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The astrophyllite supergroup: nomenclature and classification

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ABSTRACT

Here we report a nomenclature and classification for the astrophyllite-supergroup minerals. The HOH block is the main structural unit in all astrophyllite-supergroup structures; it consists of three H–O–H sheets where the T_4O_{12} astrophyllite ribbons occur in the H sheets. In each structure, HOH blocks alternate with **I** (Intermediate) blocks along [001]. The twelve minerals of the astrophyllite supergroup are divided into three groups based on (1) the type of self-linkage of HOH blocks, i.e. (a) HOH blocks link directly where they share common vertices of D octahedra, or (b) HOH blocks do not link directly; and (2) the dominant cation of the O sheet (the C group: C_7 apfu). In the astrophyllite group (HOH blocks connect via D–X^P_D–D bridges, Fe^{2+} is dominant at C_7), there are six minerals: astrophyllite, niobophyllite, zircophyllite, tarbagataite, nalivkinite and bulgakite. In the kupletskite group (HOH blocks connect via D–X^P_D–D bridges, Mn^{2+} is dominant at C_7), there are three minerals: kupletskite, niobokupletskite and kupletskite-(Cs). In the devitoite group (HOH blocks do not connect via D–X^P_D–D bridges), there are three minerals: devitoite, sveinbergeite and lobanovite. The general formula for the 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 [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 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 = 1,2; r = 1,2; A = K, Cs, Ba, H_2O, Li, Rb, Pb^{2+}, Na, □; B = Na, Ca, Ba, H_2O, □; 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. $(PO_4)_2(CO_3)$ (devitoite); X^O_D = O; X^O_A = OH, F; X^P_D = F, O, OH, H_2O, □, where *n* = 0, 1, 2 for $(X^P_D)_n$; W_A = H_2O, □.

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

Introduction

The Nomenclature Voting proposal 15-B – *"Magnesioastrophyllite" validated under the name "lobanovite", and astrophyllite supergroup classification* – has been approved by the CNMNC-IMA (in accord with Mills *et al*., 2009) with the two conclusions: (1) "Magnesioastrophyllite" has been validated under the name lobanovite, $K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$; (2) According to the new classification scheme, the astrophyllite supergroup is now divided in three groups: the astrophyllite group, the kupletskite group and the devitoite group. Following the above decision, the formal description of the lobanovite has been reported by Sokolova *et al*. (2017). In this paper, we address the second part of the Voting proposal 15-B and report the nomenclature and classification of the astrophyllite supergroup based on the work of Sokolova (2012).

Twelve minerals of the astrophyllite supergroup are listed in Table 1. The HOH block is the main structural unit in all astrophyllite-supergroup structures; it consists of a central O (Octahedral) sheet between two adjacent H (Heteropolyhedral) sheets where the T_4O_{12} astrophyllite ribbons occur in the H sheets. In each structure, HOH blocks alternate with **I** (Intermediate) blocks along [001].

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They are divided into three groups based on (1) the type of self-linkage between HOH blocks, i.e. (a) HOH blocks link directly where they share common vertices of D octahedra, or (b) HOH blocks do not link directly; and (2) the dominant cation of the O sheet (the C group: C_7 apfu). These three groups are as follows:

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

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

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

Background

For many years, the astrophyllite-group minerals have been divided into two main subgroups on the basis of the dominance of Fe^{2+} (astrophyllite; Weibye, 1848) or Mn^{2+} (kupletskite; Semenov, 1956) at the octahedrally coordinated sites in the O (Octahedral) sheet in the structure. The general crystal chemistry of the astrophyllite-group minerals was considered by Belov (1963, 1976), Piilonen *et al*. (2003*a*,*b*) and Cámara *et al.* (2010). All references pertinent to work on the general crystal chemistry of the astrophyllite-group minerals prior to 2012 are given in Sokolova (2012). Sokolova (2012) developed a structural hierarchy for the astrophyllite group and showed that in the astrophyllite group, there are two topologically distinct types of structures based on the type of self-linkage of HOH blocks: (1) HOH blocks link directly where they share common vertices of D octahedra, HOH blocks connect via $D-X^{P}_{D}-D$ bridges; and (2) HOH blocks do not link directly via polyhedra of the H sheets. For the description of atom arrangements in the intermediate space between adjacent HOH blocks in the astrophyllite-group structures, Sokolova (2012) introduced the **I** (Intermediate) block [by analogy with the **I** block in TS-block (Titanium Silicate) structures, Sokolova, 2006]. She considered nine minerals of the astrophyllite group [astrophyllite, niobophyllite, zircophyllite, tarbagataite, nalivkinite, kupletskite, niobokupletskite, kupletskite-(Cs) and lobanovite (Table 1)], suggested extending the astrophyllite group to include devitoite and sveinbergeite (Table 1), and wrote the general formula of these minerals in the form $A_{2p}B_rC_7D_2(T_4O_{12})_2I\ X^{O}_{D2}X^{O}_{A4}X^{P}_{Dn}$, where C and D are cations of the O and H sheets, $C = {}^{[6]}(Fe^{2+}, Mn, Fe^{3+}, Na, Mg$ or $Zn)$ at the $M(1–4)$ sites; $D = {}^{[6,5]}(Ti, Nb, Zr, Fe^{3+})$; T = Si, minor Al; $A_{2p}B_rI$ is the composition of the **I** block where $p = 1,2$; $r = 1,2$; A = K, Cs, Li, Ba, H_2O, □; B = Na, Ca, Ba, H_2O, □; I represents the composition of the central part of the **I** block, excluding peripheral layers of the form A_2B; $X = X^{O}_{D2}X^{O}_{A4}X^{P}_{Dn} = O$, OH, F and H_2O; $n = 0, 1, 2$.

New data

Sokolova (2012) listed zircophyllite [described by Kapustin (1972) from Tuva, Russia; $Mn > Fe^{2+}$] as a member of the kupletskite group. However Kapustin (1972) called zircophyllite a 'zirconium analogue of astrophyllite' and wrote its empirical formula as follows: $(K_{1.70}Na_{0.71}Ca_{0.24}Mn_{0.35})_{\Sigma3}(Fe^{2+}_{3.57}Mn_{3.43})_{\Sigma7}\ (Zr_{1.58}Nb_{0.25}Ti_{0.17})_{\Sigma2}(Si_{7.76}Ti_{0.24})_{\Sigma8}[O_{26.84}(OH)_{3.26}F_{0.90}]_{\Sigma31}(H_2O)_{0.9}$, where the composition of the O sheet is $C_7 = (Fe^{2+}_{3.57}Mn_{3.43})_{\Sigma7}$, i.e. $Fe^{2+} > Mn$. Following the original definition of zircophyllite, we place zircophyllite in the astrophyllite group (in accord with the nomenclature voting proposal 15-B). Here (Tables 1–3), we report some crystallographic data based on the structure refinement of zircophyllite from Mont Saint-Hilaire, Québec, Canada (Sokolova and Hawthorne, 2016).

Agakhanov *et al*. (2014, 2016) 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 crystal structure and chemical formula of nalivkinite: $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F(H_2O)_2$ (Agakhanov *et al.*, 2008; Uvarova *et al*., 2008) (Table 1). Refinement of the bulgakite and nalivkinite structures resulted in the location of H_2O groups at the *W* site in the **I** block. An H_2O group at the *W* site is a necessary ligand to complete the coordination of the cation at the *A*(2) site, where *A*(2) and *A*(1) are subsites of the *A* site. Hence the number of H_2O groups at the *W* site must equal the number of cations at the *A*(2) site. The presence of H_2O groups in the bulgakite and nalivkinite structures was confirmed by infrared spectroscopy (Agakhanov *et al*., 2014, 2016). Revision of the topology of the *A*(2) site in the astrophyllite-supergroup minerals required revision of the general formula for the astrophyllite-type structures (Sokolova, 2012), and Agakhanov *et al*. (2016) suggested writing the general formula as $A_{2p}B_rC_7D_2(T_4O_{12})_2I\ X^{O}_{D2}X^{O}_{A4}X^{P}_{Dn}W_{A2}$.

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

Mineral	Ideal 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	$K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3866 113.019	11.8821 94.578	11.6794 103.120	$P\bar{1}$	1	(1,2)
Niobophyllite	$K_2NaFe^{2+}_7(Nb,Ti)(Si_4O_{12})_2O_2(OH)_4(O,F)$	5.4022 112.990	11.8844 94.588	11.6717 103.166	$P\bar{1}$	1	(3,2)
Zircophyllite	$K_2NaFe^{2+}_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$	5.447 112.950	11.966 94.688	11.789 103.161	$P\bar{1}$	1	(4,5)
Tarbagataite	$(K\square)CaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_5$	5.3868 112.978	11.9141 94.641	11.7171 103.189	$P\bar{1}$	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	$P\bar{1}$	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	$P\bar{1}$	1	(8)
Kupletskite group	HOH blocks connect via $D–X^{P}_{D}–D$ bridges, Mn^{2+} is dominant at C_7						
Kupletskite-1*A*	$K_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3784 112.964	11.9085 94.697	11.7236 103.112	$P\bar{1}$	1	(9)
Kupletskite-2*M*	$K_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.4022	23.226 95.246	21.1782	*C*2/*c*	4	(9)
Niobokupletskite	$K_2NaMn_7(Nb,Ti)(Si_4O_{12})_2O_2(OH)_4(O,F)$	5.4303 112.927	11.924 94.750	11.747 103.175	$P\bar{1}$	1	(10)
Kupletskite-(Cs)	$Cs_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	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	$Ba_6Fe^{2+}_7Fe^{3+}_2(Si_4O_{12})_2(PO_4)_2(CO_3)O_2(OH)_4$	5.3437 91.337	11.6726 96.757	14.680 103.233	$P\bar{1}$	1	(12)
Sveinbergeite	$(H_2O)_2[Ca(H_2O)](Fe^{2+}_6Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_4$ $[OH(H_2O)]$	5.329 101.140	11.803 98.224	11.822 102.442	$P\bar{1}$	1	(13)
Lobanovite	$K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$	5.3327	23.1535 99.615	10.3775	*C*2/*m*	2	(14,15)

*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 and Hawthorne (2016); (6) Stepanov *et al.* (2012); (7) Agakhanov *et al.* (2008); (8) Agakhanov *et al.* (2016); (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*. (2017); (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				
	O sheet						2H sheets						
C_7:	2M(1)	2M(2)	2M(3)	M(4)	$2X_D^O$	$4X_A^O$	2D	nX_D^P	pA_2	rB	$2W_A$	I	Ref.
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	$^{[12]}(K\square)$	$^{[10]}Ca$			(3)
Nalivkinite	Fe_2^{2+}	Fe_2^{2+}	Fe_2^{2+}	Fe^{2+}	O_2	$(OH)_4$	Ti_2	F	Li_2	$^{[10]}Na$	$(H_2O)_2$		(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)	$(H_2O)_2$		(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	$(OH)_4$	$^{[5]}Fe_2^{3+}$	$\square_2$	$^{[12]}Ba_2$	$^{[9-11]}Ba$		$(PO_4)_2$	(7)
									$^{[12]}Ba_2$	$^{[9-11]}Ba$		(CO_3)	
Sveinbergeite	$(Fe_6^{2+}Fe^{3+})$				O_2	$(OH)_4$	Ti_2	$[OH(H_2O)]$	$(H_2O)_2$	$[^{[9]}Ca(H_2O)]$			(8)
Lobanovite*	Na	Fe_2^{2+}	Fe_2^{2+}	Mg_2	O_2	$(OH)_4$	$^{[5]}Ti_2$	$\square$	$^{[10]}K_2$	$^{[8]}Na$			(9)

X^O: anions of the O sheet; X^P: peripheral anions of the HOH block; X_D^O: common anions for three M cations in the O sheet and a D cation in the H sheet; X_A^O: monovalent anions common for three M cations in the O sheet; X_D^P: apical (anions or H_2O 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 and Hawthorne (2016); (3) Stepanov *et al.* (2012); (4) Agakhanov *et al.* (2016); (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 $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn}W_{A2}$ for the astrophyllite-supergroup minerals*.

Mineral	Ideal formula												
	A_2	B	C_7	D_2	$(T_4O_{12})_2$	I	X^O_{D2}	X^O_{A4}	X^P_D	W_{A2}	*p*	*r*	*n*
Astrophyllite group													
Astrophyllite	K_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F		1	1	1
Niobophyllite	K_2	Na	Fe^{2+}_7	$(Nb,Ti)_2$	$(Si_4O_{12})_2$		O_2	$(OH)_4$	(O,F)		1	1	1
Zircophyllite	K_2	Na	Fe^{2+}_7	Zr_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F		1	1	1
Tarbagataite	(K□)	Ca	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	(OH)		1	1	1
Nalivkinite	Li_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F	$(H_2O)_2$	1	1	1
Bulgakite	Li_2	(Ca,Na)	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	(O,F)	$(H_2O)_2$	1	1	1
Kupletskite group													
Kupletskite	K_2	Na	Mn^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F		1	1	1
Niobokupletskite	K_2	Na	Mn^{2+}_7	$(Nb,Ti)_2$	$(Si_4O_{12})_2$		O_2	$(OH)_4$	(O,F)		1	1	1
Kupletskite-(Cs)	Cs_2	Na	Mn^{2+}_7	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	F		1	1	1
Devitoite group													
Devitoite	Ba_4	Ba_2	Fe^{2+}_7	Fe^{3+}_2	$(Si_4O_{12})_2$	$(PO_4)_2(CO_3)$	O_2	$(OH)_4$	$□_2$		2	2	0
Sveinbergeite	$(H_2O)_2$	[Ca(H_2O)]	($Fe^{2+}_6Fe^{3+}$)	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	[(OH)(H_2O)]		1	2	2
Lobanovite	K_2	Na	($Fe^{2+}_4Mg_2$Na)	Ti_2	$(Si_4O_{12})_2$		O_2	$(OH)_4$	□		1	1	0

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

The HOH block in the astrophyllite-supergroup structures

General topology

The HOH block is the main structural unit in all astrophyllite-supergroup structures. In the crystal structure of astrophyllite, the M octahedra (C-group atoms) share edges to form an O sheet (Fig. 1*a*).

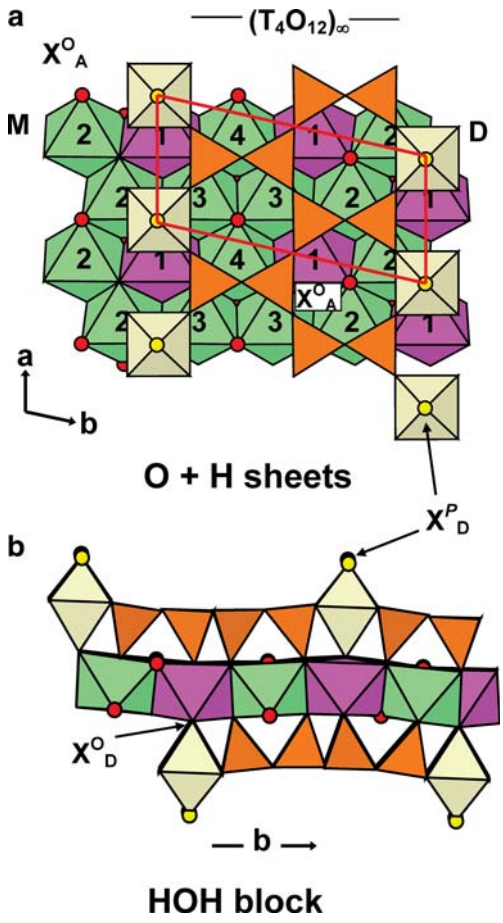

FIG. 1. The HOH block in the crystal structure of astrophyllite [atom coordinates of Sn-rich astrophyllite are taken from Cámara *et al.* (2010)]: (*a*) the O sheet and H sheets viewed perpendicular to the plane of the sheets, (*b*) the HOH block viewed down [100]. The M(1), M(2), M(3) and M(4) octahedra 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) octahedra are orange and pale yellow. The OH groups and F atoms at the X^O_A and X^P_D sites are shown as small red and yellow spheres. In (*a*), the unit cell is shown in red.

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 vertices with [6,5]-coordinated D polyhedra to form the H sheet (Fig. 1*a*). Two T_2O_7 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 $a \approx 5.4$, $b \approx 11.9$ Å, $\mathbf{a} \wedge \mathbf{b} \approx 103°$ (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).

Cation sites

In the O sheet of the crystal structure of astrophyllite, there are four *M* sites per minimal cell, $2M(1) + 2M(2) + 2M(3) + 1M(4)$, which give a total of M_7 ($= C_7$) apfu (atoms per formula unit) (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 at the *M*(1) site in lobanovite, and Zn at the *M*(4) site in kupletskite-(Cs) and Zn-rich astrophyllite (Piilonen *et al.*, 2006). In the H sheet, there are four *T* sites, mainly occupied by Si with minor Al (Piilonen *et al.*, 2003*a*,*b*). There is one *D* site which gives D_2 apfu The dominant cation at the *D* site is mainly $^{[6,5]}$Ti; $^{[6]}$Nb (niobophyllite and niobokupletskite), $^{[6]}$Zr (zircophyllite) and $^{[5]}Fe^{3+}$ (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 DT_4 apfu. The ideal cation composition of the HOH layer is C_7D_2 apfu, T atoms are considered as part of the complex anion $(T_4O_{12})^{8-}_2$ in the anion part of the structure.

Anion sites

In the HOH block, O atoms which tetrahedrally coordinate T atoms in two H sheets sum to the 24 O apfu. The D polyhedra of two H sheets share two X^O_D anions with M octahedra of the O sheet (for X^O, the O superscript defines anions of the O sheet) (Figs 1*a*, *b*), the X^O_D site is occupied by an O atom, giving $(X^O_D)_2 = O_2$ apfu. There are four anions pfu at the X^O_A sites which occur just under the interstitial *A* sites

(Fig. 1*a*) and they are occupied by monovalent anions, mainly OH groups and minor F, summing to ideally $(X^{O}_{A})_4 = (OH)_4$ pfu (Table 2). The X^{P}_{D} site is occupied by an anion at the periphery of the HOH block (P = peripheral) where the D cation is [6]-coordinated (Figs 1*a*,*b*). The X^{P}_{D} site is occupied by F, OH, O, H_2O and □, and in a structure, $X^{P}_{D} = 0$, 1 or 2 pfu (Table 2). The anion composition of the HOH block is $(T_4O_{12})_2X^{O}_{D2}X^{O}_{A4}X^{P}_{Dn}$, where $n = 0$, 1, 2. The number of X^{P}_{D} anions depends on the coordination number of the D cation (see above) and the type of self-linkage between the HOH blocks (see below).

General formula of the HOH block

The composition of the HOH block can be written as the sum of the cation and anion sites: $C_7D_2 + (T_4O_{12})_2X^{O}_{D2}X^{O}_{A4}X^{P}_{Dn} = C_7D_2(T_4O_{12})_2X^{O}_{D2}X^{O}_{A4}X^{P}_{Dn}$, where C and D are cations of the O and H sheets: $C = {}^{[6]}(Fe^{2+}$, Mn, Na, Mg, Zn, Fe^{3+}, Ca, Zr, Li); $D = {}^{[6,5]}$Ti, Nb, Zr, Sn^{4+}, $^{[5]}Fe^{3+}$, Mg, Al; T = Si, minor Al; 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. OH, F; and X^{P}_{D} are peripheral anions of the D cations, i.e. X^{P}_{D} = F, O, OH, H_2O, □, where $n = 0$, 1, 2 for $(X^{P}_{D})_n$. For astrophyllite, the ideal composition of the HOH block is $[Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F]^{3-}$ (Table 1).

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.

Type 1: HOH blocks link directly

HOH blocks link directly where they share common vertices of D octahedra, X^{P}_{D} anions, *i.e.* HOH blocks connect via D–X^{P}_{D}–D bridges (e.g. Ti–F–Ti in astrophyllite) (Fig. 2*a*). This type of self-linkage of HOH blocks occurs in astrophyllite, niobophyllite, zircophyllite, tarbagataite, nalivkinite, bulgakite, kupletskite, niobokupletskite and kupletskite-(Cs). These type-1 structures belong to the astrophyllite structure type with space group $P\bar{1}$ (or space group $C2/c$ in kupletskite-2M, Table 1). In

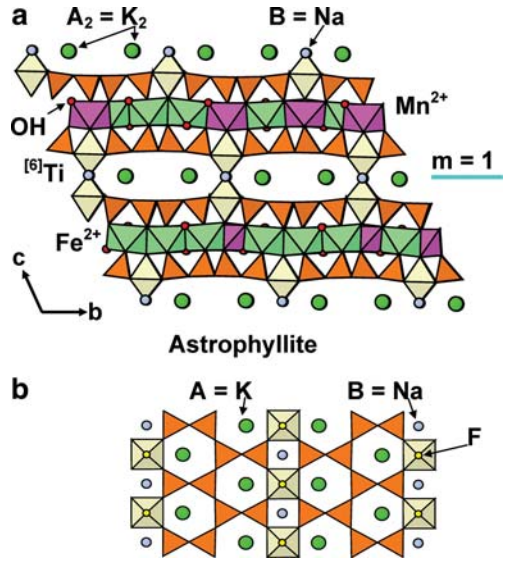

FIG. 2. Astrophyllite: (*a*) general view of the crystal structure and (*b*) the position of the *A* and *B* sites with regard to the H sheet. Legend as in Fig. 1; K and Na atoms at the *A* and *B* sites are shown as green and navy blue spheres. The position of the intermediate layer ($m = 1$, where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

the space between two HOH blocks, cations at two interstitial sites, *A* and *B*, constitute a layer of the form A_2B in the **I** block ($m = 1$, where m denotes number of cation layers in the **I** block). In astrophyllite, niobophyllite, kupletskite and niobokupletskite, the dominant cations at the *A* and *B* sites are K and Na, respectively (Figs 2*a*,*b*); other dominant cations are as follows: ^{A}Cs [kupletskite-(Cs)] and ^{B}Ca (tarbagataite) (Tables 2, 3). In bulgakite and nalivkinite, the *A* site is split into two subsites, *A*(1) and *A*(2), which are occupied mainly by K and Li, respectively, where Li > K (Fig. 3*a*). Hence we write the ideal composition of the *A* site as Li_2 apfu (Tables 1–3). Li and K at the *A*(1) and *A*(2) sites occur at short distances and must be locally mutually exclusive. Figure 3*b* gives a short-range order model for Li + H_2O and K in the structure of nalivkinite. The large K cation at the *A*(1) site is coordinated by thirteen O atoms, and a smaller Li cation at the *A*(2) site is coordinated by five 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, $Na_3Fe^{2+}_{10}Ti_2(Si_6O_{17})_2O_2(OH)_6F\ (H_2O)_2$ (Cámara *et al.*, 2014).

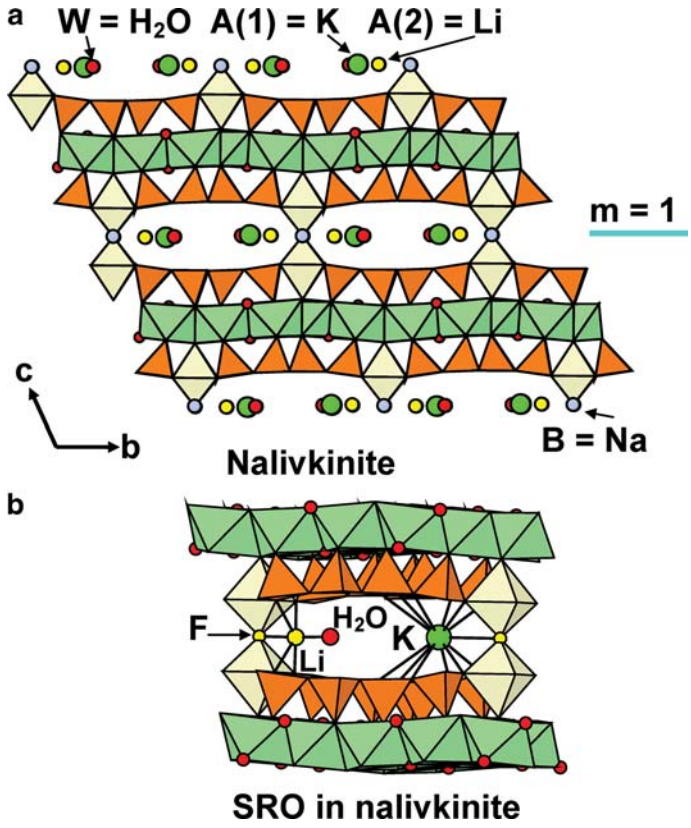

FIG. 3. Nalivkinite: (*a*) general view of the crystal structure and (*b*) the short-range order of K [*A*(1) site] and Li [*A*(2) site] plus H_2O [*W* site] in the **I** block. Legend as in Fig. 2; K and Li atoms at the *A*(1) and *A*(2) sites are shown as green and larger yellow spheres, H_2O groups are shown as larger red spheres.

On the basis of the dominant cation of the O sheet, we divide the nine minerals listed above into two groups (Tables 1–3):

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

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

Type 2: HOH blocks do not link directly

HOH blocks do not link directly via polyhedra of the H sheets, i.e. HOH blocks do not connect via $D–X^P_D–D$ bridges. The type-2 structure occurs in lobanovite, sveinbergeite and devitoite. In lobanovite, with [5]-coordinated Ti in the H sheet, HOH layers connect via K at the *A* site and Na at the *B* site, which constitute an **I** block ($m = 1$) of the form A_2B (Fig. 4*a*). In sveinbergeite, the **I** block ($m = 1$) is characterized by both cation and anion disorder (Fig. 4*b*) (Khomyakov *et al.*, 2011). The *A* site is occupied mainly by H_2O groups, giving ideally $(H_2O)_2$ pfu (Table 2). The *B* site splits into the *B*(1) and *B*(2) sites which are separated by < 1 Å and are occupied by $(Ca,\square)_2$ and $(H_2O,\square)_2$, giving ideally $[Ca(H_2O)]$ pfu. Short-range order of Ca and H_2O at the *B*(1,2) sites affects the composition of the X^P_D site, ideally $[(OH)(H_2O)]$ pfu. The ideal composition of the **I** block in sveinbergeite is the sum of the constituents at the *A* (2 apfu) and *B* (2 apfu) sites: $(H_2O)_2 + [Ca(H_2O)] = Ca(H_2O)_3$ pfu. Devitoite is the only known mineral with the astrophyllite-type HOH block where [5]-coordinated *D* sites are occupied by Fe^{3+} (Kampf *et al.*, 2010) (Tables 1–3). In the devitoite structure, HOH layers alternate with **I** blocks along [001] (Fig. 4*c*). In the **I** block,

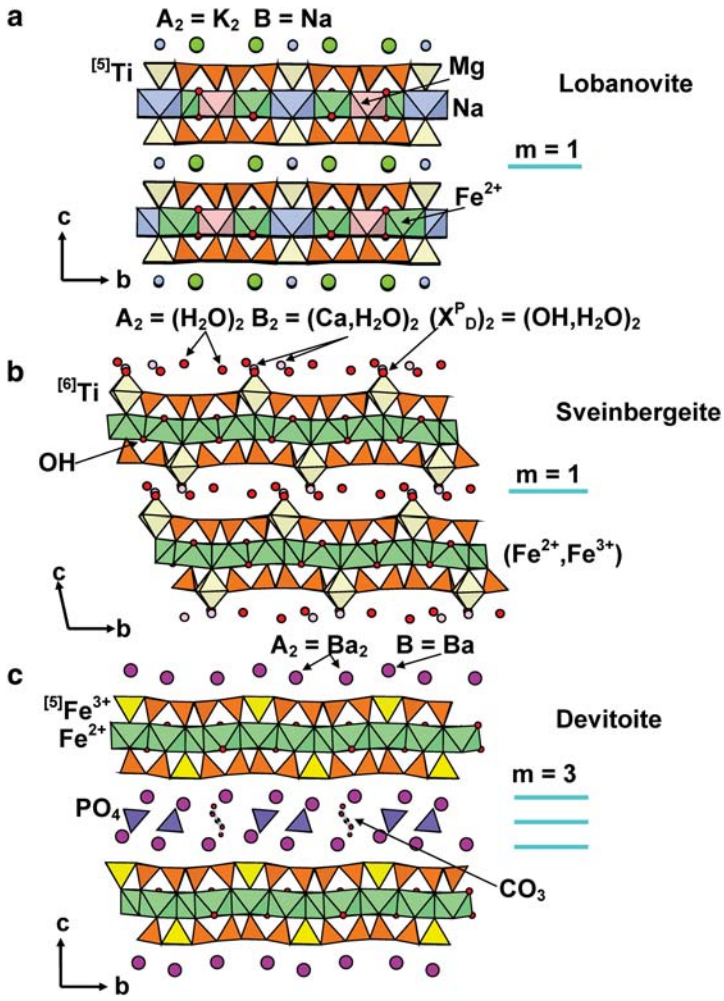

FIG. 4. General view of the crystal structures of (*a*) lobanovite, (*b*) sveinbergeite and (*c*) devitoite. Legend as in Fig. 2; the Mg and Na octahedra are pink and navy blue, the [5]-coordinated Fe^{3+} polyhedra are yellow; Ca (at the *B* site in sveinbergeite) and Ba (at the *A* and *B* sites in devitoite) atoms and H_2O groups (at the *A*, *B* and X^P_D sites in sveinbergeite) are shown as pink, raspberry and red spheres, respectively; PO_4 tetrahedra are purple, CO_3 groups are shown as small black spheres (C atoms) bonded to small red spheres (O atoms of CO_3 groups). The positions of the intermediate layer in lobanovite and sveinbergeite and the three intermediate layers in devitoite are shown by turquoise lines.

there are three layers of cations ($m = 3$). Two peripheral layers of the **I** block are topologically identical to the layer of the form A_2B in astrophyllite (Fig. 2*a*). In the peripheral layer of the **I** block in devitoite, the *A* and *B* sites are occupied by Ba (Fig. 4*c*), giving Ba_2 (A_2) + Ba (*B*) = Ba_3 apfu. The central layer of the **I** block in devitoite is occupied by PO_4 tetrahedra and CO_3 groups, giving $(PO_4)_2(CO_3)$ pfu. The ideal composition of the **I** block in devitoite is the sum of the two peripheral layers and the central layer: 2 x Ba_3 + $(PO_4)_2(CO_3)$ = $Ba_6(PO_4)_2(CO_3)$ pfu.

Taking into account that devitoite (Kampf *et al.*, 2010) was described prior to sveinbergeite (Khomyakov *et al.*, 2011) and lobanovite (Sokolova *et al.*, 2017), we list devitoite, sveinbergeite and lobanovite in the:

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

General formula for the astrophyllite-supergroup minerals

*The **I** block*

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, H_2O, □; B = Na, Ca, Ba, H_2O, □; W = H_2O, □; 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. $(PO_4)_2(CO_3)$ in devitoite.

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** block, $A_{2p}B_rIW_{A2}$, into a general formula for the astrophyllite-supergroup minerals:

$$A_{2p}B_rC_7D_2(T_4O_{12})_2I\,X^O_{D2}X^O_{A4}X^P_{Dn}W_{A2},$$

where C [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 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 $p = 1,2$; $r = 1,2$; A = K, Cs, Ba, H_2O, Li, Rb, Pb^{2+}, Na, □; B = Na, Ca, Ba, H_2O, □; 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. $(PO_4)_2(CO_3)$ (devitoite); $X^O_D = O$; X^O_A = OH, F; X^P_D = F, O, OH, H_2O, □, where $n = 0$, 1, 2 for $(X^P_D)_n$; $W_A = H_2O$, □.

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