Mineralogical Magazine, August 2012, Vol. 76(4), pp. 863–882

Further developments in the structure topology of the astrophyllite-group minerals

E. SOKOLOVA[1,2,*]

[1] Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada
[2] Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Moscow 119017, Russia

[*Received 1 November 2011; Accepted 2 February 2012; Associate Editor: G. Diego Gatta*]

ABSTRACT

The structure topology and crystal chemistry have been considered for ten astrophyllite-group minerals that contain the HOH layer, a central trioctahedral (O) sheet and two adjacent (H) sheets of [5]- and [6]-coordinated D polyhedra and the astrophyllite (T_4O_{12}) ribbons. The HOH layer is characterized by a planar cell with a ~5.4, b ~11.9 Å and $\mathbf{a}$^$\mathbf{b}$ ~103°. The ideal composition of the O sheet is Fe^{2+}_7 (astrophyllite) or Mn^{2+}_7 (kupletskite). All structures consist of an HOH layer and an **I** (intermediate) block that consists of atoms between two HOH layers. In the astrophyllite group, there are two types of structures based on the type of linkage of HOH layers: (1) HOH layers link directly where they share common vertices of D octahedra, and (2) HOH layers do not link directly via polyhedra of the H sheets. The type-1 structure occurs in astrophyllite, niobophyllite, nalivkinite, tarbagataite, kupletskite, niobokupletskite and kupletskite-(Cs); the type-2 structure occurs in magnesioastrophyllite, sveinbergeite and devitoite. The general formulae for the eight astrophyllite-group minerals (astrophyllite, niobophyllite, nalivkinite, tarbagataite, kupletskite, niobokupletskite, kupletskite-(Cs), magnesioastrophyllite) and for the extended astrophyllite group including devitoite and sveinbergeite are $A_2BC_7D_2T_8O_{26}(OH)_4X_{0-1}$ and $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn}$, respectively, where C and D are cations of the O and H sheets, C = $^{[6]}$(Fe^{2+}, Mn, Fe^{3+}, Na, Mg, 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 = O, OH, F and H_2O; n = 0, 1, 2. Two topological issues have been considered: (1) the pattern of sizes of the M octahedra in the O sheet, M(1) > M(2) > M(3) > M(4) and (2) different topologies of the HOH layer in magnesioastrophyllite and all other structures of the astrophyllite group.

KEYWORDS: astrophyllite group, general formula, endmember formula, topology, HOH layer, intermediate block, magnesioastrophyllite.

Introduction

THE astrophyllite-group minerals are 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 trioctahedral (O) sheet in the structure. There has been extensive work on the structure and composition of the astrophyllite-group minerals. Piilonen *et al.* (2003*a*,*b*) reviewed previous work, presented a considerable amount of data (crystal-structure refinements, electron-microprobe analyses and Mössbauer spectra), and generalized the crystal chemistry of the astrophyllite-group minerals using the *HOH layer* notation of Ferraris *et al.* (1996) for the description of the *Three-Layer*

---

* E-mail: elena_sokolova@umanitoba.ca
DOI: 10.1180/minmag.2012.076.4.04

Packet as pioneered by Belov (1963, 1976). Piilonen *et al.* (2003*a*) wrote the general formula as $A_2BC_7D_2T_8O_{26}(OH)_4X_{0-1}$, where $^{[10-13]}A$ = K, Rb, Cs, Na, H_3O^+, H_2O or □; $^{[10]}B$ = Na or Ca; $^{[6]}C$ = Fe^{2+}, Mn, Fe^{3+}, Na, Mg or Zn at the *M*(1−4) sites; $^{[6]}D$ = Ti, Nb or Zr; $^{[4]}T$ = Si or Al and X = F, OH, O or □. In accord with the general formula, Piilonen *et al.* (2003*a*) revised the formulae for astrophyllite, $K_2Na(Fe^{2+},Mn)_7Ti_2Si_8O_{26}(OH)_4F$, magnesioastrophyllite, $K_2Na[Na(Fe^{2+},Mn)_4Mg_2]Ti_2Si_8O_{26}(OH)_4\square$, niobophyllite, $K_2Na(Fe^{2+},Mn)_7(Nb,Ti)_2Si_8O_{26}(OH)_4(F,O)$, kupletskite, $K_2Na(Mn,Fe^{2+})_7(Ti,Nb)_2Si_8O_{26}(OH)_4F$, kupletskite-(Cs), $(Cs,K)_2Na(Mn,Fe,Li)_7(Ti,Nb)_2Si_8O_{26}(OH)_4F$, niobokupletskite, $K_2Na(Mn,Zn,Fe^{2+})_7(Nb,Zr,Ti)_2Si_8O_{26}(OH)_4(O,F)$, and zircophyllite, $K_2(Na,Ca)(Mn,Fe^{2+})_7(Zr,Nb)_2Si_8O_{26}(OH)_4F$. Recent work on the crystal chemistry of the astrophyllite group includes a crystal-structure refinement of magnesioastrophyllite (Sokolova and Cámara, 2008) and determinations of the crystal structures for Zn-rich kupletskite (Piilonen *et al.*, 2006), and niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite (Cámara *et al.*, 2010). Piilonen *et al.* (2003*b*) and Sokolova and Cámara (2008) emphasized that there are two different topologies of the HOH layer: the first occurs in astrophyllite and all other astrophyllite-group minerals except magnesioastrophyllite, which has a different topology. Cámara *et al.* (2010) suggested writing the general formula of the astrophyllite-group minerals as $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X_{0-1}$ as this (i) preserves the correct formula of the silicate radical in the structure, the (Si_4O_{12}) astrophyllite ribbon, and (ii) identifies the O_2 anion component of the structure as not bonded to Si. In the first publication on the crystal structure of astrophyllite, Peng and Ma (1963) wrote the astrophyllite-ribbon component as $[Si_4O_{12}]_2$. In his discussion of common features for micas, astrophyllite-group minerals and Ti-disilicates of the bafertisite group, Belov (1976) also gave the formula of the astrophyllite ribbon as $[Si_4O_{12}]$. Therefore, the general formula of Cámara *et al.* (2010) is in accord with the original crystal-chemical form of the astrophyllite group. The discovery of four new Fe^{2+}-dominant members of the astrophyllite group, nalivkinite, ideally $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$ (Agakhanov *et al.*, 2008; Uvarova *et al.*, 2008), tarbagataite, ideally $(K\square)CaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_5$ (Stepanov *et al.*, 2012), devitoite, ideally $[Ba_6(PO_4)_2(CO_3)]Fe^{2+}_7Fe^{3+}_2(Si_4O_{12})_2O_2(OH)_4$ (Kampf *et al.*, 2010), and sveinbergeite, ideally $Ca(Fe^{2+}_6Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_5(H_2O)_4$ (Khomyakov *et al.*, 2011) further extends the structural and chemical diversity of the astrophyllite-group minerals. Minerals of the astrophyllite group are listed in Table 1. However, the stoichiometries of devitoite and sveinbergeite cannot be described by a general formula of the form $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X_{0-1}$ (Cámara *et al.*, 2010; modified after Piilonen *et al.*, 2003*a*).

In this paper, I develop a structural hierarchy for the astrophyllite group and write a general formula and individual endmember formulae for the astrophyllite-group minerals. I also address two features of the topology of the HOH layer that are not yet understood: (1) in the O sheet of the HOH layer, the sizes of M octahedra follow the pattern M(1) > M(2) > M(3) > M(4), and (2) the topology of the HOH layer in magnesioastrophyllite is different from that in all other structures of the astrophyllite-group minerals.

The HOH layer in the astrophyllite structure

General topology

In the crystal structure of astrophyllite, the M octahedra (C-group atoms) share edges to form a trioctahedral (O) sheet [Fig. 1*a*; the sample RUS8 (Piilonen *et al.*, 2003*b*) is taken as an example for all references to the astrophyllite structure, including diagrams]. The characteristic feature of the astrophyllite structure is the (T_4O_{12}) astrophyllite ribbon [a branched silicate chain in the terminology of Liebau (1985)] that extends along [100] (Fig. 1*b*). 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*b*, Table 1). The astrophyllite ribbons share common vertices with [6,5]-coordinated D polyhedra to form the heteropolyhedral (H) sheet (Fig. 1*b*). In the H sheet, T tetrahedra and D polyhedra form six-membered rings (five T tetrahedra and a D polyhedron: −T−T−T−T−T−D−) and four-membered rings (two T tetrahedra and two D polyhedra: −T−D−T−D−). The H and O sheets are characterized by a minimal planar cell with *a* ~5.4, *b* ~11.9 Å and **a** ^ **b** ~103° (Table 1, Fig. 1*a*,*b*). Two H sheets and a central O sheet form the HOH layer (Fig. 1*c*,*d*). In the HOH layer, H sheets are identical as they are related by an inversion centre.

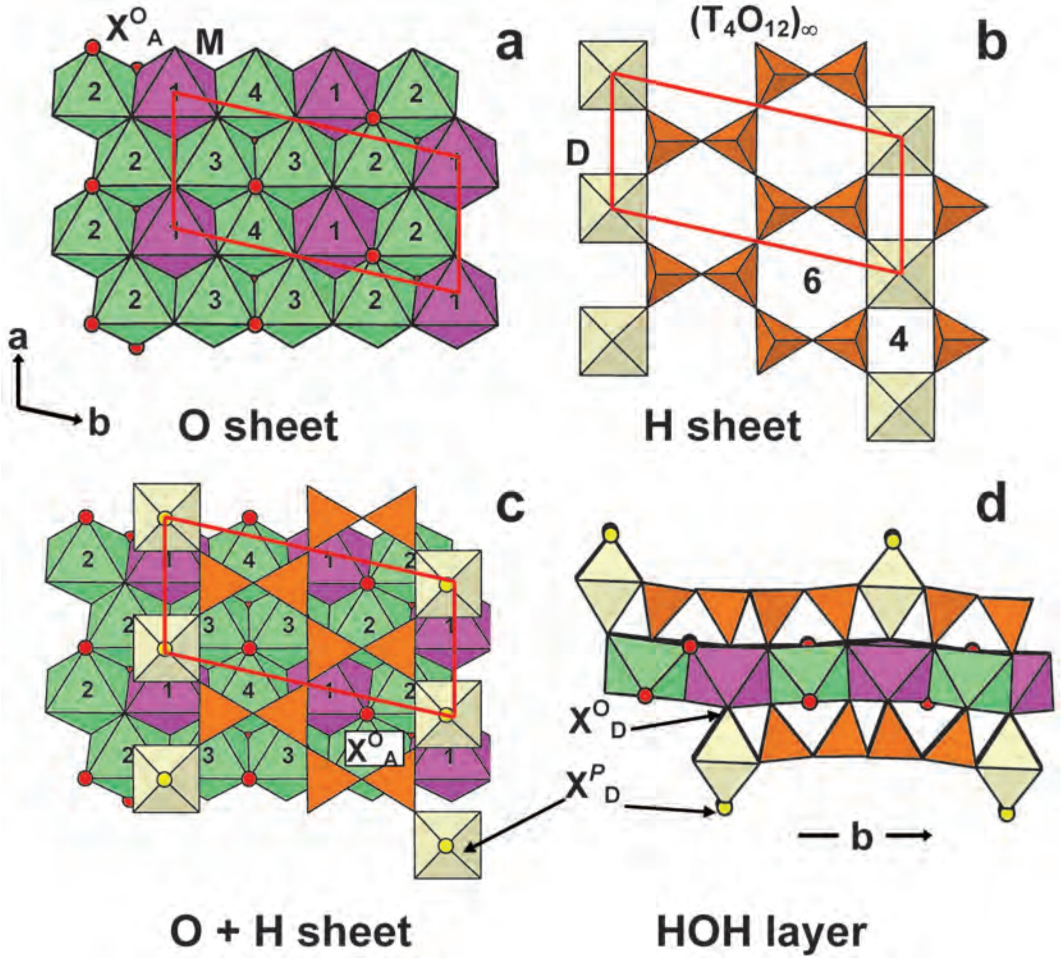

FIG. 1. The HOH layer in the crystal structure of astrophyllite (atom coordinates of sample RUS8 are taken from Piilonen *et al.* (2003*b*), ICSD #17194): (*a*) the O sheet viewed perpendicular to the plane of the sheet, (*b*) the H sheet viewed perpendicular to the plane of the sheet, six-membered rings (–T–T–T–T–T–D–) and four-membered rings (–T–D–T–D–) are labelled 6 and 4, respectively; (*c*) linkage of the O and H sheets, (*d*) the HOH layer 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 red and yellow spheres. In (*a–c*), the unit cell is shown in red.

Cation sites

In the O sheet of the crystal structure of astrophyllite, there are four *M* sites per minimal cell, 2*M*(1) + 2*M*(2) + 2*M*(3) + 1*M*(4), which give a total of M_7 (= C_7) a.p.f.u. (atoms per formula unit) (Fig. 1*a*). In astrophyllite-group minerals, the dominant cations at the *M* sites are mainly Fe^{2+} and Mn^{2+} (Table 2). Other dominant M cations are rare (Table 2): Mg at the *M*(4) site and Na at the *M*(1) site in magnesioastrophyllite, 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 a.p.f.u. The dominant cation at the *D* site (Fig. 1*b*) is mainly $^{[6,5]}$Ti; $^{[6]}$Nb (niobophyllite and niobokupletskite) and $^{[5]}Fe^{3+}$ (devitoite) are less common (Table 2). In

Table 1. Endmember formulae and unit-cell parameters for the astrophyllite-group minerals.

Mineral	Endmember formula	a (Å) α (°)	b (Å) β (°)	c (Å) γ (°)	Space group	Z	Ref.[‡]
Fe^{2+}-dominant members							
Astrophyllite	$K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3754 113.133	11.8970 94.638	11.6634 103.081	$P\bar{1}$	1	(1)
Magnesioastrophyllite	$K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$	5.3327	23.1535 99.615	10.3775	$C2/m$	2	(2)
Niobophyllite	$K_2NaFe^{2+}_7(Nb,Ti)(Si_4O_{12})_2O_2(OH)_4(O,OH)$	5.4022 112.990	11.8844 94.588	11.6717 103.166	$P\bar{1}$	1	(3)
Nalivkinite	$Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.3745 113.325	11.930 94.524	11.651 103.080	$P\bar{1}$	1	(4)
Tarbagataite	$(Ko)CaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_5$	5.3868 112.978	11.9141 94.641	11.7171 103.189	$P\bar{1}$	1	(5)
Sveinbergeite	$Ca(H_2O)(Fe^{2+}_6Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_5(H_2O)_4$	5.329 101.140	11.80 98.224	11.822 102.442	$P\bar{1}$	1	(6)
Devitoite	$Ba_6(PO_4)_2(CO_3)Fe^{2+}_7Fe^{3+}_2(Si_4O_{12})_2O_2(OH)_4$	5.3437 91.337	11.6726 96.757	14.680 103.233	$P\bar{1}$	1	(7)
Mn^{2+}-dominant members							
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	(8)
Kupletskite-2*M*	$K_2NaMn_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$	5.4022	23.226 95.246	21.1782	$C2/c$	4	(8)
Niobokupletskite	$K_2NaMn_7(Nb,Ti)(Si_4O_{12})_2O_2(OH)_4(O,OH)$	5.4303 112.927	11.924 94.750	11.747 103.175	$P\bar{1}$	1	(9)
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	(10)
Zircophyllite*	$K_2NaMn_7Zr_2(Si_4O_{12})_2O_2(OH)_4F$		n.d.		n.d.	n.d.	(11)

* No structural data is available; the abbreviation n.d. means not determined.

[‡] References (the latest and the first references on structure are the first and second entries in the numbered list of references, respectively): (1) Piilonen *et al.* (2003*b*, sample RUS8), Woodrow (1967) and Peng and Ma (1963), model; (2) Sokolova and Cámara (2008), Shi *et al.* (1998); (3) Cámara *et al.* (2010); (4) Uvarova *et al.* (2008); (5) Stepanov *et al.*, 2012; (6) Khomyakov *et al.* (2011); (7) Kampf *et al.* (2010); (8) Piilonen *et al.* (2001), Peng and Ma (1964); (9) Piilonen *et al.* (2000); (10) Cámara *et al.* (2010); (11) Kapustin (1973).

TABLE 2. Ideal chemical compositions of the astrophyllite-group minerals.

	HOH layer								Intermediate (**I**) block		
	O sheet						2H sheets				
Mineral	C_7: 2M(1)	2M(2)	2M(3)	M(4)	$2X^O_D$	$4X^O_A$	2D	nX^P_D	pA_2	rB	Ref.‡
Fe^{2+}-dominant members											
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)
*Magnesioastrophyllite	Na	Fe^{2+}_2	Fe^{2+}_2	Mg_2	O_2	$(OH)_4$	$^{[5]}Ti_2$	□	$^{[10]}K_2$	$^{[8]}Na$	(2)
Niobophyllite	Mn^{2+}_2	Fe^{2+}_2	Fe^{2+}_2	Fe^{2+}	O_2	$(OH)_4$	$(Nb,Ti)_2$	(O,OH)	$^{[13]}K_2$	$^{[10]}Na$	(3)
Nalivkinite	Mn^{2+}_2	Fe^{2+}_2	Fe^{2+}_2	Fe^{2+}	O_2	$(OH)_4$	Ti_2	F	$^{[5]}Li_2$	$^{[10]}Na$	(4)
Tarbagataite	Mn^{2+}_2	Fe^{2+}_2	Fe^{2+}_2	Fe^{2+}	O_2	$(OH)_4$	Ti_2	OH	$^{[12]}(K\square)$	$^{[10]}Ca$	(5)
Sveinbergeite	$(Fe^{2+}_6Fe^{3+})$				O_2	$(OH)_4$	Ti_2	$[OH(H_2O)]$	$(H_2O)_2$	$[^{[9]}Ca(H_2O)]$	(6)
Devitoite	Fe^{2+}_2	Fe^{2+}_2	Fe^{2+}_2	Fe^{2+}	O_2	$(OH)_4$	$^{[5]}Fe^{3+}_2$	$\square_2$	$^{[12]}Ba_2$ $^{[12]}Ba_2$ $(PO_4)_2$	$^{[9-11]}Ba$ $^{[9-11]}Ba$ (CO_3)	(7)
Mn^{2+}-dominant members											
Kupletskite	Mn^{2+}_2	Mn^{2+}_2	Mn^{2+}_2	Mn^{2+}	O_2	$(OH)_4$	Ti_2	F	$^{[12]}K_2$	$^{[10]}Na$	(8)
Niobokupletskite	Mn^{2+}_2	Mn^{2+}_2	Mn^{2+}_2	Mn^{2+}	O_2	$(OH)_4$	$(Nb,Ti)_2$	(O,OH)	$^{[8,9]}K_2$	$^{[10]}Na$	(9)
Kupletskite-(Cs)	Mn^{2+}_2	Fe^{2+}_2	Mn^{2+}_2	Zn	O_2	$(OH)_4$	Ti_2	F	$^{[13]}Cs_2$	$^{[10]}Na$	(10)

X^O and X^P: anions of the O sheet and peripheral anions; 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 of D cations at the periphery of the HOH layer; ( ), [ ] cations and anions are disordered and substitute for each other; coordination numbers (CN) for cations are shown if CN $\neq$ 6.

* For magnesioastrophyllite the O sheet is M(1), 2M(2), 2M(3), 2M(4).

‡References: (1) Piilonen *et al.* (2003*b*, sample RUS8); (2) Sokolova and Cámara (2008); (3) Cámara *et al.* (2010); (4) Uvarova *et al.* (2008); (5) Stepanov *et al.*, 2012; (6) Khomyakov *et al.* (2011); (7) Kampf *et al.* (2010); (8) Piilonen *et al.* (2001); (9) Piilonen *et al.* (2000); (10) Cámara *et al.* (2010).

the minimal cell, there are one *D* site and one minimal repeat of the astrophyllite ribbon (Fig. 1*b*), and the ideal composition of the H sheet is DT_4 a.p.f.u. I write the ideal cation composition of the HOH layer as the sum of the cations of the O sheet and two H sheets: C_7D_2 a.p.f.u., T atoms are considered as part of the complex anion $(T_4O_{12})_2^{8-}$ in the anion part of the structure.

Anion sites

In the astrophyllite structure, O atoms which tetrahedrally coordinate T atoms sum to 24 O a.p.f.u., corresponding to two astrophyllite ribbons (two H sheets). The D polyhedra of two H sheets share two X^O_D anions with M octahedra of the O sheet (for X^O, O superscript defines anions of the O sheet) (Fig. 1*d*), the X^O_D site receives bond-valence contributions from three M^{2+} cations and a D cation, and hence is occupied by an O atom (Table 2), giving $2X^O_D = O_2$ a.p.f.u. There are four anions p.f.u. at the X^O_A sites which occur just under the interstitial *A* sites (Fig. 1*a*,*c*) which receive bond-valence contributions from three M^{2+} cations and are therefore occupied by monovalent anions (Table 2), mainly OH groups and minor F, giving ideally $X^O_{A4} = (OH)_4$ p.f.u. Details of hydrogen bonding involving OH groups at the X^O_A sites are given in Cámara *et al.* (2010). The X^P_D site is occupied by an anion at the periphery of the HOH layer (*P* = *peripheral*) where the D cation is [6]-coordinated (Fig. 1*c*,*d*) [the *X* site in the terminology of Piilonen *et al.* (2003*a*)]. 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 p.f.u. (Table 2). I write the anion composition of the HOH layer as $(T_4O_{12})_2X^O_{D2}X^O_{A4}X^P_{Dn}$, 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 linkage between the HOH layers in a structure (see below).

General formula

I write the composition of the HOH layer 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 = $^{[6]}(Fe^{2+}, Mn, Fe^{3+}, Na, Mg$ or Zn); D = $^{[6,5]}(Ti, Nb, Zr, Fe^{3+})$; T = Si, minor Al; X are anions: X^O_D 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. OH, F, H_2O, O, with n = 0, 1, 2. For astrophyllite, the ideal composition of the HOH layer is $[Fe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F]^{3-}$ (Table 2).

Linkage of HOH layers: the intermediate (I) block

I divide all structures of the astrophyllite-group minerals into two types on the basis of the type of linkage of the HOH layers: (1) HOH layers link directly where they share common vertices of D octahedra, and (2) HOH layers do not link directly via polyhedra of the H sheets.

Type 1

The HOH layers link directly where they share common vertices of D octahedra, X^P_D anions, forming Ti–F–Ti bridges as in astrophyllite (Fig. 2*a*). This type of linkage of HOH layers occurs in astrophyllite, niobophyllite, nalivkinite, tarbagataite, kupletskite, niobokupletskite and kupletskite-(Cs). The type-1 structures belong to the *astrophyllite* structure type with space group $P\bar{1}$ (or space group $C2/c$ in kupletskite-2*M*, Table 1). In the intermediate space between two HOH layers, cations at two interstitial sites, *A* and *B*, constitute a layer of the form A_2B. I name this layer an *intermediate* (**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; other dominant species are as follows: ^{A}Li (nalivkinite), ^{A}Cs [kupletskite-(Cs)] and ^{B}Ca (tarbagataite) (Table 2). A review of cation disorder at the *A* site is given by Cámara *et al.* (2010).

Type 2

The HOH layers do not link directly via polyhedra of the H sheets. The type-2 structure occurs in magnesioastrophyllite, sveinbergeite and devitoite. In magnesioastrophyllite, 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. 2*b*). In astrophyllite and magnesioastrophyllite, the geometry of the **I** block is identical: the *A* and *B* sites are centred above six-membered rings (–T–T–T–T–D–) and four-membered rings of polyhedra (–T–D–T–D–) in the H sheet, respectively (Fig. 2*c*). In sveinbergeite, the **I** block (m = 1) is

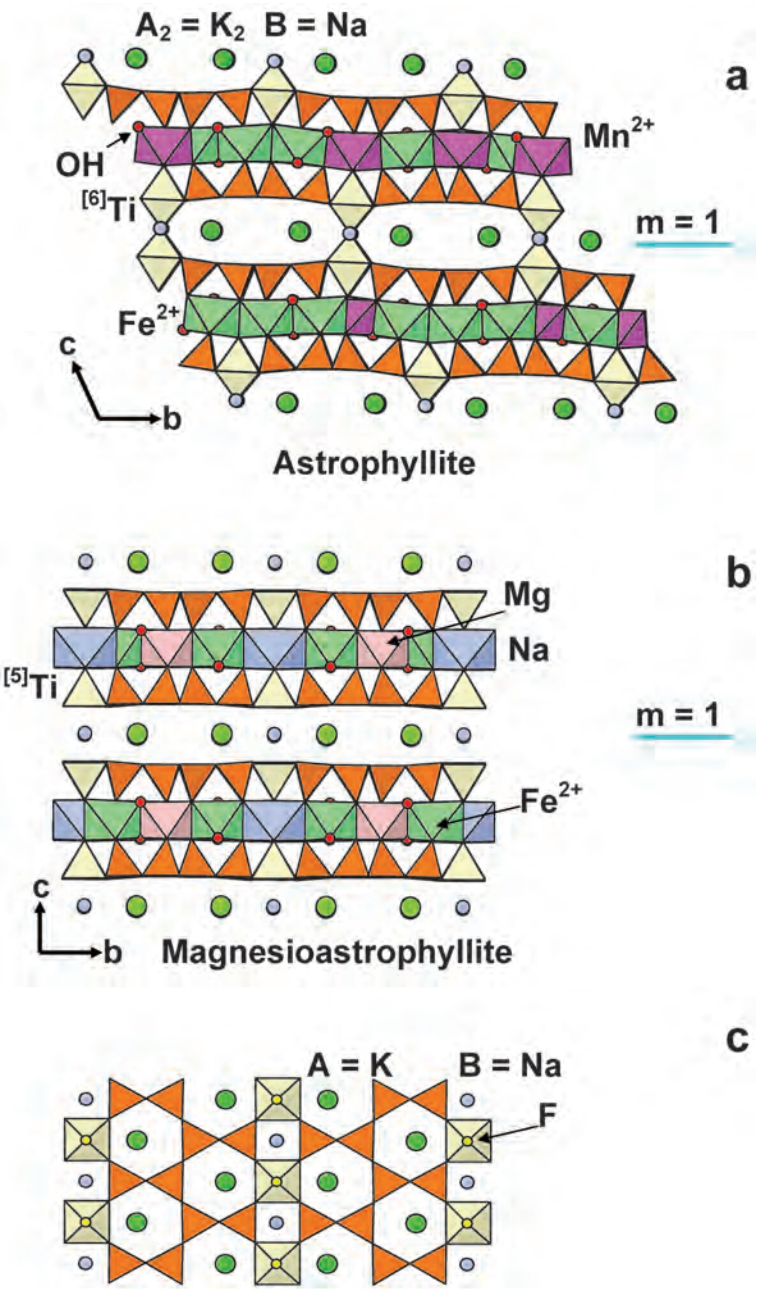

FIG. 2. General view of the crystal structures of (*a*) astrophyllite, (*b*) magnesioastrophyllite and (*c*) the position of the *A* and *B* sites with regard to the H sheet in astrophyllite. The Mn- and Fe^{2+}-dominant octahedra are magenta and green. The T(=Si) tetrahedra and D(=Ti,Nb) octahedra are orange and pale yellow. The OH groups and F atoms at the X_A^O and X_D^P sites are shown as red and yellow spheres. The Na and Mg-dominant octahedra are navy blue and pink; K and Na atoms at the *A* and *B* sites are shown as green and blue spheres. The position of the intermediate layer (m = 1, where m is a number of intermediate layers) is shown by a turquoise line.

characterized by both cation and anion disorder (Fig. 3*a*) (Khomyakov *et al.*, 2011). The *A* site is occupied mainly by H_2O groups, giving ideally $(H_2O)_2$ p.f.u. (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 $[Ca(H_2O)]$ p.f.u. Short-range order of Ca and H_2O at the *B*(1,2) sites affects the composition of the X^P_D site, ideally $[(OH)(H_2O)]$ p.f.u. The ideal composition of the **I** block in sveinbergeite is the sum of the *A* (2 a.p.f.u.) and *B* (2 a.p.f.u.) sites: $(H_2O)_2 + [Ca(H_2O)] = Ca(H_2O)_3$ p.f.u. (Table 2). Devitoite is the only known mineral with the astrophyllite-type HOH layer where [5]-coordinated *D* sites are occupied by Fe^{3+} (Kampf *et al.*, 2010) (Table 2). In the devitoite structure, HOH layers alternate with **I** blocks along [001] (Fig. 3*b*). In the **I** block, 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 (Figs 3*b* and 2*c*). In the peripheral layer of the **I** block in devitoite, the *A* and *B* sites are occupied by Ba, giving 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) tetrahedra and (CO_3) groups, giving $(PO_4)_2(CO_3)$ p.f.u. The ideal composition of the **I** block in devitoite is the sum of the two peripheral layers and the central layer: $2 \times Ba_3 + (PO_4)_2(CO_3) = Ba_6(PO_4)_2(CO_3)$ p.f.u.

General and individual endmember formulae for the astrophyllite-group minerals

The general formula of the astrophyllite-group minerals of the form $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X_{0-1}$ (Cámara *et al.*, 2010; modified after Piilonen *et al.*, 2003*a*) describes the stoichiometry of all eight astrophyllite-group minerals, astrophyllite, niobophyllite, nalivkinite, tarbagataite, kupletskite, niobokupletskite, kupletskite-(Cs) and magnesioastrophyllite, but not for devitoite, ideally $[Ba_6(PO_4)_2(CO_3)]Fe^{2+}_7Fe^{3+}_2(Si_4O_{12})_2O_2(OH)_4$, and sveinbergeite, ideally $Ca(Fe^{2+}_6Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_5(H_2O)_4$, which differ in the stoichiometries of the intermediate block $[Ba_6(PO_4)_2(CO_3)]$ (devitoite) and $Ca(H_2O)_3$ (sveinbergeite) (cf. A_2B in the general formula above).

To incorporate devitoite and sveinbergeite into the astrophyllite group, I propose writing the composition of the **I** block in the astrophyllite-group minerals as $A_{2p}B_rI$, where p is the number of layers of the form A_2B and is equal to 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, i.e. $(PO_4)_2(CO_3)$ in devitoite. For astrophyllite, the ideal composition of the **I** block is $[K_2Na]^{3+}$ ($A_2 = K_2$, p = 1; B_r = Na, r = 1) (Table 2). I combine general formulae for the HOH layer, $C_7D_2(T_4O_{12})_2X^O_{D2}X^O_{A4}X^P_{Dn}$, and the **I** block, $A_{2p}B_rI$, into a general formula for the extended astrophyllite group including devitoite and sveinbergeite:

$$A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn},$$

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 = O, OH, F and H_2O; n = 0, 1, 2.

For astrophyllite, an endmember formula is of the form $A_2BC_7D_2(T_4O_{12})_2O_2(OH)_4X$: $K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$. Individual endmember formulae are given in Table 3.

Understanding the linkage of O and H sheets

In the astrophyllite-group structures, the periodicity of the H sheet has to match the periodicity of the O sheet in order to form the HOH layer. This restriction is a major constraint on the chemical variability of both O and H sheets.

Articulation of the astrophyllite ribbon

As the geometry of the astrophyllite ribbon is controlled by the stereochemistry of Si, I will discuss the Si_4O_{12} (not T_4O_{12}) ribbon. The minimal repeat of the astrophyllite ribbon is defined by two Si_2O_7 groups oriented perpendicular to [100] (Fig. 1*b*), which I designate as *basic* Si_2O_7 groups. For a better understanding of the articulation of the astrophyllite ribbon, I also designate a *connecting* Si_2O_7 group, which is composed of two adjacent SiO_4 tetrahedra of two basic groups. Connecting Si_2O_7 groups form a chain along [100] (Fig. 1*b*). Consider the effective size of an Si_2O_7 group in astrophyllite and in magnesioastrophyllite, two structures that have different topologies of the HOH layer. The size of an Si_2O_7 group in the H and O sheets can be defined as the $(O-O)^H$ and $(O-O)^O$ separations,

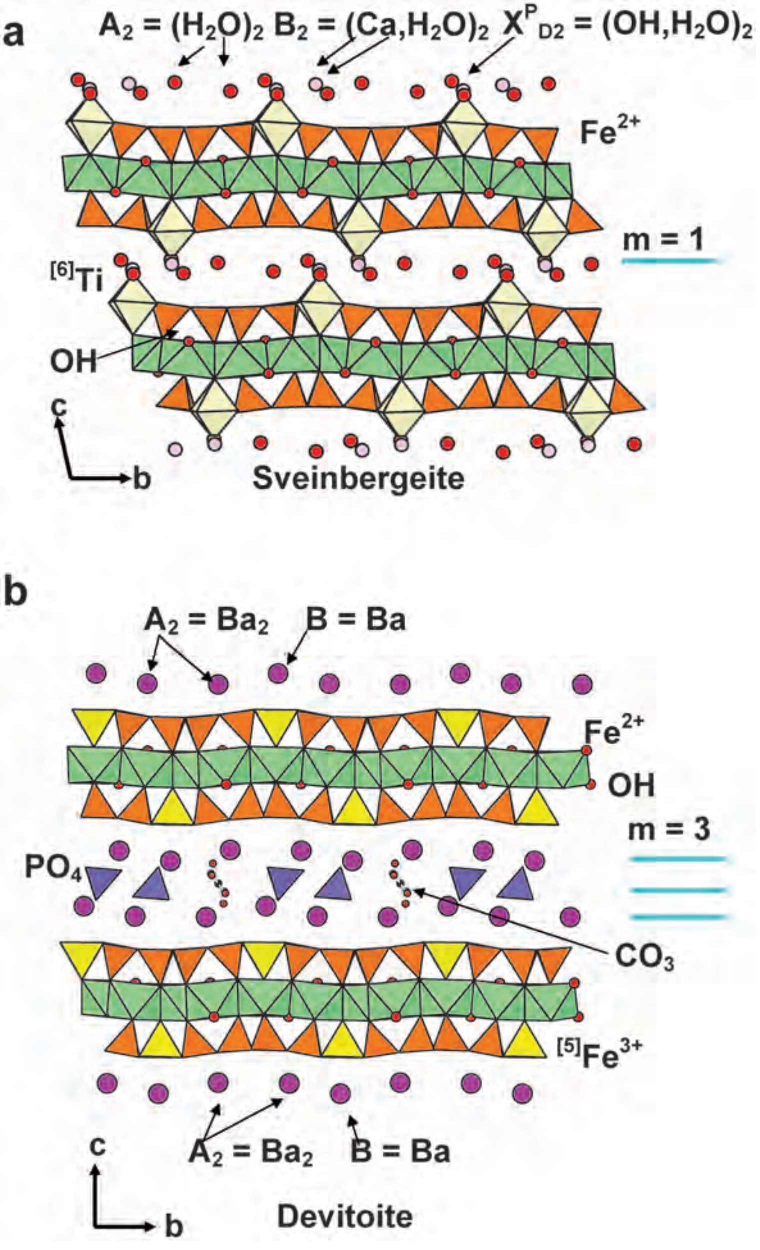

FIG. 3. General view of the crystal structures of (*a*) sveinbergeite and (*b*) devitoite. The T(=Si) tetrahedra and D(=Ti,Nb) octahedra are orange and pale yellow. The [5]-coordinated Fe^{3+} polyhedra are yellow; Ca (at the *B* site in sveinbergeite) and Ba (at the *A* and *B* sites in devitoite) atoms and H_2O groups (at the *A*, *B* and X_D^P 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 sveinbergeite and the three intermediate layers in devitoite are shown by turquoise lines.

TABLE 3. Endmember formula of the form $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^P_{Dn}$ for the astrophyllite-group minerals.

Mineral	Endmember formula								p	r	n
	A_2	**B**	**C_7**	**D_2**	**$(T_4O_{12})_2$**	**X^O_{D2}**	**X^O_{A4}**	**X^P_D**	1	1	1
Astrophyllite	K_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F			
Niobophyllite	K_2	Na	Fe^{2+}_7	$(Nb,Ti)_2$	$(Si_4O_{12})_2$	O_2	$(OH)_4$	(O,OH)			
Nalivkinite	Li_2	Na	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F			
Tarbagataite	(K□)	Ca	Fe^{2+}_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	(OH)			
Kupletskite	K_2	Na	Mn^{2+}_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F			
Niobokupletskite	K_2	Na	Mn^{2+}_7	$(Nb,Ti)_2$	$(Si_4O_{12})_2$	O_2	$(OH)_4$	(O,OH)			
Zircophyllite*	K_2	Na	Mn^{2+}_7	Zr_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F			
Kupletskite-(Cs)	Cs_2	Na	Mn^{2+}_7	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	F			
	A_2	**B**	**C_7**	**D_2**	**$(T_4O_{12})_2$**	**X^O_{D2}**	**X^O_{A4}**		1	1	0
Magnesioastrophyllite	K_2	Na	$(Fe^{2+}_4Mg_2Na)$	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$				
	A_2	**B_2**	**C_7**	**D_2**	**$(T_4O_{12})_2$**	**X^O_{D2}**	**X^O_{A4}**	**X^P_{D2}**	1	2	2
Sveinbergeite	$(H_2O)_2$	$[Ca(H_2O)]$	$(Fe^{2+}_6Fe^{3+})$	Ti_2	$(Si_4O_{12})_2$	O_2	$(OH)_4$	$[(OH)(H_2O)]$			
	A_4	**B_2**	**C_7**	**D_2**	**$(T_4O_{12})_2$**	**I**	**X^O_{D2}**	**X^O_{A4}**	2	2	0
Devitoite	Ba_4	Ba_2	Fe^{2+}_7	Fe^{3+}_2	$(Si_4O_{12})_2$	$(PO_4)_2(CO_3)$	O_2	$(OH)_4$			

* Possible endmember formula as the crystal structure has not yet been refined.

respectively (Sokolova, 2006) (Fig. 4*a*). The relation between the $(O{-}O)^H$ and $(O{-}O)^O$ separations of an Si_2O_7 group is very important as they reflect periodicities of the O and H sheets that must match in order to form the HOH layer. For astrophyllite (Fig. 4*b*) and magnesioastrophyllite (Fig. 4*c*), the Si−O−Si angles for the basic Si_2O_7 groups are ~143° and ~139°, and for connecting Si_2O_7 groups, they are ~139° and ~138°, respectively. It is notable that the Si_2O_7 groups in the astrophyllite ribbon have a very restricted range of Si−O−Si angles, 143−138°, particularly when compared to the Si_2O_7 groups in the Ti-silicate minerals with the TS (titanium silicate) block which have a wider range of Si−O−Si angles, varying from ~206 to ~134° (Sokolova, 2006). In the astrophyllite structure, the mean effective size of an Si_2O_7 group in the H and O sheets varies from 4.48 to 4.56 Å and 3.10 to 3.27 Å, respectively (Fig. 4*b*). In the magnesioastrophyllite structure, the effective size of an Si_2O_7 group in the H and O sheets varies from 4.49 to 4.52 Å and 3.06 to 3.14 Å, respectively (Fig. 4*c*). In the H sheet, the effective size of a basic Si_2O_7 group is smaller (4.48 Å in astrophyllite and 4.49 Å in magnesioastrophyllite) than that of a connecting Si_2O_7 group (4.56 Å in astrophyllite and 4.52 Å in magnesioastrophyllite). In the O sheet, the effective size of a basic Si_2O_7 group is larger (3.27 Å in astrophyllite and 3.14 Å in magnesioastrophyllite) than that of a connecting Si_2O_7 group (3.10 Å in astrophyllite and 3.06 Å in magnesioastrophyllite). Therefore in the astrophyllite-group structure, the larger size of an Si_2O_7 group in the H sheet corresponds to the smaller size of an Si_2O_7 group in the O sheet, e.g. in astrophyllite: ${}^{H}4.48$ Å → ∠143° → ${}^{O}3.27$ Å (basic Si_2O_7) and ${}^{H}4.56$ Å → ∠139° → ${}^{O}3.10$ Å (connecting Si_2O_7). This pattern follows that for Ti silicates of Group II: ${}^{H}4.23$ Å → 141° → ${}^{O}3.42$ Å (Sokolova, 2006).

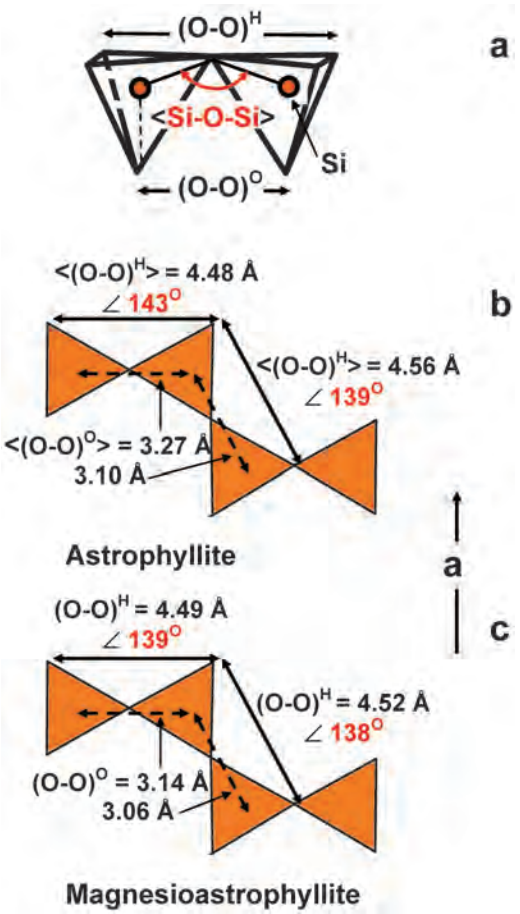

FIG. 4. Articulation of the astrophyllite ribbon: (*a*) the geometry of the Si_2O_7 group, with the $(O{-}O)^H$ and $(O{-}O)^O$ anion separations defining its effective size in the H and O sheets, respectively [after Sokolova (2006): fig. 33*c*]; the astrophyllite ribbon in (*b*) astrophyllite and (*c*) magnesioastrophyllite. In (*a*) Si atoms are shown as orange spheres; in (*b*,*c*) SiO_4 tetrahedra are orange; the $(O{-}O)^H$ and $(O{-}O)^O$ anion separations are shown as black double-headed arrows and dashed lines, respectively; the ∠Si−O−Si is given in red for each Si_2O_7 group (see text).

To summarize, the sizes of Si_2O_7 groups do not vary significantly in two structures with different topologies of the HOH layer, astrophyllite and magnesioastrophyllite, and hence the periodicity of the astrophyllite ribbon is practically identical in all astrophyllite-group structures.

The periodicity of the H sheet

The H sheet is composed of D polyhedra and astrophyllite ribbons (Figs 1*b*,*c*, and 2*c*) and its size is defined by the size of these two components. The periodicity of the astrophyllite ribbon is practically identical in all astrophyllite-group structures (see above). The size of the D polyhedron can be described by the length of its edge in the plane of the H sheet. For [6]-coordinated Ti and Nb (*r* = 0.605 and 0.64 Å; Shannon, 1976) and [5]-coordinated Ti and Fe^{3+} (*r* = 0.51 and 0.58 Å), the size of that edge varies from 2.70 and 2.84 to 2.67 and

2.69 Å, respectively. Hence, the size of the D polyhedron does not vary greatly. As the sizes of the astrophyllite ribbon and the D polyhedron do not vary significantly, the size of the H sheet is almost identical in all astrophyllite-group structures.

In the H sheet (astrophyllite), there are two important types of Si–Si distances perpendicular to [100]: 3.09 Å (within the basic Si_2O_7 group) and 3.96 Å (two SiO_4 tetrahedra in the four-membered –Si–D–Si–D– ring) (Fig. 5*a*). For a connecting Si_2O_7 group, Si–Si = 3.07 Å. As all SiO_4 tetrahedra share common anions with the M octahedra of the O sheet, specific anion separations in the O sheet must correspond to the anion separations related to the Si–Si distances in the H sheet.

Sizes of the M octahedra: M(1) > M(2) > M(3) > M(4)

In the astrophyllite-group structures, the sizes of the M octahedra follow the pattern M(1) > M(2) > M(3) > M(4) (Piilonen *et al*., 2003*b*). In the crystal structure of astrophyllite (RUS8), <M(1)–O> = 2.195 Å, <M(2)–O> = 2.159 Å, <M(3)–O> = 2.145 Å, <M(4)–O> = 2.127 Å (Piilonen *et al*., 2003*b*). In the HOH layer of astrophyllite, all M octahedra in the O sheet share at least one edge with an Si_2O_7 group of the H sheet (Fig. 5*a*). The M(1) and M(3) octahedra share one edge with a smaller connecting Si_2O_7 group of an astrophyllite ribbon (shown by dashed lines in Fig. 5*b*): $(O-O)^O$ = 3.12 Å [M(1)] and 3.09 Å [M(3)]. The M(2) and M(4) octahedra share one and two edges, respectively, with a larger basic Si_2O_7 group of an astrophyllite ribbon (Fig. 5*b*): $(O-O)^O$ = 3.27 Å [M(2)] and 2 × 3.24 Å [M(4)]. The M(1) octahedron and M(2,3) octahedra share two edges and one edge with a DO_6 octahedron and an SiO_4 group (shown by dotted lines in Fig. 5*b*). These edges are 3.25 Å [M(1)] and 3.20 Å [M(2,3)] long, respectively; they are compatible with $(O-O)^O$ for basic Si_2O_7 groups (3.24 and 3.27 Å) and larger than $(O-O)^O$ for connecting Si_2O_7 groups (3.09 and 3.12 Å). Hence the M(1–3) octahedra exhibit different types of linkage with the two H sheets and the sizes of their *trans* edges, shared with those H sheets (they are oriented perpendicular [100]), are different: 3.19 and 3.55 Å for M(1), 3.27 and 3.42 Å for M(2) and 3.20 and 3.36 Å for M(3) (the positions of *trans* edges are shown as horizontal black lines in Fig. 5*b*).

The M(4) octahedron shares two *trans* edges with Si_2O_7 groups of the two H sheets, the *trans* edges shared with Si_2O_7 groups contract to 3.24 Å (Fig. 5*b*), and M(4) is the smallest octahedron, <M(4)–O> = 2.127 Å.

The M(1) cation shares two anions with Si atoms, and the corresponding *trans* edge is 3.55 Å in length (Fig. 5*a*,*b*). The M(1) octahedron is the largest in the structure, <M(1)–O> = 2.195 Å, as in the O sheet, it provides the largest anion separation (3.55 Å) to match the periodicity of the H sheet, i.e. apical O atoms of two SiO_4 tetrahedra of the four-membered –Si–D–Si–D– ring (Si–Si = 3.96 Å) (Fig. 5*a*).

The M(2,3) octahedra are medium-sized, and the M(3) octahedron is smaller than the M(2) octahedron, <M(3)–O> = 2.145 *vs*. <M(2)–O> = 2.159 Å. The topology of linkage of the M(2) and M(3) octahedra to one H sheet is identical: each octahedron shares an edge of 3.20 Å with a DO_6 octahedron and an SiO_4 group, with adjacent *trans* edges of 3.42 and 3.36 Å, respectively. There is a slight difference in the linkage of the M(2) and M(3) octahedra to the other H sheet: the M(2) octahedron shares an edge with a basic Si_2O_7 group [$(O-O)^O$ = 3.27 Å], and the M(3) octahedron shares an edge with a connecting Si_2O_7 group [$(O-O)^O$ = 3.09 Å] (Fig. 5*b*). Above, I showed that in the O sheet of the astrophyllite-group structures, the connecting Si_2O_7 group has a shorter anion separation than the basic Si_2O_7 group (Fig. 4*b*,*c*). Linkage of the M(3) and M(2) octahedra to connecting and basic Si_2O_7 groups results in a shorter *trans* edge adjacent to the connecting Si_2O_7 group for the M(3) octahedron, 3.20 Å, and a longer *trans* edge shared with a basic Si_2O_7 group for the M(2) octahedron, 3.27 Å (Fig. 5*b*,*c*). Hence, due to linkages to a basic Si_2O_7 group and a connecting Si_2O_7 group, the M(2) octahedron is larger than the M(3) octahedron: [<M(2)–O> = 2.159 Å] > [<M(3)–O> = 2.145 Å].

To conclude, the sizes of the M octahedra in the O sheet follow the pattern M(1) > M(2) > M(3) > M(4) due to the different linkage of M octahedra to the polyhedra of the H sheets*. To maintain linkage of the O and H sheets, the M octahedra distort. Figure 5*c* shows two rows of octahedra of the O sheet and a corresponding fragment of the H

---

* The *M*(1) > *M*(2) > *M*(3) > *M*(4) pattern does not occur in sveinbergeite and devitoite.

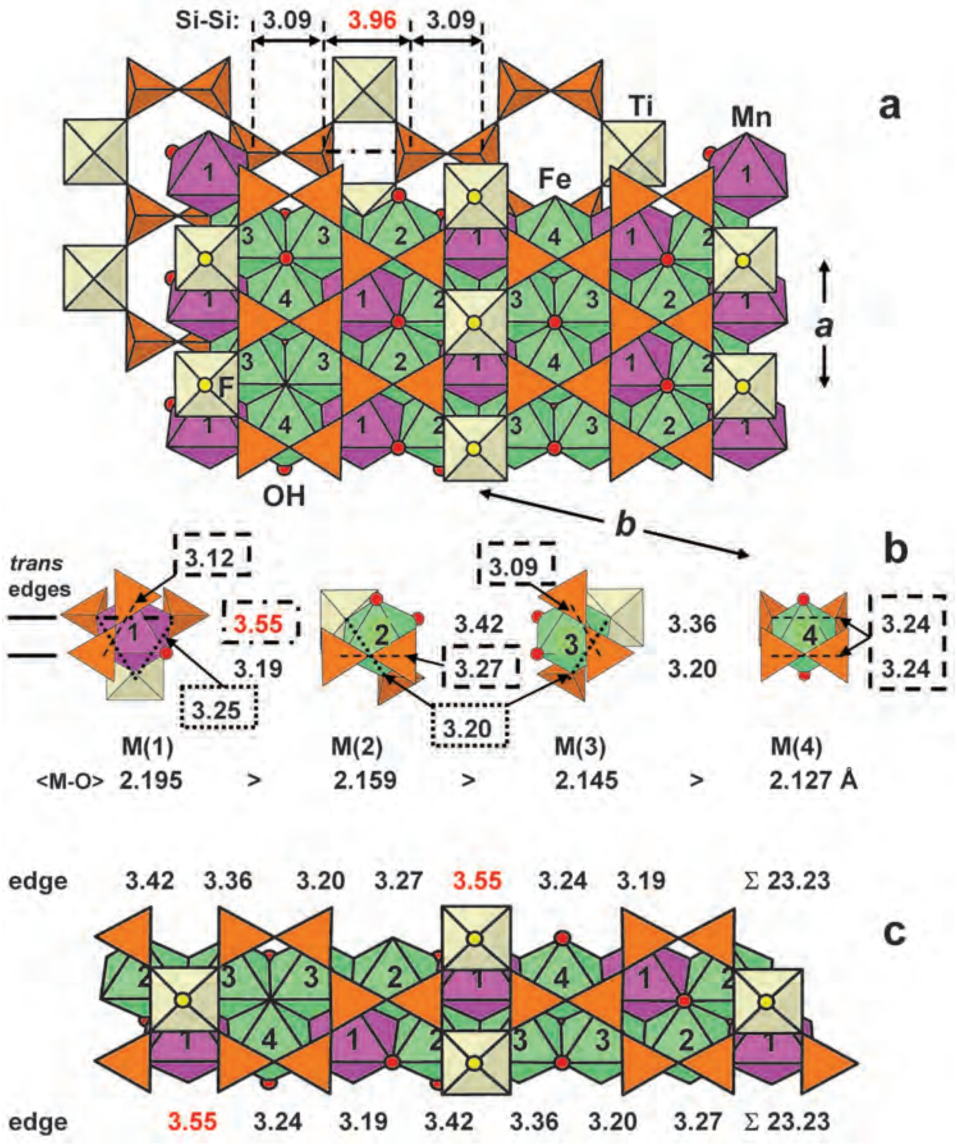

FIG. 5. Details of the topology of the HOH layer in the crystal structure of astrophyllite: (*a*) the HOH layer viewed perpendicular to the plane of the layer; (*b*) linkage of the individual M(1−4) octahedra in the O sheet to the polyhedra in the H sheets; in (*b*), the mean bond-length <M−O> (Å) is given below each polyhedron, lengths of *trans* edges of M octahedra oriented perpendicular to [100] (Å) are given to the right of each M octahedron, edges of M octahedra shared with an Si_2O_7 group are shown by dashed lines, and corresponding $(O-O)^O$ anion separations (Å) are given in a dashed frame, edges of M octahedra shared with a D octahedron and an SiO_4 group are shown by dotted lines and their lengths (Å) are given in a dotted frame, an edge of the M(1) octahedron linking to two Si tetrahedra of the four-membered ring (−Si−D−Si−D−) is shown by a dot−dash line and its length (Å) is given in red; (*c*) linkage of seven M octahedra in two rows in the O sheet (from left to right in the upper row: 2-3-3-2-1-4-1; lower row: 1-4-1-2-3-3-2) and polyhedra of the H sheet, sizes of horizontal edges of M octahedra are given only for one side of the O sheet. 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 red and yellow spheres.

sheet. Each row has a repeat of seven octahedra: 2-3-3-2-1-4-1 from left to right in the upper row and 1-4-1-2-3-3-2 in the lower row. As the H sheets are identical, both sides of the O sheet must be the same size to match the H sheet. This requirement is satisfied where each of the M(1–3) octahedra exhibits two types of linkage and shares two edges of different length with each H sheet. For example, in the lower row, one M(1) octahedron (first from the left) shares two vertices with two SiO_4 tetrahedra of the four-membered –Si–D–Si–D– ring, and the corresponding horizontal edge is 3.55 Å; another M(1) octahedron (third from the left) shares one edge with an Si_2O_7 group, with a corresponding horizontal edge of 3.19 Å. Horizontal edges of seven M octahedra in each row, 2M(1), 2M(2), 2M(3) and M(4), sum to ~23.23 Å. In the H sheet, four Si_2O_7 groups [defined by $(O–O)^H$ = 4.48 Å, see above] and edges of two D octahedra (2.71 Å) (Fig. 2*c*), sum to 23.34 Å.

Topology of the HOH layer in magnesioastrophyllite

Magnesioastrophyllite, ideally $K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$, is monoclinic, space group *C*2/*m* (Sokolova and Cámara, 2008). In the H sheet, the [5]-coordinated *D* site is occupied by Ti. In the O sheet, the *M*(1) site is fully occupied by Na, the *M*(2), *M*(3) and *M*(4) sites are occupied by (Fe^{2+} > Mn), (Fe^{2+} > Mg) and (Mg > Fe^{2+}), respectively (Fig. 6*a*, Table 2). Magnesioastrophyllite is the only mineral of the astrophyllite group where a site in the O sheet is fully occupied by Na, giving 1 Na a.p.f.u. Piilonen *et al.* (2003*a*,*b*) showed that in all other astrophyllite-group minerals, the Na content at the *M*(1) site in the O sheet varies from 0.02 to 0.60 a.p.f.u. (excluding sample RUS6 from Khibina, where the Na content in the O sheet is 1 a.p.f.u., with Mg = 1.90 a.p.f.u., which is probably a magnesioastrophyllite). Note that the *M*(1) site in magnesioastrophyllite (1 a.p.f.u.) does not correspond to the *M*(1) site in astrophyllite (2 a.p.f.u). In magnesioastrophyllite, the H sheets link to the O sheet such that each M octahedron has identical linkage with polyhedra of the two H sheets, and their horizontal *trans* edges are the same length: 3.80 Å for M(1) > 3.43 Å for M(2) > 3.14 Å for M(3) > 3.12 Å for M(4) (Fig. 6*b*). Only two octahedra, M(3) and M(4), share edges with Si_2O_7 groups (Fig. 6*b*). The M(1) cation shares four anions with Si atoms of four SiO_4 tetrahedra belonging to two four-membered –Si–D–Si–D– rings, with *trans* edges of 3.80 Å (Fig. 6*a*,*b*). The M(1) octahedron is the largest, <M(1)–O> = 2.372 Å, as it provides the largest anion separation in the O sheet (3.80 Å) to match the longest Si–Si distance of 3.96 Å. The M(3,4) octahedra are small, and the M(4) octahedron is smaller than the M(3) octahedron: <M(4)–O> = 2.094 *vs*. <M(3)–O> = 2.113 Å. The M(3) octahedron shares two edges with basic Si_2O_7 groups [$(O–O)^O$ = 3.14 Å], and the M(4) octahedron shares two edges with connecting Si_2O_7 groups [$(O–O)^O$ = 3.06 Å] (Fig. 6*b*). In the O sheet, the connecting Si_2O_7 group has a shorter anion separation than the basic Si_2O_7 group (3.06 *vs*. 3.14 Å). Linkage of the M(4) and M(3) octahedra to connecting and basic Si_2O_7 groups results in shorter *trans* edges adjacent to the connecting Si_2O_7 group for the M(4) octahedron, 3.12 Å, and slightly longer *trans* edges shared with basic Si_2O_7 groups for the M(3) octahedron, 3.14 Å (Fig. 6*b*,*c*). Hence, due to linkages to basic and connecting Si_2O_7 groups, the M(3) octahedron is slightly larger than the M(4) octahedron, [<M(3)–O> = 2.113 Å] > [<M(4)–O> = 2.094 Å].

The M(2) octahedron is larger than the M(3,4) octahedra as it does not share edges with (Si_2O_7) groups. Hence in the magnesioastrophyllite structure, the sizes of the M octahedra follow the pattern M(1) > M(2) > M(3) > M(4): <M(1)–O> = 2.372 Å, <M(2)–O> = 2.166 Å, <M(3)–O> = 2.113 Å, <M(4)–O> = 2.094 Å as in other astrophyllite-group structures. Note that the *M*(1–4) sites in astrophyllite do not correspond to the *M*(1–4) sites in magnesioastrophyllite.

Figure 6*c* shows two rows of octahedra of the O sheet and a corresponding fragment of the H sheet. These two rows are related by an inversion centre at (¼,½,0) which occurs in the middle of the edge between two M(4) octahedra in an M(4) chain. Horizontal edges of seven M octahedra in each row, M(1), 2M(2), 2M(3) and 2M(4), sum to ~23.18 Å (cf. 23.23 Å for astrophyllite RUS8). In the H sheet, four Si_2O_7 groups [defined by $(O–O)^H$ = 4.49 Å, Fig. 4*c*] and edges of two D semi-octahedra (2.67 Å) (Fig. 6*c*), sum to 23.30 Å (cf. 23.34 Å for astrophyllite RUS8).

Different topology of the HOH layer in magnesioastrophyllite and all other structures of the astrophyllite group

Above, I showed that (1) the periodicity of the H sheet is approximately the same in all structures

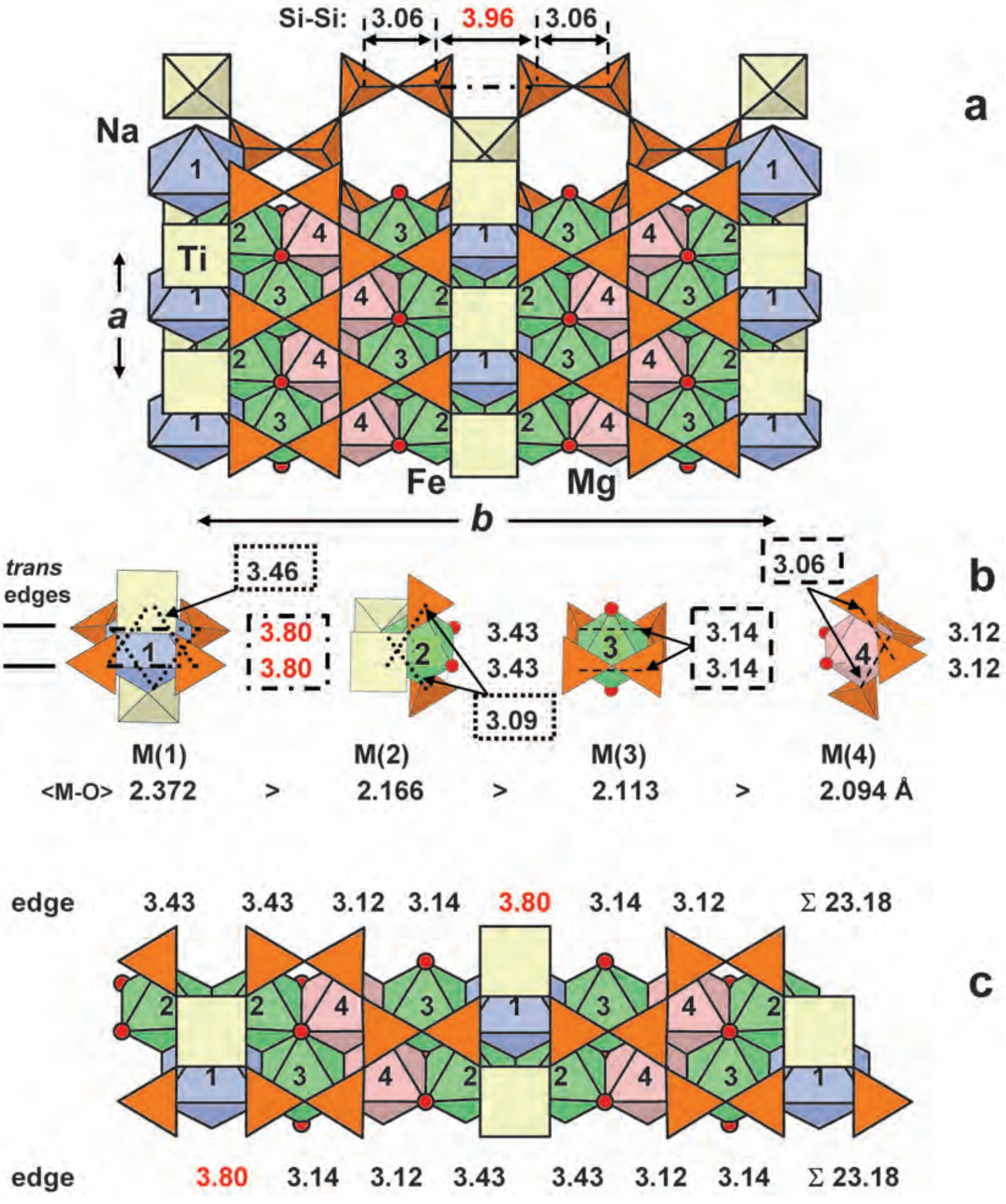

FIG. 6. Details of the topology of the HOH layer in the crystal structure of magnesioastrophyllite: (*a*) the HOH layer viewed perpendicular to the plane of the layer; (*b*) linkage of the individual M(1–4) octahedra in the O sheet to the polyhedra in the H sheets; (*c*) linkage of seven M octahedra in two rows in the O sheet (from left to right in the upper row: 2-2-4-3-1-3-4; lower row: 1-3-4-2-2-4-3) and polyhedra of the H sheet, sizes of horizontal edges of M octahedra are given only for one side of the O sheet. The Fe^{2+}-dominant octahedra are green. The T(=Si) tetrahedra and D(=Ti,Nb) octahedra are orange and pale yellow. The OH groups and F atoms at the X_A^O and X_D^P sites are shown as red and yellow spheres. The Na and Mg octahedra are navy blue and pink.

of the astrophyllite group (Fig. 4), and (2) the periodicity of the O sheet is approximately the same for astrophyllite and magnesioastrophyllite (Figs 5*c* and 6*c*). However, the topologies of the HOH layer in astrophyllite, ideally $K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$, and magnesioastrophyllite, ideally $K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$, are different. In astrophyllite (and all other

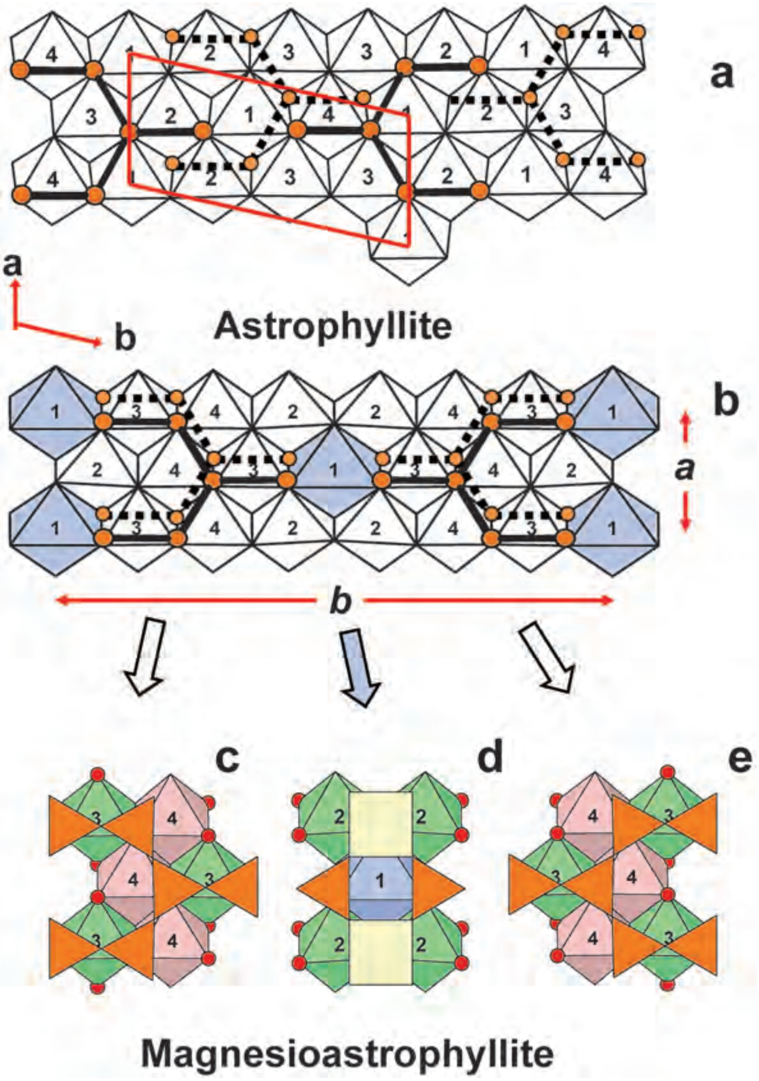

FIG. 7. Linkage of astrophyllite ribbons and M polyhedra of the O sheet in (*a*) astrophyllite and (*b*) magnesioastrophyllite; specific structural fragments of the O sheet for magnesioastrophyllite are given in (*c–e*): (*c*) a convoluted ribbon of M octahedra linking to the astrophyllite ribbon along [100] (left), (*d*) M(1) and M(2) octahedra, (*e*) a convoluted ribbon of M octahedra linking to the astrophyllite ribbon along [100] (right). The legend for (*a*,*b*) is as follows: astrophyllite ribbons in the H sheets above and below the plane of the O sheet are shown as Si atoms (orange spheres) connected by solid black lines and Si atoms (smaller orange spheres) connected by dashed black lines, respectively; M^{2+}-dominant M octahedra are white, Na octahedra are blue; for astrophyllite, the unit cell is shown by red lines. The legend for (*c–e*) is as follows: the Fe^{2+}-dominant octahedra are green; the T(=Si) tetrahedra and D(=Ti,Nb) octahedra are orange and pale yellow; the Na and Mg octahedra are navy blue and pink. The arrows relate structure fragments (*c–e*) to the general structure of magnesioastrophyllite (*b*).

astrophyllite-group structures, except for magnesioastrophyllite), H sheets link to the O sheet such that each M octahedron shares at least one edge with an Si_2O_7 group of the astrophyllite ribbon (Fig. 7*a*). In magnesioastrophyllite, H sheets link to the O sheet such that Si_2O_7 groups of the astrophyllite ribbon share edges only with M(3,4) octahedra (Fig. 7*b*), which I designate as a convoluted ribbon of M(3,4) octahedra (Figs 6*a* and 7*c*,*e*).

In magnesioastrophyllite, the *M*(1) site is fully occupied by Na^+. The radius of $^{[6]}Na^+$ [1.02 Å; Shannon (1976)] is significantly larger than of $^{[6]}Fe^{2+}$ (0.78 Å) and $^{[6]}Mn$ (0.83 Å), which are dominant cations at the *M*(1) site in the astrophyllite structure. Hence the M(1) octahedron in magnesioastrophyllite [<M(1)–O> = 2.372 Å] is significantly larger than the M(1) octahedron in astrophyllite [<M(1)–O> = 2.195 Å]. In the astrophyllite-group structures, the anion separations of Si_2O_7 groups in the O sheet, $(O–O)^O$, vary from 3.06 (magnesioastrophyllite) to 3.27 Å (astrophyllite). There are six edges of the M(1) octahedron which are not shared with other M octahedra in the O sheet, and they are 3.46 and 3.80 Å long (Fig. 6*b*). These six edges are too long to be shared with Si_2O_7 groups of the astrophyllite ribbon, cf. $(O–O)^O$ = 3.12 Å, M(1), astrophyllite (Fig. 5*b*). Therefore the M(1) octahedron is too large to share an edge (or edges) with an Si_2O_7 group(s) of the astrophyllite ribbon and the HOH layer with the astrophyllite topology (where each octahedron shares an edge with an Si_2O_7 group) cannot occur in magnesioastrophyllite. The position of the M(2) octahedra, between the M(1) octahedra (Fig. 7*d*) and the convoluted chains of M(3,4) octahedra underlying the astrophyllite ribbons (Fig. 7*c*,*e*), means that the M(2) octahedra do not share edges with Si_2O_7 groups.

To summarize, the dominance of Na^+ at the *M*(1) site in the O sheet makes the M(1) octahedron too large to share an edge with an Si_2O_7 group of the astrophyllite ribbon. Hence the astrophyllite ribbons of both H sheets link to the M(3,4) octahedra. The chemical composition of the O sheet ($Fe^{2+}_4Mg_2Na$) and the dominance of Na^+ at a specific site in the O sheet of magnesioastrophyllite results in a different linkage of H and O sheets, i.e. a different topology of the HOH layer. Magnesioastrophyllite would have better been named sodiumastrophyllite, as it is Na^+ and not Mg^{2+} that makes the HOH layer topologically different from all other structures in the astrophyllite group.

Summary

(1) In the astrophyllite group, there are two types of structures based on the type of linkage of HOH layers: (i) HOH layers link directly where they share common vertices of D octahedra, and (ii) HOH layers do not link directly via polyhedra of the H sheets. The type-1 structure occurs in astrophyllite, niobophyllite, nalivkinite, tarbagataite, kupletskite, niobokupletskite and kupletskite-(Cs); the type-2 structure occurs in magnesioastrophyllite, sveinbergeite and devitoite.

(2) The sizes of the M octahedra in the O sheet follow the pattern M(1) > M(2) > M(3) > M(4) due to the different linkage of M octahedra and the polyhedra of the H sheets.

(3) The topology of the HOH layer in magnesioastrophyllite is different from all other structures of the astrophyllite-group minerals due to the different chemical composition of the O sheet ($Fe^{2+}_4Mg_2Na$) and the dominance of Na^+ at the *M*(1) site which makes the M(1) polyhedron too large to share edges with Si_2O_7 groups of astrophyllite ribbons and results in a different linkage of H and O sheets, i.e. a different topology of the HOH layer.

(4) The general formulae for the eight astrophyllite-group minerals (astrophyllite, niobophyllite, nalivkinite, tarbagataite, kupletskite, niobokupletskite, kupletskite-(Cs), magnesioastrophyllite) and for the extended astrophyllite group including devitoite and sveinbergeite are $A_2BC_7D_2T_8O_{26}(OH)_4X_{0-1}$ and $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^{P}_{Dn}$, respectively, where: $A_{2p}B_rC_7D_2(T_4O_{12})_2IX^O_{D2}X^O_{A4}X^{P}_{Dn}$, 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 = O, OH, F and H_2O; n = 0, 1, 2.

(5) The general formula of the form $A_2BC_7D_2(T_4O_{12})_2X^O_{D2}X^O_{A4}X^{P}_{D}$ applies to astrophyllite, ideally $K_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$; niobophyllite, ideally $K_2NaFe^{2+}_7(Nb,Ti)_2(Si_4O_{12})_2O_2(OH)_4(O,OH)$; nalivkinite, ideally $Li_2NaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$; tarbagataite, ideally $(K\square)CaFe^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4(OH)$; kupletskite, ideally $K_2NaMn^{2+}_7Ti_2(Si_4O_{12})_2O_2(OH)_4F$; niobokupletskite, ideally $K_2NaMn^{2+}_7(Nb,Ti)_2(Si_4O_{12})_2O_2(OH)_4(O,OH)$; zircophyllite,

ideally $K_2NaMn_7^{2+}Zr_2(Si_4O_{12})_2O_2(OH)_4F$; and kupletskite-(Cs), ideally $Cs_2NaMn_7^{2+}Ti_2(Si_4O_{12})_2O_2(OH)_4F$.

The general formula of the form $A_2BC_7D_2(T_4O_{12})_2X^{O}_{D2}X^{O}_{A4}$ applies to magnesioastrophyllite, ideally $K_2Na(Fe_4^{2+}Mg_2Na)Ti_2(Si_4O_{12})_2O_2(OH)_4$.

The general formula of the form $A_2B_2C_7D_2(T_4O_{12})_2X^{O}_{D2}X^{O}_{A4}X^{P}_{D2}$ applies to sveinbergeite, ideally $(H_2O)_2[Ca(H_2O)](Fe_6^{2+}Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_4[(OH)(H_2O)]$.

The general formula of the form $A_4B_2C_7D_2(T_4O_{12})_2\mathbf{I}X^{O}_{D2}X^{O}_{A4}$ applies to devitoite, ideally $Ba_4Ba_2Fe_7^{2+}Fe_2^{3+}(Si_4O_{12})_2(PO_4)_2(CO_3)O_2(OH)_4$.

Acknowledgements

I dedicate this paper to Mark Welch, a friend and colleague for many years. I thank reviewers Yulia Uvarova and Andy McDonald, Technical Editor Fernando Cámara and Guest Editor Diego Gatta for useful comments and Frank C. Hawthorne for his interest in this work and numerous critical comments.

References

Agakhanov, A.A., Pautov L.A., Uvarova, Y.A., Sokolova E., Hawthorne, F.C. and Karpenko V.Yu. (2008) Nalivkinite, $Li_2NaFe_7^{2+}Ti_2(Si_8O_{24})O_2(OH)_4F$, a new mineral of the astrophyllite group from the Darai-Pioz massif, Tadjikistan. *New Data on Minerals*, **43**, 5–12.

Belov, N.V. (1963) Essays on structural mineralogy. XIV. 97. Ba,Fe-titanosilicate - bafertisite. 98. Anion role of Ti and Zr. Titanates, zirconates, titanosilicates, zirconosilicates. *Mineralogicheskii Sbornik L'vovskogo Geologicheskogo Obshchestva*, N17, 22–29, [in Russian].

Belov, N.V. (1976) *Essays on structural mineralogy*. Nedra, Moscow, [in Russian].

Cámara, F., Sokolova, E., Abdu, Y. and Hawthorne, F.C. (2010) The crystal structures of niobophyllite, kupletskite-(Cs) and Sn-rich astrophyllite; revisions to the crystal chemistry of the astrophyllite-group minerals. *The Canadian Mineralogist*, **48**, 1–16.

Christiansen, C.C., Johnsen, O. and Stahl, K. (1998) Crystal structure of kupletskite from the Kangerdlugssuaq intrusion, East Greenland. *Neues Jahrbuch für Mineralogie, Monatshefte*, N6, 253–264.

Ferraris, G., Ivaldi, G., Khomyakov, A.P., Soboleva, S.V., Belluso, E. and Pavese, A. (1996) Nafertisite, a layer titanosilicate member of a polysomatic series including mica. *European Journal of Mineralogy*, **8**, 241–249.

Kampf, A.R., Rossman, G.R., Steele, I.M., Pluth, J.J., Dunning, G.E. and Walstrom, R.E. (2010) Devitoite, a new heterophyllosilicate mineral with astrophyllite-like layers from eastern Fresno County, California. *The Canadian Mineralogist*, **48**, 29–40.

Kapustin, Yu. L. (1973) Zircophyllite, the zirconium analogue of astrophyllite. *International Geology Review*, **15**, 621–625.

Khomyakov, A.P., Cámara, F., Sokolova, E., Hawthorne, F.C. and Abdu, Y. (2011) Sveinbergeite, $Ca(Fe_6^{2+}Fe^{3+})Ti_2(Si_4O_{12})_2O_2(OH)_5(H_2O)_4$, a new astrophyllite-group mineral species from the Larvik plutonic complex, Oslo region, Norway: description and crystal structure. *Mineralogical Magazine*, **75**, 2687–2702.

Liebau, F. (1985) *Structural Chemistry of Silicates*. Springer-Verlag, Berlin.

Ma, Z.-S., Li, G.-W., Shi, N.-C., Zhou, H.-Y., Ye, D.-I. and Pushcharovskii, D.Yu. (2001) Structure refinement of astrophyllite. *Science in China Series D*, **44**, 508–516.

Nickel, E.H., Rowland, J.F. and Charette, D.J. (1964) Niobophyllite – the niobium analogue of astrophyllite; a new mineral from Seal Lake, Labrador. *The Canadian Mineralogist*, **8**, 40–52.

Peng, C.C. and Ma, C.S. (1963) Discovery of a new Si–O ribbon – crystal-structure analysis of astrophyllite. *Scientia Sinica*, **12**, 272–276, [in Russian].

Peng, C.C. and Ma, C.S. (1964) Crystal structure of triclinic manganoastrophyllite. *Scientia Sinica*, **13**, 1180–1183, [in Russian].

Piilonen, P.C., Lalonde, A.E., McDonald, A.M. and Gault, R.A. (2000) Niobokupletskite, a new astrophyllite-group mineral from Mont Saint-Hilaire, Quebec, Canada: description and crystal structure. *The Canadian Mineralogist*, **38**, 627–639.

Piilonen, P.C., McDonald, A.M. and Lalonde, A.E. (2001) Kupletskite polytypes from the Lovozero massif, Kola Peninsula, Russia: kupletskite-1*A* and kupletskite-*Ma2b2c*. *European Journal of Mineralogy*, **13**, 973–984.

Piilonen, P.C., Lalonde, A.E., McDonald, A.M., Gault, R.A. and Larsen, A.O. (2003*a*) Insights into astrophyllite-group minerals. I. Nomenclature, composition and development of a standardized general formula. *The Canadian Mineralogist*, **41**, 1–26.

Piilonen, P.C., McDonald, A.M. and Lalonde, A.E. (2003*b*) Insights into astrophyllite-group minerals. II. Crystal chemistry. *The Canadian Mineralogist*, **41**, 27–54.

Piilonen, P.C., Pekov, I.V., Back, M., Steede, T. and Gault, R.A. (2006) Crystal-structure refinement of a Zn-rich kupletskite from Mont Saint-Hilaire, Quebec, with contributions to the geochemistry of zinc in peralkaline environments. *Mineralogical*

Magazine, **70**, 565–578.

Semenov, E.I. (1956) Kupletskite, a new mineral of the astrophyllite group. *Doklady Akademii Nauk SSSR*, **108**, 933–936, [in Russian].

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, **A32**, 751–767.

Shi, N.-C., Ma, Z.S., Li, G.W., Yamnova, N.A. and Pushcharovskii, D.Yu. (1998) Structure refinement of monoclinic astrophyllite. *Acta Crystallographica*, **B54**, 109–114.

Sokolova, E. (2006) From structure topology to chemical composition: I. Structural hierarchy and stereochemistry in titanium disilicate minerals. *The Canadian Mineralogist*, **44**, 1273–1330.

Sokolova, E. and Cámara, F. (2008) Re-investigation of the crystal structure of magnesium astrophyllite. *European Journal of Mineralogy*, **20**, 253–260.

Stepanov, A.V., Bekenova, G.K., Levin, V.I., Sokolova, E., Hawthorne, F.C. and Dobrovol'skaya, E.A. (2012) Tarbagataite, $(K,\square)_2(Ca,Na)(Fe^{2+},Mn)_7Ti_2(Si_4O_{12})_2O_2(OH)_4(OH,F)$, a new astrophyllite-group mineral species from the Verkhnee Espe deposit, Akjailyautas Mountains, Kazakhstan: description and crystal structure. *The Canadian Mineralogist*, **50**, 159–168.

Uvarova, Y.A., Sokolova, E., Hawthorne, F.C., Agakhanov, A.A. and Pautov, L.A. (2008) The crystal structure of nalivlinite, a new lithium member of the astrophyllite group. *The Canadian Mineralogist*, **46**, 651–659.

Weibye, P.C. (1848) Beiträge zur topographischen Mineralogie Norwegens. *Archiv für Mineralogie, Geognosie Bergbau und Hüttenkunde*, **22**, 465–544.

Woodrow, P.J. (1967) The crystal structure of astrophyllite. *Acta Crystallographica*, **22**, 673–678.

Yamnova, N.A., Egorov Tismenko, Yu.K., Zlykhenskaya, I.V. and Khomyakov, A.P (2000) Refined crystal structure of iron-rich triclinic astrophyllite. *Crystallography Reports*, **45**, 585–590.

Appendix

In the Inorganic Crystal Structure Database (ICSD), the data on the astrophyllite-group minerals are rather confusing. Several of them are given wrong names (e.g. astrophyllite instead of kupletskite), and there are several double entries. Working on this paper, I encountered some problems with the ICSD entries on the astrophyllite-group structures and I thought it would be helpful for others to know which entry corresponds to a particular mineral (and a sample). Table 1A (*overleaf*) assigns correct names to the ICSD entries and identifies double ICSD entries.

TABLE 1A. Astrophyllite-group structures in the ICSD (International Crystal Structure Database).

ICSD code	Space group	O sheet	Ref.[‡]	Sample	Mineral
Listed under the name astrophyllite					
24911	$A\bar{1}$	Fe > Mn	(1)		astrophyllite
91547	$A\bar{1}$	Fe > Mn	(2)		astrophyllite
94308	$P\bar{1}$	Fe > Mn	(3)		astrophyllite
171937	$P\bar{1}$	Fe > Mn	(4)	LAB3	astrophyllite
171938	$P\bar{1}$	Fe > Mn	(4)	NOR1	astrophyllite
171939	$P\bar{1}$	Fe > Mn	(4)	NOR17	astrophyllite
171940	$P\bar{1}$	Fe > Mn	(4)	RUS4	astrophyllite
171941	$P\bar{1}$	Fe > Mn	(4)	RUS8	astrophyllite
171944	$P\bar{1}$	Fe > Mn	(4)	US5	astrophyllite
171953	$P\bar{1}$	Fe > Mn	(4)	MSH33A	astrophyllite[†]
171954	$P\bar{1}$	Fe > Mn	(4)	MSH34A	astrophyllite
171945	$P\bar{1}$	Mn > Fe	(4)	MSH2	kupletskite
171946	$P\bar{1}$	Mn > Fe	(4)	MSH3	kupletskite
171947	$P\bar{1}$	Mn > Fe	(4)	MSH8	kupletskite
171948	$P\bar{1}$	Mn > Fe	(4)	MSH9	kupletskite
171949	$P\bar{1}$	Mn > Fe	(4)	MSH15	kupletskite
171950	$P\bar{1}$	Mn > Fe	(4)	MSH15A	kupletskite
171951	$P\bar{1}$	Mn > Fe	(4)	MSH19A	kupletskite
171952	$P\bar{1}$	Mn > Fe	(4)	MSH20	kupletskite
171955	$P\bar{1}$	Mn > Fe	(4)	MSH38A	kupletskite
171942*	$C2/c$	Mn > Fe	(4)	RUS9	kupletskite-2*M*
171943*	$P\bar{1}$	Mn > Fe	(4)	RUS12	kupletskite-1*A*
171956*	$P\bar{1}$	Mn > Fe	(4)	MSH42	niobokupletskite
166994	$P\bar{1}$	Fe > Mn	(5)		astrophyllite[††]
160475	$C2/m$	Fe > Mn	(6)		magnesioastrophyllite
Listed under the name magnesiumastrophyllite					
280456**	$A2$	Fe > Mn	(7)		magnesioastrophyllite
56848**	$A2/m$	Fe > Mn	(7)		magnesioastrophyllite
Listed under the name niobophyllite					
109075***	$P\bar{1}$	Fe > Mn	(8)		niobophyllite
166992	$P\bar{1}$	Fe > Mn	(5)		niobophyllite
Listed under the name kupletskite					
86867	$P\bar{1}$	Mn > Fe	(9)		kupletskite
89859*	$P\bar{1}$	Mn > Fe	(10)		niobokupletskite
92945*	$P\bar{1}$	Mn > Fe	(11)	RUS12	kupletskite-1*A*
92946*	$C2/c$	Mn > Fe	(11)	RUS9	kupletskite-2*M*
166993	$P\bar{1}$	Mn > Fe	(5)		kupletskite-(Cs)
Other astrophyllite-group minerals					
161277	$P\bar{1}$	Fe > Mn	(12)		nalivkinite
166995	$P\bar{1}$	Fe > Mn	(13)		devitoite

* Piilonen *et al.* (2000, 2001) published 3 sets of structural data that were subsequently listed by Piilonen *et al.* (2003*b*). The data of Piillonen *et al.* (2003*b*) were assigned different ICSD codes from the identical data in Piilonen *et al.* (2000, 2001). These pairs are as follows: 89859 is equivalent to 171956, 92945 is equivalent to 171943, 92946 is equivalent to 171942.

** The atom coordinates of (7) (sp. gr. *A*2, #280456) were changed to match sp. gr. *A*2/*m* by ICSD #56848; however, they gave an incorrect chemical formula. For the correct chemical formula see #160475 (6).

*** Atom coordinates are quoted from (8) which does not have atom coordinates.

[†] *D* site: Zr > Ti; zircophyllite?

[††] Sn-rich.

[‡] References: (1) Woodrow (1967); (2) Yamnova *et al*. (2000); (3) Ma *et al*. (2001); (4) Piilonen *et al.* (2003*b*); (5) Cámara *et al*. (2010); (6) Sokolova and Cámara (2008); (7) Shi *et al.* (1998); (8) Nickel *et al.* (1964); (9) Christiansen *et al*. (1998); (10) Piilonen *et al*. (2000); (11) Piilonen *et al.* (2001); (12) Uvarova *et al*. (2008); (13) Kampf *et al*. (2010).