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18 Abstract

19

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 (the C group: C₇ a.p.f.u.). In the astrophyllite group (HOH blocks connect via $D-X_{D}^{P}-D$ bridges, 26 Fe^{2+} is dominant at C₇), there are six minerals: astrophyllite, niobophyllite, zircophyllite, 27 tarbagataite, nalivkinite and bulgakite. In the kupletskite group (HOH blocks connect via $D-X_{D}^{\rho}$ 28 D bridges. Mn²⁺ is dominant at C₇), there are three minerals: kupletskite, niobokupletskite and 29 kupletskite-(Cs). In the devitoite group (HOH blocks do not connect via $D-X_{D}^{P}-D$ bridges), there 30 31 are three minerals: devitoite, sveinbergeite and lobanovite. The general formula for the astrophyllite-supergroup minerals is of the form $A_{2n}B_rC_7D_2(T_4O_{12})_2|X_{D2}^OX_{A4}X_{Dn}^PW_{A2}$, where C 32 [cations at the M(1-4) sites in the O sheet] = Fe²⁺, Mn, Na, Mg, Zn, Fe³⁺, Ca, Zr, Li; D (cations in 33 the H sheets) = ${}^{[6,5]}$ Ti, Nb, Zr, Sn⁴⁺, ${}^{[5]}$ Fe³⁺, Mg, Al; T = Si, minor Al; A_{2p}B_rIW_{A2} (I block) where p = 34 1,2; r = 1,2; A = K, Cs, Ba, H₂O, Li, Rb, Pb²⁺, Na, \Box ; B = Na, Ca, Ba, H₂O, \Box ; I represents the 35 36 composition of the central part of the I block, excluding peripheral layers of the form $A_{2p}B_rW_{A2}$, e.g. $(PO_4)_2(CO_3)$ (devitoite); $X_D^{O} = O$; $X_A^{O} = OH$, F; $X_D^{P} = F$, O, OH, H₂O, \Box , where n = 0, 1, 2 37 for $(X_{D}^{P})_{n}$; $W_{A} = H_{2}O, \Box$. 38 39

Here we report a nomenclature and classification for the astrophyllite-supergroup minerals. The

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

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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 been validated under the name lobanovite, K₂Na(Fe²⁺₄Mg₂Na)Ti₂(Si₄O₁₂)₂O₂(OH)₄; (2) According 47 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 $D-X_{D}^{P}-D$ bridges, Fe²⁺ is dominant at C₇; 62 Kupletskite group: HOH blocks connect via $D-X_{D}^{P}-D$ bridges, Mn²⁺ is dominant at C₇; 63 Devitoite group: HOH blocks do not connect via $D-X_{D}^{P}-D$ 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. 1976), Piilonen et al. (2003a,b) and Cámara et al. (2010). All references pertinent to work on the 70 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 formula of these minerals in the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX_{D2}^{O}X_{A4}^{O}X_{Dn}^{P}$, where C and D are 83 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 =84 $^{[6,5]}$ (Ti, Nb, Zr, Fe³⁺); T = Si, minor Al; $A_{2p}B_r$ is the composition of the I block where p = 1,2; r = 85 1,2; A = K, Cs, Li, Ba, H₂O, \Box ; B = Na, Ca, Ba, H₂O, \Box ; I represents the composition of the 86 central part of the I block, excluding peripheral layers of the form A₂B; $X = X_{D2}^{O}X_{A4}^{O}X_{Dn}^{P} = O$, 87 88 OH, F and H₂O; n = 0, 1, 2.

89

90 New data

91 Sokolova (2012) listed zircophyllite [described by Kapustin (1972) from Tuva, Russia; Mn >

92 Fe²⁺] 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 $(K_{1.70}Na_{071}Ca_{0.24}Mn_{0.35}Sr_{0.02})_{\Sigma 3}(Fe^{2+}_{3.57}Mn_{3.43})_{\Sigma 7}(Zr_{1.58}Nb_{0.25}Ti_{0.17})_{\Sigma 2}(Si_{7.76}Ti_{0.24})_{\Sigma 8}[O_{26.84}]$

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95 $(OH)_{3.26}F_{0.90}]_{\Sigma 31}(H_2O)_{0.9}$, where the composition of the O sheet is $C_7 = (Fe^{2+}_{3.57}Mn_{3.43})_{\Sigma 7}$, i.e. Fe^{2+} 96 > 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, $Li_2(Ca,Na)Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)(H_2O)_2$, a Ca-analogue of nalivkinite, and revised the 101 crystal structure and chemical formula of nalivkinite: Li₂NaFe²⁺₇Ti₂(Si₄O₁₂)₂O₂(OH)₄F(H₂O)₂ 102 103 (Agakhanov et al., 2008; Uvarova et al., 2008) (Table 1). Refinement of the bulgakite and 104 nalivkinite structures resulted in the location of H₂O groups at the W site in the I block. An H₂O 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 H₂O groups at the W 107 site must equal the number of cations at the A(2) site. The presence of H₂O 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 A_{2p}B_rC₇D₂(T₄O₁₂)₂I $X^{O}_{D2}X^{O}_{A4}X^{P}_{Dn}W_{A2}$ 112

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}
- astrophyllite ribbon that extends along [100] (Fig. 1*a*). The astrophyllite ribbons share common
- 120 vertices with [6,5]-coordinated D polyhedra to form the H (Heteropolyhedral) sheet (Fig. 1*a*).

121 Two T₂O₇ groups oriented perpendicular to [100] constitute the minimal repeat of the

astrophyllite ribbon which defines the *a* cell parameter of ~5.4 Å (Fig. 1*a*, Table 1). The H and O sheets are characterized by a minimal planar cell with *a* ~ 5.4, *b* ~ 11.9 Å, **a** ^ **b** ~ 103° (Table 1, Fig. 1*a*). Two H sheets and a central O sheet form the HOH block (Fig. 1*b*). The linkage of O and H sheets is identical in all astrophyllite-supergroup structures, except for lobanovite (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 M₇ (= C₇) a.p.f.u. (atoms per formula unit)

131 (Fig. 1*a*). In the astrophyllite-supergroup minerals, the dominant cations at the *M* sites are

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.*, 2003*a*,*b*). There is one *D* site which gives D₂ 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]Fe³⁺

137 (devitoite) are less common (Table 2). In the minimal cell, there are one *D* site and one minimal

repeat of the astrophyllite ribbon (Fig. 1*a*), and the ideal composition of the H sheet is DT₄

a.p.f.u. The ideal cation composition of the HOH layer is C₇D₂ 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. 1*a*,*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 anions, mainly OH groups and minor F, summing to ideally $(X^{O}_{A})_{4} = (OH)_{4}$ p.f.u. (Table 2). The 148 X^{P}_{D} site is occupied by an anion at the periphery of the HOH block (*P* = *peripheral*) where the D 149 150 cation is [6]-coordinated (Figs. 1a,b). The X_{D}^{P} site is occupied by F, OH, O, H₂O and \Box , and in a structure, $X_{D}^{P} = 0$, 1 or 2 p.f.u. (Table 2). The anion composition of the HOH block is 151 $(T_4O_{12})_2 X_{D2}^{O} X_{A4}^{O} X_{Dn}^{P}$, where n = 0, 1, 2. The number of X_D^{P} anions depends on the coordination 152 153 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 + $(T_4O_{12})_2 X^O_{D2} X^O_{A4} X^P_{Dn} = C_7 D_2 (T_4O_{12})_2 X^O_{D2} X^O_{A4} X^P_{Dn}$, where C and D are cations of the O and H 158 sheets: C = ^[6](Fe²⁺, Mn, Na, Mg, Zn, Fe³⁺, Ca, Zr, Li); D = ^[6,5]Ti, Nb, Zr, Sn⁴⁺, ^[5]Fe³⁺, Mg, Al; T = 159 160 Si, minor AI; X are anions: X^O_D anions coordinate three M cations in the O sheet and a D cation in the H sheet, i.e. O; X^O_A (monovalent anions) coordinate three M cations in the O sheet, i.e. 161 OH, F; and X_{D}^{P} are peripheral anions of the D cations, i.e. X_{D}^{P} = F, O, OH, H₂O, \Box , where n = 0, 162 1, 2 for $(X_D^{P})_n$. For astrophyllite, the ideal composition of the HOH block is 163 [Fe²⁺₇Ti₂(Si₄O₁₂)₂O₂(OH)₄F]³⁻ (Table 1). 164

165

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

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

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173 Type 1: HOH blocks link directly

HOH blocks link directly where they share common vertices of D octahedra, X_{D}^{P} anions, *i.e.* 174 HOH blocks connect via $D-X_{D}^{P}-D$ bridges (e.g. Ti-F-Ti in astrophyllite) (Fig. 2a). This type of 175 176 self-linkage of HOH blocks occurs in astrophyllite, niobophyllite, zircophyllite, tarbagataite, 177 nalivkinite, bulgakite, kupletskite, niobokupletskite and kupletskite-(Cs). These type-1 structures belong to the astrophyllite structure type with space group $P\overline{1}$ (or space group C2/c in 178 179 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. 2a,b; other dominant cations are as follows: ^ACs [kupletskite-(Cs)] and ^BCa (tarbagataite) 183 184 (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 Li > 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 Li + H_2O 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 Na + H_2O and K has been reported for nafertisite, Na₃Fe²⁺₁₀Ti₂(Si₆O₁₇)₂O₂(OH)₆F (H₂O)₂ (Cámara *et al.*, 2014). 191 192 Based on the dominant cation of the O sheet, we divide the nine minerals listed above 193 into two groups (Tables 1–3): Astrophyllite group: HOH blocks connect via $D-X_{D}^{P}-D$ bridges, Fe^{2+} is dominant at C_{7} ; 194 HOH blocks connect via $D-X_{D}^{P}-D$ bridges, Mn^{2+} is dominant at C_{7+} Kupletskite group: 195 196 197 198

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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 $D-X_{p}^{P}-D$ 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 Å and are occupied by 207 $(Ca,\Box)_2$ and $(H_2O,\Box)_2$, giving ideally $[Ca(H_2O)]$ p.f.u. Short-range order of Ca and H₂O at the B(1,2) sites affects the composition of the X_D^{P} site, ideally [(OH)(H₂O)] p.f.u. The ideal 208 209 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 the astrophyllite-type HOH block where [5]-coordinated D sites are occupied by Fe^{3+} (Kampf et 211 212 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 PO₄ 217 tetrahedra and CO₃ 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

sveinbergeite (Khomyakov et al., 2011) and lobanovite (Sokolova et al., 2015), we list devitoite,

sveinbergeite and lobanovite in the:

223

Devitoite group: HOH blocks do not connect via $D-X_{D}^{P}-D$ bridges.

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_{A2},

where p is the number of layers of the form A_2BW_{A2} and is equal to 1, 2; r = 1, 2; A = K, Cs, Li, Ba, H₂O, \Box ; B = Na, Ca, Ba, H₂O, \Box ; W = H₂O, \Box ; I represents the composition of the central part of the I block, excluding peripheral layers of the form A_2B and A_2BW_{A2} , i.e. (PO₄)₂(CO₃) in devitoite.

232 We combine general formulae for the HOH block, $C_7D_2(T_4O_{12})_2X^O_{D2}X^O_{A4}X^P_{Dn}$, and the I 233 block, $A_{2p}B_rIW_{A2}$, into a general formula for the astrophyllite-supergroup minerals:

234
$$A_{2p}B_{r}C_{7}D_{2}(T_{4}O_{12})_{2}IX^{O}{}_{D2}X^{O}{}_{A4}X^{P}{}_{Dn}W_{A2}$$

where C [cations at the M(1-4) sites in the O sheet] = Fe²⁺, Mn, Na, Mg, Zn, Fe³⁺, Ca, Zr, Li; D (cations in the H sheets) = ^[6,5]Ti, Nb, Zr, Sn⁴⁺, ^[5]Fe³⁺, Mg, Al; T = Si, minor Al; A_{2p}B_rIW_{A2} (I block) where p = 1,2; r = 1,2; A = K, Cs, Ba, H₂O, Li, Rb, Pb²⁺, Na, \Box ; B = Na, Ca, Ba, H₂O, \Box ; I represents the composition of the central part of the I block, excluding peripheral layers of the form A_{2p}B_rW_{A2}, e.g. (PO₄)₂(CO₃) (devitoite); X^O_D = O; X^O_A = OH, F; X^P_D = F, O, OH, H₂O, \Box , where n = 0, 1, 2 for (X^P_D)_n; W_A = H₂O, \Box .

241

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- 331 Fig. 1. The HOH block in the crystal structure of astrophyllite [atom coordinates of Sn-rich
- 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-
- and Fe^{2+} -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

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

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Fig. 3. Nalivkinite: (*a*) general view of the crystal structure and (*b*) the short-range order of K [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 at the A(1) and A(2) sites are shown as green and larger yellow spheres, H₂O groups are shown as larger red spheres.

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Fig. 4. General view of the crystal structures of (*a*) lobanovite, (*b*) sveinbergeite and (*c*)

devitoite. Legend as in Fig. 2; the Mg and Na octahedra are pink and navy blue, the [5]-

351 coordinated Fe^{3+} 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

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.

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Mineral	Endmember formula	a (Å)	b (Å)	c (Å)	Space	Ζ	Ref.
		α(°)	β (°)	γ (°)	group		
Astrophyllite gro	Dup HOH blocks connect via $D-X_{D}^{P}$ -D bridges,	Fe ²⁺ is domi	inant at C7				
Astrophyllite	$K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3866 113.019	11.8821 94.578	11.6794 103.120	<i>P</i> 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	<i>P</i> 1	1	(3,2)
Zircophyllite	$K_2NaFe^{2+}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$	5.447 112.950	11.966 94.690	11.789 103.116	<i>P</i> 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	<i>P</i> 1	1	(6)
Nalivkinite	$Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$	5.374 113.360	11.948 94.538	11.676 103.01	<i>P</i> 1	1	(7,8)
Bulgakite	$Li_2(Ca,Na)Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(O,F)(H_2O)_2$	5.374 113.457	11.965 94.533	11.65 103.08	<i>P</i> 1	1	(8)
Kupletskite grou	<i>up</i> HOH blocks connect via $D-X_{D}^{P}-D$ bridges,	Mn ²⁺ is dom	inant at C7				
Kupletskite-1A	$K_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3784 112.964	11.9085 94.697	11.7236 103.112	<i>P</i> 1	1	(9)
Kupletskite-2M	$K_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.4022	23.226 95.246	21.1782	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	<i>P</i> 1	1	(10)
Kupletskite-(Cs)	$Cs_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3850 113.117	11.9350 94.614	11.7793 103.075	<i>P</i> 1	1	(11,2)
Devitoite group	HOH blocks do not connect via D-X ^{P} _D -D b	ridges					
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	P1	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	<i>P</i> 1	1	(13)
Lobanovite	K₂Na(Fe ²⁺ ₄Mg₂Na)Ti₂(Si₄O₁₂)₂O₂(OH)₄	5.3327	23.1535 99.615	10.3775	C2/m	2	(14,15)

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

*The ideal formula is of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^o_{D2}X^o_{A4}X^P_{Dn}W_{A2}$ (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).

				— н	OH blo	ck ——			I (Intermediate) block — F				
Mineral	O sheet -			heet —			2H sheets		-				
C ₇ :	2M(1)	2M(2)	2M(3)	M(4)	$2X^{\rm O}{}_{\rm D}$	$4X^{O}_{A}$	2D	nX^P_D	pA ₂	rB	$2W_{\text{A}}$	I	
Astrophyllite gr	oup												
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	$Mn^{2+}{}_{2}$	$\mathrm{Fe}^{2^{+}}{}_{2}$	$\mathrm{Fe}^{2^{+}}{}_{2}$	Fe ²⁺	O ₂	(OH) ₄	(Nb,Ti) ₂	(O,F)	^[13] K ₂	^[10] Na			(1)
Zircophyllite	Mn ²⁺ 2	$\mathrm{Fe}^{2^{+}}{}_{2}$	$\mathrm{Fe}^{2^{+}}_{2}$	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	ОН	^[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	$\mathrm{Fe}^{2^{+}}_{2}$	$\mathrm{Fe}^{2^{+}}{}_{2}$	Fe ²⁺	O ₂	(OH) ₄	Ti ₂	(O,F)	Li 2	^[10] (Ca,Na)	(H ₂ O) ₂		(4)
Kupletskite gro	ир												
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	\square_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)

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

 X° : anions of the O sheet; X^{ρ} : peripheral anions of the HOH block; X°_{D} : common anions for three M cations in the O sheet and a D cation in the H sheet; X°_{A} : monovalent anions common for three M cations in the O sheet; X^{ρ}_{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 \neq 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).

Mineral			Idea	al formula									
	A ₂	В	C ₇	D ₂	(T ₄ O ₁₂) ₂	I	Х⁰ D2	X ⁰ _{A4}	X ^P D	W _{A2}	р	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	\square_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	$(Fe^{2+}_{4}Mg_2Na)$	Ti ₂	(Si ₄ O ₁₂) ₂		O ₂	(OH) ₄			1	1	0

Table 3. Detailed ideal formulae of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2|X^O_{D2}X^O_{A4}X^P_{Dn}W_{A2}$ for the astrophyllite-supergroup minerals*.

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



HOH block

Fig. 1



Astrophyllite



Fig. 2



