 HOH blocks do not link directly via polyhedra of the H sheets, i.e. HOH blocks do not connect
201 via $D-X_D^P-D$ bridges. The type-2 structure occurs in lobanovite, sveinbergeite and devitoite. In
202 lobanovite, with [5]-coordinated Ti in the H sheet, HOH layers connect *via* K at the A site and Na
203 at the B site, which constitute an I block ($m = 1$) of the form A_2B (Fig. 4a). In sveinbergeite, the I
204 block ($m = 1$) is characterized by both cation and anion disorder (Fig. 4b) (Khomyakov *et al.*,
205 2011). The A site is occupied mainly by H_2O groups, giving ideally $(H_2O)_2$ p.f.u. (Table 2). The B
206 site splits into the B(1) and B(2) sites which are separated by $< 1 \text{ \AA}$ and are occupied by
207 $(Ca, \square)_2$ and $(H_2O, \square)_2$, giving ideally $[Ca(H_2O)]$ p.f.u. Short-range order of Ca and H_2O at the
208 B(1,2) sites affects the composition of the X_D^P site, ideally $[(OH)(H_2O)]$ p.f.u. The ideal
209 composition of the I block in sveinbergeite is the sum of the constituents at the A (2 a.p.f.u.) and
210 B (2 a.p.f.u.) sites: $(H_2O)_2 + [Ca(H_2O)] = Ca(H_2O)_3$ p.f.u. Devitoite is the only known mineral with
211 the astrophyllite-type HOH block where [5]-coordinated D sites are occupied by Fe^{3+} (Kampf *et*
212 *al.*, 2010) (Tables 1–3). In the devitoite structure, HOH layers alternate with I blocks along [001]
213 (Fig. 4c). In the I block, there are three layers of cations ($m = 3$). Two peripheral layers of the I
214 block are topologically identical to the layer of the form A_2B in astrophyllite (Fig. 2a). In the
215 peripheral layer of the I block in devitoite, the A and B sites are occupied by Ba (Fig. 4c), giving
216 $Ba_2 (A_2) + Ba (B) = Ba_3$ a.p.f.u. The central layer of the I block in devitoite is occupied by PO_4
217 tetrahedra and CO_3 groups, giving $(PO_4)_2(CO_3)$ p.f.u. The ideal composition of the I block in
218 devitoite is the sum of the two peripheral layers and the central layer: $2 \times Ba_3 + (PO_4)_2(CO_3) =$
219 $Ba_6(PO_4)_2(CO_3)$ p.f.u.

220 Taking into account that devitoite (Kampf *et al.*, 2010) was described prior to
221 sveinbergeite (Khomyakov *et al.*, 2011) and lobanovite (Sokolova *et al.*, 2015), we list devitoite,
222 sveinbergeite and lobanovite in the:

223 Devitoite group: HOH blocks do not connect via $D-X_D^P-D$ bridges.

224

225 **General formula for the astrophyllite-supergroup minerals**

226 *The I block*

227 We write the composition of the I block in the astrophyllite-supergroup minerals as $A_{2p}B_rIW_{A_2}$,
228 where p is the number of layers of the form $A_2BW_{A_2}$ and is equal to 1, 2; r = 1, 2; A = K, Cs, Li,
229 Ba, H₂O, □; B = Na, Ca, Ba, H₂O, □; W = H₂O, □; I represents the composition of the central
230 part of the I block, excluding peripheral layers of the form A_2B and $A_2BW_{A_2}$, i.e. (PO₄)₂(CO₃) in
231 devitoite.

232 We combine general formulae for the HOH block, $C_7D_2(T_4O_{12})_2X^O_{D_2}X^O_{A_4}X^P_{D_n}$, and the I
233 block, $A_{2p}B_rIW_{A_2}$, into a general formula for the astrophyllite-supergroup minerals:

234
$$A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D_2}X^O_{A_4}X^P_{D_n}W_{A_2},$$

235 where C [cations at the M(1–4) sites in the O sheet] = Fe²⁺, Mn, Na, Mg, Zn, Fe³⁺, Ca, Zr, Li; D
236 (cations in the H sheets) = ^[6,5]Ti, Nb, Zr, Sn⁴⁺, ^[5]Fe³⁺, Mg, Al; T = Si, minor Al; $A_{2p}B_rIW_{A_2}$ (I
237 block) where p = 1,2; r = 1,2; A = K, Cs, Ba, H₂O, Li, Rb, Pb²⁺, Na, □; B = Na, Ca, Ba, H₂O, □; I
238 represents the composition of the central part of the I block, excluding peripheral layers of the
239 form $A_{2p}B_rW_{A_2}$, e.g. (PO₄)₂(CO₃) (devitoite); X^O_D = O; X^O_A = OH, F; X^P_D = F, O, OH, H₂O, □,
240 where n = 0, 1, 2 for (X^P_D)_n; W_A = H₂O, □.

241

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329

330 **Figure captions**

331 Fig. 1. The HOH block in the crystal structure of astrophyllite [atom coordinates of Sn-rich
332 astrophyllite are taken from Cámara *et al.* (2010)]: (a) the O sheet and H sheets viewed
333 perpendicular to the plane of the sheets, (b) the HOH block viewed down [100]. The M(1), M(2),
334 M(3) and M(4) octahedra in the O sheet (C-group of atoms) are labelled 1, 2, 3 and 4. The Mn-
335 and Fe²⁺-dominant octahedra are magenta and green. The T(=Si) tetrahedra and D(=Ti,Nb)
336 octahedra are orange and pale yellow. The OH groups and F atoms at the X_A^O and X_D^P sites are
337 shown as small red and yellow spheres. In (a), the unit cell is shown in red.

338

339 Fig. 2. Astrophyllite: (a) general view of the crystal structure and (b) the position of the A and B
340 sites with regard to the H sheet. Legend as in Fig. 1; K and Na atoms at the A and B
341 sites are shown as green and navy blue spheres. The position of the intermediate layer (m = 1, where m
342 is a number of intermediate layers) is shown by a turquoise line.

343

344 Fig. 3. Nalivkinite: (a) general view of the crystal structure and (b) the short-range order of K
345 [A(1) site] and Li [A(2) site] plus H₂O [W site] in the I block. Legend as in Fig. 2; K and Li atoms
346 at the A(1) and A(2) sites are shown as green and larger yellow spheres, H₂O groups are shown
347 as larger red spheres.

348

349 Fig. 4. General view of the crystal structures of (a) lobanovite, (b) sveinbergeite and (c)
350 devitoite. Legend as in Fig. 2; the Mg and Na octahedra are pink and navy blue, the [5]-
351 coordinated Fe³⁺ polyhedra are yellow; Ca (at the B site in sveinbergeite) and Ba (at the A and
352 B sites in devitoite) atoms and H₂O groups (at the A, B and X_D^P sites in sveinbergeite) are
353 shown as pink, raspberry and red spheres, respectively; PO₄ tetrahedra are purple, CO₃ groups
354 are shown as small black spheres (C atoms) bonded to small red spheres (O atoms of CO₃

355 groups). The positions of the intermediate layer in lobanovite and sveinbergeite and the three
356 intermediate layers in devitoite are shown by turquoise lines.

Table 1. Ideal formulae* and unit-cell parameters for the astrophyllite-supergroup minerals.

Mineral	Endmember formula	a (Å) α (°)	b (Å) β (°)	c (Å) γ (°)	Space group	Z	Ref.
Astrophyllite group HOH blocks connect via D-X ^P _D -D bridges, Fe ²⁺ is dominant at C ₇							
Astrophyllite	K ₂ NaFe ²⁺ ₇ Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ F	5.3866 113.019	11.8821 94.578	11.6794 103.120	P $\bar{1}$	1	(1,2)
Niobophyllite	K ₂ NaFe ²⁺ ₇ (Nb,Ti)(Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ (O,F)	5.4022 112.990	11.8844 94.588	11.6717 103.166	P $\bar{1}$	1	(3,2)
Zircophyllite	K ₂ NaFe ²⁺ ₇ Zr ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ F	5.447 112.950	11.966 94.690	11.789 103.116	P $\bar{1}$	1	(4,5)
Tarbagataite	(K□)CaFe ²⁺ ₇ Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₅	5.3868 112.978	11.9141 94.641	11.7171 103.189	P $\bar{1}$	1	(6)
Nalivkinite	Li ₂ NaFe ²⁺ ₇ Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ F(H ₂ O) ₂	5.374 113.360	11.948 94.538	11.676 103.01	P $\bar{1}$	1	(7,8)
Bulgakite	Li ₂ (Ca,Na)Fe ²⁺ ₇ Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ (O,F)(H ₂ O) ₂	5.374 113.457	11.965 94.533	11.65 103.08	P $\bar{1}$	1	(8)
Kupletskite group HOH blocks connect via D-X ^P _D -D bridges, Mn ²⁺ is dominant at C ₇							
Kupletskite-1A	K ₂ NaMn ₇ Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ F	5.3784 112.964	11.9085 94.697	11.7236 103.112	P $\bar{1}$	1	(9)
Kupletskite-2M	K ₂ NaMn ₇ Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ F	5.4022 95.246	23.226 95.246	21.1782 95.246	C2/c	4	(9)
Niobokupletskite	K ₂ NaMn ₇ (Nb,Ti)(Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ (O,F)	5.4303 112.927	11.924 94.750	11.747 103.175	P $\bar{1}$	1	(10)
Kupletskite-(Cs)	Cs ₂ NaMn ₇ Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ F	5.3850 113.117	11.9350 94.614	11.7793 103.075	P $\bar{1}$	1	(11,2)
Devitoite group HOH blocks do not connect via D-X ^P _D -D bridges							
Devitoite	Ba ₆ Fe ²⁺ ₇ Fe ³⁺ ₂ (Si ₄ O ₁₂) ₂ (PO ₄) ₂ (CO ₃)O ₂ (OH) ₄	5.3437 91.337	11.6726 96.757	14.680 103.233	P $\bar{1}$	1	(12)
Sveinbergeite	(H ₂ O) ₂ [Ca(H ₂ O)](Fe ²⁺ ₆ Fe ³⁺)Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄ [OH(H ₂ O)]	5.329 101.140	11.803 98.224	11.822 102.442	P $\bar{1}$	1	(13)
Lobanovite	K ₂ Na(Fe ²⁺ ₄ Mg ₂ Na)Ti ₂ (Si ₄ O ₁₂) ₂ O ₂ (OH) ₄	5.3327 99.615	23.1535 99.615	10.3775 99.615	C2/m	2	(14,15)

*The ideal formula is of the form A_{2p}B_rC₇D₂(T₄O₁₂)₂IX^O_{D2}X^O_{A4}X^P_{Dn}W_{A2} (see text);

References (description of a new mineral, the latest work on the structure): (1) Weibye (1848); (2) Cámara *et al.* (2010); (3) Nickel *et al.* (1964); (4) Kapustin (1972); (5) Sokolova *et al.* (in preparation); (6) Stepanov *et al.* (2012); (7) Agakhanov *et al.* (2008); (8) Agakhanov *et al.* (2015); (9) Piilonen *et al.* (2001); (10) Piilonen *et al.* (2000); (11) Yefimov *et al.* (1971); (12) Kampf *et al.* (2010); (13) Khomyakov *et al.* (2011); (14) Sokolova *et al.* (2015); (15) Sokolova and Cámara (2008).

Table 2. Cation and anion sites in the structures of the astrophyllite-supergroup minerals.

Mineral	HOH block								I (Intermediate) block		Ref.
	O sheet				2H sheets				rB	2W _A	
C ₇ :	2M(1)	2M(2)	2M(3)	M(4)	2X ^O _D	4X ^O _A	2D	nX ^P _D			pA ₂
Astrophyllite group											
Astrophyllite	Mn ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺	O ₂	(OH) ₄	Ti ₂	F	[¹²]K ₂	[¹⁰]Na	(1)
Niobophyllite	Mn ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺	O ₂	(OH) ₄	(Nb,Ti) ₂	(O,F)	[¹³]K ₂	[¹⁰]Na	(1)
Zircophyllite	Mn ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺	O ₂	(OH) ₄	Ti ₂	F	[¹³]K ₂	[¹⁰]Na	(2)
Tarbagataite	Mn ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺	O ₂	(OH) ₄	Ti ₂	OH	[¹²](K□)	[¹⁰]Ca	(3)
Nalivkinite	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺	O ₂	(OH) ₄	Ti ₂	F	Li ₂	[¹⁰]Na	(H ₂ O) ₂ (4)
Bulgakite	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺	O ₂	(OH) ₄	Ti ₂	(O,F)	Li ₂	[¹⁰](Ca,Na)	(H ₂ O) ₂ (4)
Kupletskite group											
Kupletskite	Mn ²⁺ ₂	Mn ²⁺ ₂	Mn ²⁺ ₂	Mn ²⁺	O ₂	(OH) ₄	Ti ₂	F	[¹²]K ₂	[¹⁰]Na	(5)
Niobokupletskite	Mn ²⁺ ₂	Mn ²⁺ ₂	Mn ²⁺ ₂	Mn ²⁺	O ₂	(OH) ₄	(Nb,Ti) ₂	(O,F)	[^{8,9}]K ₂	[¹⁰]Na	(6)
Kupletskite-(Cs)	Mn ²⁺ ₂	Fe ²⁺ ₂	Mn ²⁺ ₂	Zn	O ₂	(OH) ₄	Ti ₂	F	[¹³]Cs ₂	[¹⁰]Na	(1)
Devitoite group											
Devitoite	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺ ₂	Fe ²⁺	O ₂	(OH) ₄	[⁵]Fe ³⁺ ₂	□ ₂	[¹²]Ba ₂ [¹²]Ba ₂	[⁹⁻¹¹]Ba [⁹⁻¹¹]Ba	(PO ₄) ₂ (CO ₃) (7)
Sveinbergeite	(Fe ²⁺ ₆ Fe ³⁺)				O ₂	(OH) ₄	Ti ₂	[OH(H ₂ O)]	(H ₂ O) ₂	[⁹]Ca(H ₂ O)]	(8)
Lobanovite*	Na	Fe ²⁺ ₂	Fe ²⁺ ₂	Mg ₂	O ₂	(OH) ₄	[⁵]Ti ₂	□	[¹⁰]K ₂	[⁸]Na	(9)

X^O: anions of the O sheet; X^P: peripheral anions of the HOH block; X^O_D: common anions for three M cations in the O sheet and a D cation in the H sheet; X^O_A: monovalent anions common for three M cations in the O sheet; X^P_D: apical (anions or H₂O groups) of D cations at the periphery of the HOH block; (), [] cations and anions are disordered and substitute for each other; coordination numbers (CN) for cations are shown where CN ≠ 6; n = 0, 1, 2; p = 1, 2; r = 1, 2.

*M(1), 2M(2), 2M(3), 2M(4).

References: (1) Cámara *et al.* (2010); (2) Sokolova *et al.* (in preparation); (3) Stepanov *et al.* (2012); (4) Agakhanov *et al.* (2015); (5) Piilonen *et al.* (2001); (6) Piilonen *et al.* (2000); (7) Kampf *et al.* (2010); (8) Khomyakov *et al.* (2011); (9) Sokolova and Cámara (2008).

Table 3. Detailed ideal formulae of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2lX_{D2}^O X_{A4}^O X_{Dn}^P W_{A2}$ for the astrophyllite-supergroup minerals*.

Mineral	Ideal formula												
	A_2	B	C_7	D_2	$(T_4O_{12})_2$	l	X_{D2}^O	X_{A4}^O	X_D^P	W_{A2}	p	r	n
Astrophyllite group													
Astrophyllite	K ₂	Na	Fe ²⁺ ₇	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	F		1	1	1
Niobophyllite	K ₂	Na	Fe ²⁺ ₇	(Nb,Ti) ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	(O,F)		1	1	1
Zircophyllite	K ₂	Na	Fe ²⁺ ₇	Zr ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	F		1	1	1
Tarbagataite	(K□)	Ca	Fe ²⁺ ₇	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	(OH)		1	1	1
Nalivkinite	Li ₂	Na	Fe ²⁺ ₇	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	F	(H ₂ O) ₂	1	1	1
Bulgakite	Li ₂	(Ca,Na)	Fe ²⁺ ₇	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	(O,F)	(H ₂ O) ₂	1	1	1
Kupletskite group													
Kupletskite	K ₂	Na	Mn ²⁺ ₇	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	F		1	1	1
Niobokupletskite	K ₂	Na	Mn ²⁺ ₇	(Nb,Ti) ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	(O,F)		1	1	1
Kupletskite-(Cs)	Cs ₂	Na	Mn ²⁺ ₇	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	F		1	1	1
Devitoite group													
Devitoite	Ba ₄	Ba ₂	Fe ²⁺ ₇	Fe ³⁺ ₂	(Si ₄ O ₁₂) ₂	(PO ₄) ₂ (CO ₃)	O ₂	(OH) ₄	□ ₂		2	2	0
Sveinbergeite	(H ₂ O) ₂	[Ca(H ₂ O)]	(Fe ²⁺ ₆ Fe ³⁺)	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	[(OH)(H ₂ O)]		1	2	2
Lobanovite	K ₂	Na	(Fe ²⁺ ₄ Mg ₂ Na)	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄	□		1	1	0

*Data are taken from the structure work (see references in Table 2).

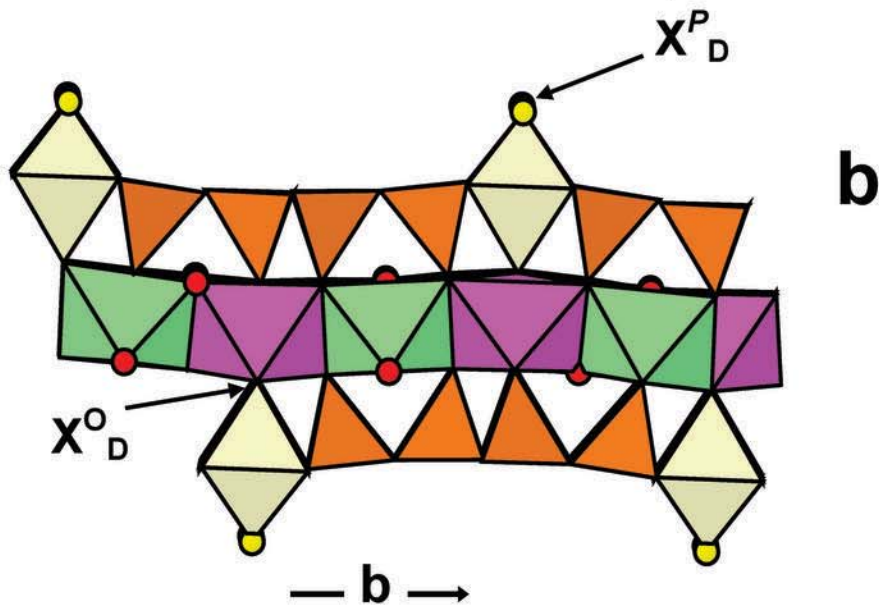
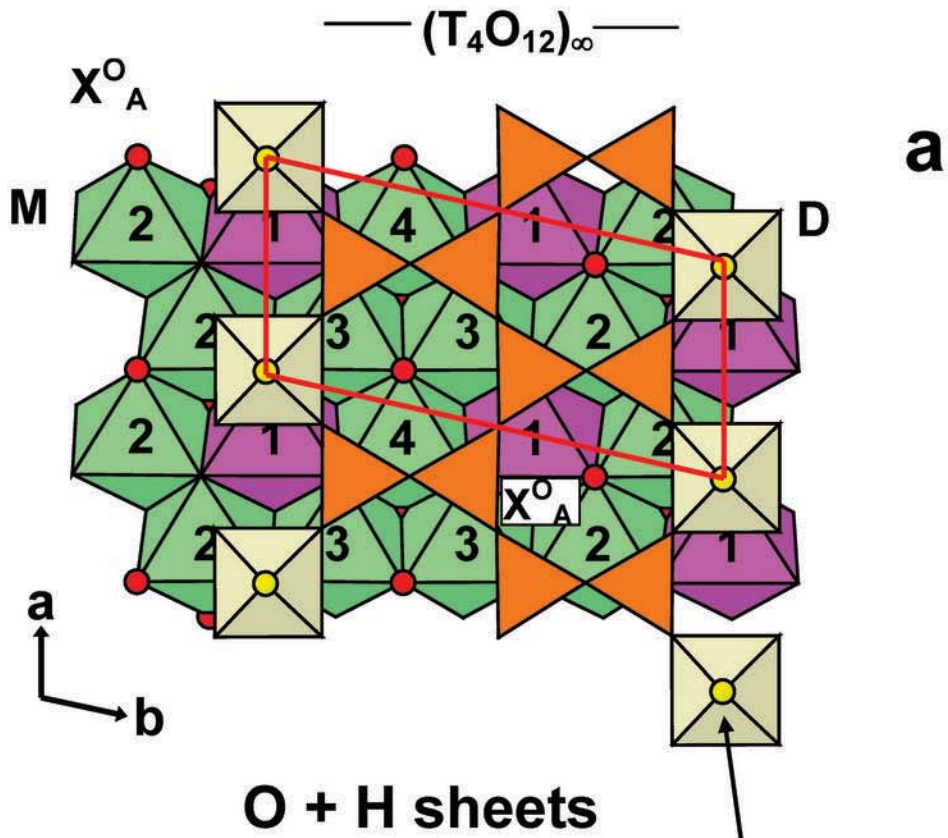


Fig. 1

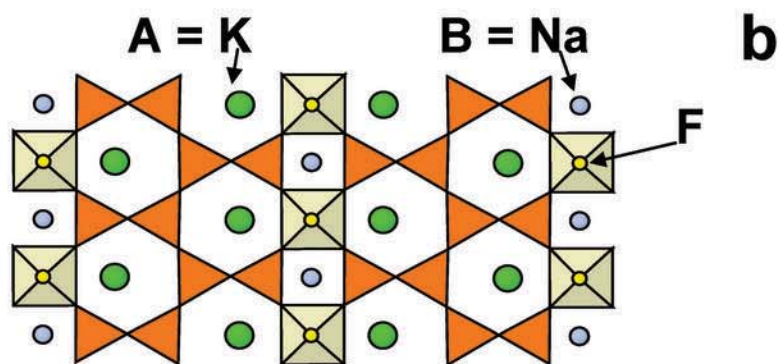
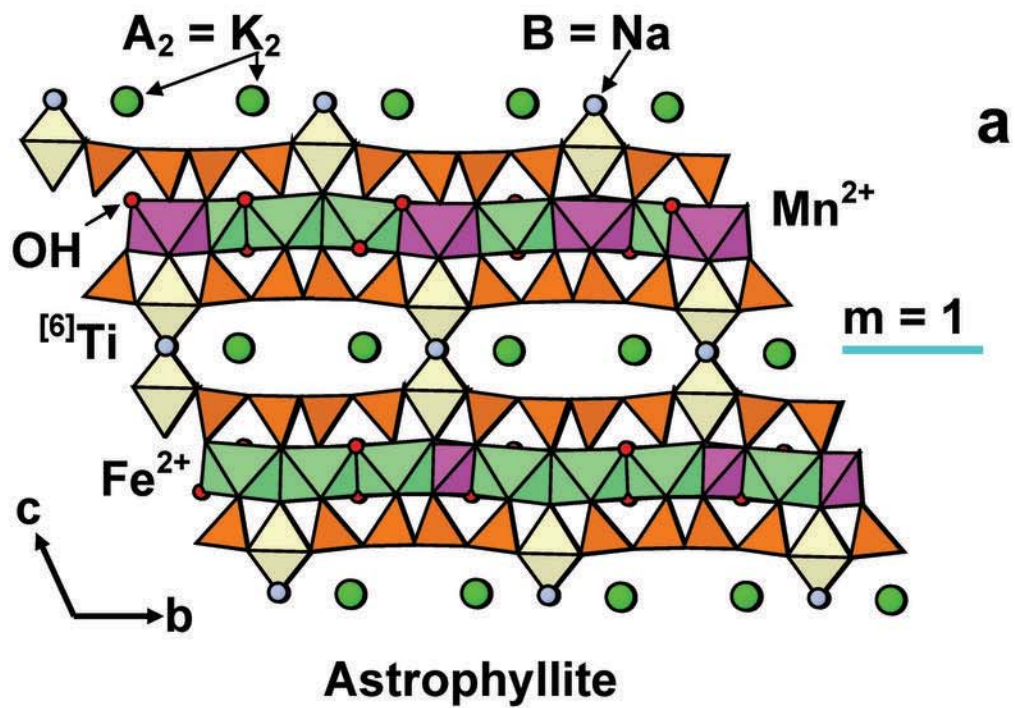


Fig. 2

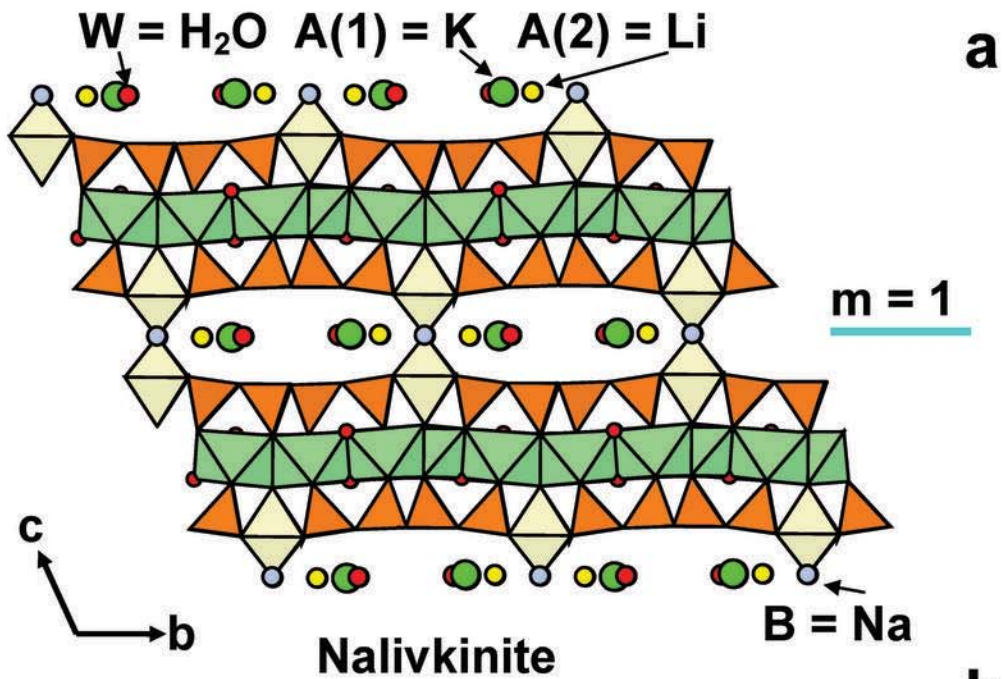


Fig. 3

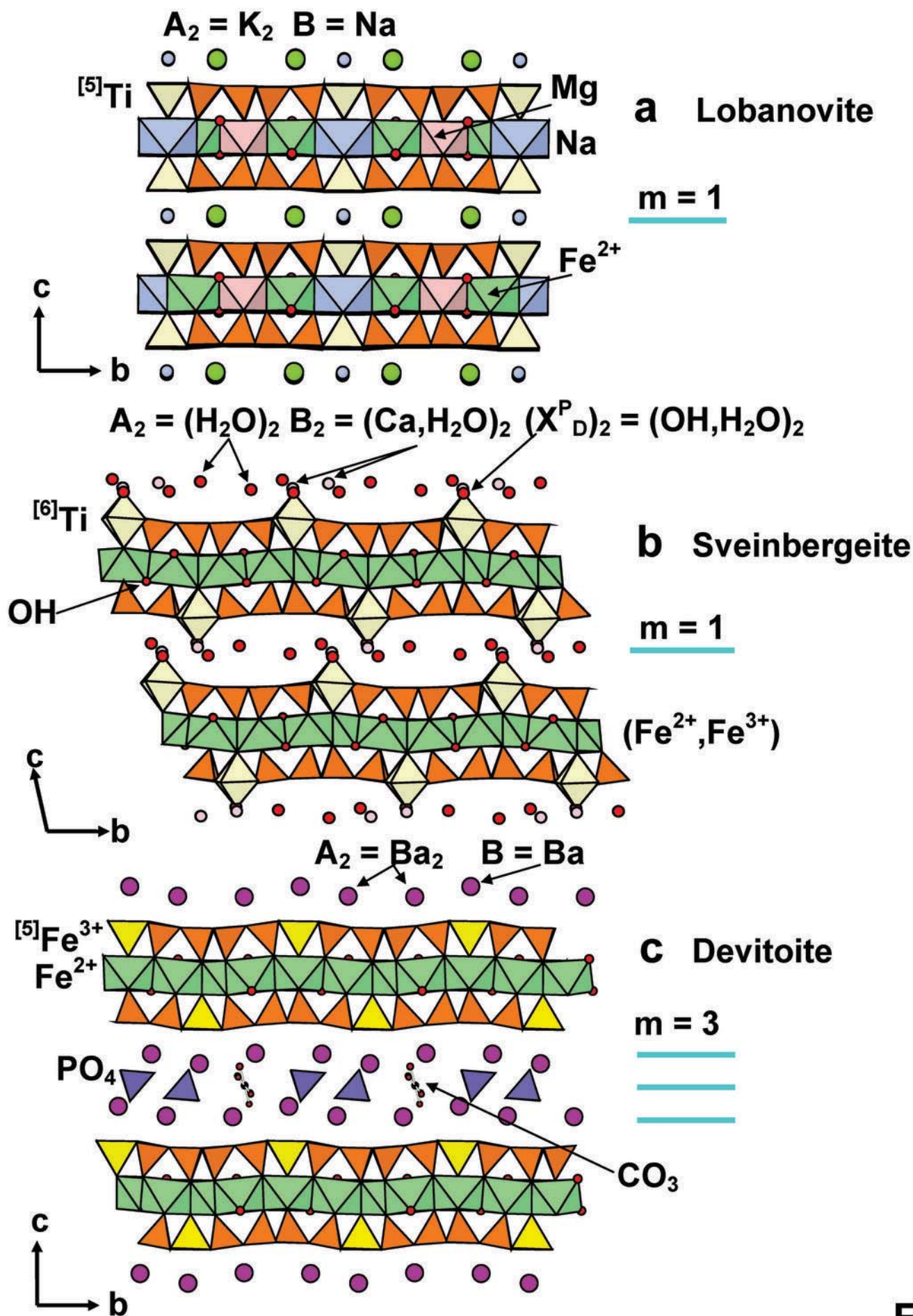


Fig. 4