Structure refinement of astrophyllite

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Abstract The crystal structure of astrophyllite $K_2Na(Fe, Mn, Mg, \square)_7[Ti_2(Si_4O_{12})_2|O_3](OH, F)_4$ has been refined. The dimensions of the triclinic unit cell are: a = 0.5359(2) nm, b = 1.1614(4) nm, c = 1.1861(4) nm, α = 113.16(2)°, β = 103.04(2)°, γ = 94.56(2)°, V = 0.6495(5) nm^3, Z = 1, space group P1, R=0.057 for 5308 reflections $|F_o|>3\sigma|F_o|$. According to structural and compositional differences the monoclinic astrophyllite $K_2NaNa(Fe, Mn)_4Mg_2Ti_2[Si_4O_{12}]_2(OH)_4(OH, F)_2$ and astrophyllite should be considered as two different mineral species. Astrophyllite, monoclinic astrophyllite, bafertisite and lamprophyllite contain heteropolyhedral sheets which topologically are related with Si, O sheets of mica where one or several SiO_4 tetrahedra are replaced by TiO_n polyhedra. Therefore this heterophyllotitanosilicate series represents a kind of functional substitution in inorganic crystals.

Keywords: astrophyllite, crystal structure, functional substitution.

Astrophyllite is a kind of Fe-Mn silicates which are characterized chemically by the presence of large amounts of potassium, sodium and titanium. It occurs in super-alkaline igneous rocks, pegmatite and metamorphite. There are a lot of reports about its occurrence, for example, Khibiny alkaline massifs of Russia, Vigo of Spain, Labrador of Canada and a super-alkaline igneous complex in Mount Gharib from Egypt[1]. Recently, astrophyllite was discovered in igneous Cabonate vein of granulite facies metamorphite group, Namjabarwa area, the eastern Himalayan syntaxis, Eastern Tibet, China[2].

In 1963 Peng Zhizhong and Ma Zhesheng investigated astrophyllite from Khibina area and revealed its two polymorphs: (i) monoclinic astrophyllite[3], space group A2/m, unit cell: a = 1.043(2) nm, b = 2.300(5) nm, c = 0.535(1) nm, α = 102°; (ii) triclinic astrophyllite[4], space $P\bar{1}$, unit cell a = 1.177 nm, b = 1.186 nm, c = 0.542 nm, α = 101° 53′, β = 94° 25′, γ=113° 21′. Using Weissenberg multiplefilm method, the diffraction intensities were estimated. The x, y atomic coordinates of monoclinic astrophyllite were determined. The most specific feature of this structure was a new type of silicate chain $[Si_4O_{12}]_n^{8n-}$ which was later termed as a branched tetrahedral chain. In 1998, the structure of monoclinic astrophyllite was refined with intensity data col-

lected using the single crystal diffractometer[5].

In 1967, Woodrow determined the crystal structure of triclinic astrophyllite using the multiplefilm techniques for the measurements of diffraction intensities[6]. In order to facilitate the comparison of this structure with that of biotite, a centred setting of the unit cell was selected: a = 0.536 nm, b = 1.176 nm, c = 2.108 nm, $\alpha = 85^\circ 08'$, $\beta = 90^\circ 00'$, $\gamma = 103^\circ 13'$. All atomic coordinates were reported, although x coordinates were evaluated by graphic method.

Thus so far the lack of the accurate structure data related to triclinic astrophyllite did not permit to examine the comparative crystal chemistry of the whole astrophyllite family in detail. The results of its structure refinement are reported below.

1 Experimental

1.1 Occurrence, physical and chemical properties

The crystals of astrophyllite appropriate for structure determination (sample No. 3098) provided by Russian mineralogist A. P. Khomyakov were discovered in alkaline rocks in Eveclogchorr Mountain, south-eastern part of Khibiny alkaline massif (Kola Peninsula). Crystals yellow brown in colour have glass lustre and their form is a plate prismatic. They exhibit two kinds of cleavage: {100} is perfect and {010} is good.

The total chemical analyses of the studied samples are listed in table 1. The atomic proportions recalculated on the basis of 31 oxygen atoms were generalized in the chemical formula:

$$(K_{1.5790}Na_{0.9902}Ca_{0.5242}Ba_{0.0114})_{3.1048}(Fe_{5.1815}Mn_{0.9876}Mg_{0.3719})_{6.5410}$$
$$[(Ti_{1.7748}Nb_{0.0558}Zr_{0.0520}TR_{0.0051})_{1.8877}(Si_{7.3877}Al_{0.4747})_{7.8624}O_{24}](O_{1.4304}(OH)_{4.4276}F_{1.1420})_7$$

Table 1 The chemical composition of astrophyllite (wt%)

Mineral	Astrophyllite[a)]	Astrophyllite	Kupletskite[7]	Astrophyllite	Niobophyllite[8]	Hydro-astrophyllite[9]	Monoclinic astrophyllite
Place	Russia	Russia	Russia	Tibet, China	Canada	Sichuan, China	Russia
SiO_2	34.86	39.05	32.60	35.79	33.40	25.72	37.98
TiO_2	11.13	9.36	12.04	11.48	2.94	9.63	12.18
ZrO_2	0.51		1.19				
Nb_2O_5	0.56		0.66		14.76	5.01	
Ta_2O_5					0.32	0.82	
TR_2O_3	0.086				1.50		
Al_2O_3	1.91	4.27	1.68	1.17	0.89	3.92	1.11
Fe_2O_3		12.08			23.74	24.24	2.95
FeO	29.28	20.21	5.44	28.65		0.05	17.91
MnO_2						3.77	
MnO	5.51	1.22	27.65	5.28	9.83	8.05	4.00
MgO	1.17	0.92	2.98	1.52	0.16	0.51	6.39
CaO	2.31	1.53	3.60	1.69	0.72	2.40	1.15
BaO	0.14					0.32	
K_2O	5.83	5.58	4.38	5.88	5.51	1.28	7.28
Na_2O	2.42	1.42	2.14	2.55	2.49	0.53	5.38
H_2O+	3.08	4.55	3.83		3.64	6.65	3.44
H_2O-	0.048		1.08		0.08	5.74	
F	1.71	0.55	1.22		0.46	1.83	0.45
Total	100.55	100.74	100.49	94.01	100.44	100.47	100.22
System	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic

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1.2 The determination of crystal structure

A single crystal with approximate dimensions 0.2 × 0.2 × 0.1 mm^3 was selected for X-ray study, which was carried on a Rigaku AFC-6 four circle diffractometer using graphite monochromatized Mo$K\alpha$ radiation (λ = 0.071073 nm). The unit cell parameters were derived by a least square fit using 15 reflections $2\theta>25^\circ$: a = 0.5359(2) nm, b = 1.1614(4) nm, c = 1.1861(4) nm, α=113.16(2)°, β=103.04(2)°, γ= 94.56(2)°, V = 0.6495(5) nm^3, space group P1, Z = 1, Dx = 3.359 Mgm^{-3}, μ= 4.936 mm^{-1}, $F(000)$ = 620. This unit cell is very similar to that reported by Woodrow (1967), because the unit cell from Woodrow can transfer to a = 0.536 nm, b = 1.1625 nm, c = 1.1756 nm, α= 112.10°, β= 103.13°, γ= 96.64° by a matrix ($\bar{1}$ 0 0, 0 $\bar{1}$ / 2 1/2, 1 1 0). 6457 reflections were collected using the scan mode $2\theta/\omega$, scan speed 4°/min, scan width $\Delta\omega$ = 1.51±0.5 tanθ, scan range $3^\circ < 2\theta < 70^\circ$ for reciprocal space, h:–18—18, k:–19—19, l:0—8. LP corrections were carried out for diffraction intensities. 5308 reflections with $|F_o|>3\sigma|F_o|$ were used for crystal structure determination and refinement.

Heavy atom method revealed the atomic sites of Fe, Ti, Si, K, and Na (software package SHELX- 86[10]). The consequent Fourier syntheses were allowed to localize the positions of O atoms. The refinement of the structure with anisotropic displacement parameters for all atoms led to $R[F^2>2\sigma(F^2)]$ = 0.057, $wR(F^2)$ = 0.1776 and GoF = 0.823[11]. Refined atomic coordinates, occupancies, isotropic thermal parameters and interatomic distances are given in tables 2 and 3 respectively. The final electron density map was featureless: $\Delta\rho_{max}$(enm^{-3}) = 0.00343, $\Delta\rho_{min}$(enm^{-3}) = –0.00158.

Table 2 Fractional atomic coordinates, isotropic and occupancy parameters of astrophyllite

Atom	x	y	z	Ueq	Occupancies
Fe1	–0.3211(3)	0.0548(2)	0.0977(2)	0.0098(1)	0.890(2)
Fe2	–0.7435(1)	0.0681(1)	0.2441(1)	0.0112(2)	0.931(3)
Fe3	–0.1692(1)	0.0740(1)	0.3907(1)	0.0094(2)	0.887(3)
Fe4	–0.6006(1)	0.0646(1)	0.5289(1)	0.0090(2)	0.921(3)
Fe5	–0.0394(1)	0.0437(1)	0.6647(1)	0.0116(2)	0.947(3)
Fe6	–0.4707(1)	0.0356(1)	0.8038(1)	0.0101(2)	0.876(3)
Fe7	0.1029(1)	0.0420(1)	0.9503(1)	0.0085(2)	0.862(3)
Ti1	–0.4004(1)	0.3541(1)	0.5090(1)	0.0076(2)	1.000(3)
Ti2	–0.2412(1)	–0.2457(1)	0.6841(1)	0.0085(2)	1.000(4)
K1	0.5333(5)	0.5569(2)	0.3287(2)	0.0504(7)	0.927(6)
K2	0.8002(5)	0.5477(2)	0.8613(2)	0.0359(6)	0.948(6)
Na	0.1724(6)	0.5533(3)	0.5950(3)	0.0027(2)	1.000(5)
Si1	–0.5086(3)	–0.1931(1)	0.1413(1)	0.0112(3)	1
Si2	–0.9416(3)	–0.1901(1)	0.2713(1)	0.0110(3)	1
Si3	–0.8157(3)	–0.2096(1)	0.5285(1)	0.0103(3)	1
Si4	–0.6448(2)	–0.2130(1)	0.8682(1)	0.0091(3)	1
Si5	–0.1384(3)	0.3000(1)	0.0494(1)	0.0106(3)	1
Si6	0.0008(3)	0.3226(1)	0.3243(1)	0.0108(3)	1
Si7	–0.8291(3)	0.3178(1)	0.6638(1)	0.0100(3)	1

(*To be continued on the next page*)

(*Continued*)

Atom	*x*	*y*	*z*	Ueq	Occupancies
Si8	0.2971(3)	0.2982(1)	0.9209(1)	0.0104(3)	1
O1	–0.1778(8)	–0.0740(3)	0.7547(4)	0.0159(9)	1
O2	–0.5956(8)	–0.0601(3)	0.9164(4)	0.0178(9)	1
O3	–0.0296(9)	–0.0464(4)	0.0548(4)	0.0217(11)	1
O4	–0.4538(8)	–0.0370(3)	0.2068(4)	0.0149(8)	1
O5	–0.8755(7)	–0.0325(3)	0.3382(4)	0.0123(8)	1
O6	–0.3156(9)	–0.0344(4)	0.4772(4)	0.0237(10)	1
O7	–0.7564(8)	–0.0552(3)	0.6076(4)	0.0140(8)	1
O8	0.2348(8)	0.1466(4)	0.8517(4)	0.0124(8)	1
O9	–0.1993(6)	0.1505(4)	0.9902(3)	0.0077(7)	1
O10	–0.6245(7)	0.1525(3)	0.1325(3)	0.0077(7)	1
O11	–0.0471(6)	0.1676(3)	0.2781(3)	0.0082(8)	1
O12	–0.4695(6)	0.1828(4)	0.4333(4)	0.0131(9)	1
O13	–0.8988(6)	0.1666(4)	0.5767(3)	0.0082(7)	1
O14	–0.3350(6)	0.1483(3)	0.7099(4)	0.0085(7)	1
O15	–0.4708(10)	–0.2798(4)	0.7772(4)	0.0321(11)	1
O16	–0.9319(10)	–0.2790(5)	0.7806(5)	0.0360(12)	1
O17	–0.6005(11)	–0.2529(4)	0.9893(4)	0.0267(12)	1
O18	–0.7385(10)	–0.2464(4)	0.1828(5)	0.0278(12)	1
O19	–1.2452(8)	–0.2445(5)	0.1854(5)	0.0305(14)	1
O20	–0.9128(11)	–0.2465(4)	0.3768(4)	0.0299(13)	1
O21	–1.0446(10)	–0.2788(4)	0.5587(5)	0.0332(11)	1
O22	–0.5725(10)	–0.2765(4)	0.5562(6)	0.0343(15)	1
O23	0.2360(10)	0.3575(4)	0.8169(4)	0.0222(10)	1
O24	0.6047(9)	0.3552(4)	0.0066(5)	0.0223(11)	1
O25	0.1104(8)	0.3546(4)	0.0102(4)	0.0206(10)	1
O26	–0.0626(11)	0.3580(5)	0.2036(4)	0.0248(12)	1
O27	0.3005(9)	0.3857(4)	0.4009(6)	0.0306(13)	1
O28	–0.2119(9)	0.3824(4)	0.3932(5)	0.0287(10)	1
O29	–0.5784(10)	0.3811(4)	0.6433(5)	0.0302(12)	1
O30	–1.0794(10)	0.3791(5)	0.6379(6)	0.0350(12)	1
O31	–0.3157(11)	0.5543(6)	0.5967(7)	0.0076(14)	1
H13	–0.067(18)	–0.141(9)	0.006(9)	0.042(31)	1
H26	–0.377(18)	–0.122(9)	0.443(10)	0.068(37)	1
H310	–0.540(20)	0.240(9)	0.183(10)	0.043(33)	1
H414	–0.291(17)	0.252(8)	0.753(9)	0.022(30)	1

2 Discussion

The perspective views of astrophyllite crystal structure are shown in figs.1—6. The silicate "open-branched two periodicity single chains"[12] (in terms of F. Liebau crystal chemical classification of silicates) with chemical formula $[Si_4O_{12}]_n^{8n-}$ are linked with TiO_6 octahedra to form heteropolyhedral anionic (H) sheets. The (Fe, Mn, Mg)O_6 octahedra with isomorphic replacement between central Fe, Mn and Mg cations and linked each other by edge-sharing form the octahedral (O) sheets which can be considered as the most rigid part of the structure. The octahedral sheets are sandwiched between two neighbouring heterogeneous sheets $[Ti_2(Si_4O_{12})_2|O_3]$ with the formation of 3-layered HOH complex sheets. The interlayers are filled by large cations K, Na and Ca.

Table 3 Interatomic distances (nm) of astrophyllite

(Fe, Mn, Mg)-O octahedra		Ti-O octahedral and Si-O tetrahedra within heterogeneous anionic sheets		Large cations in the interlayers	
Fe1-O3	0.2064(5)	Ti1-O12	0.1797(4)	Na-O21#6	0.2477(7)
Fe1-O10	0.2081(4)	Ti1-O30#2	0.1941(5)	Na-O16#6	0.2512(7)
Fe1-O11	0.2127(4)	Ti1-O27#3	0.1971(5)	Na-O15#6	0.2517(5)
Fe1-O2#4	0.2138(4)	Ti1-O29	0.1971(5)	Na-O22#6	0.2561(7)
Fe1-O9#4	0.2159(5)	Ti1-O28	0.1986(6)	Na-O30#2	0.2619(8)
Fe1-O4	02167(5)	Ti1-O31	0.2101(7)	Na-O31	0.2622(7)
Fe2-O4	0.2069(4)	Ti2-O1	0.1802(4)	Na-O27	0.2638(7)
Fe2-O5	0.2089(5)	Ti2-O15	0.1940(5)	Na-O29#2	0.2663(7)
Fe2-O11#3	0.2091(4)	Ti2-O21#6	0.1948(6)	Na-O28	0.2701(6)
Fe2-O10	0.2104(4)	Ti2-O16#2	0.1950(6)	Na-O31#2	0.2737(7)
Fe2-O12	0.2195(4)	Ti2-O22	0.1959(5)	K1-O27	0.2769(7)
Fe2-O3#3	0.2222(4)	Ti2-O31#10	0.2097(7)	K1-O28#2	0.2784(6)
Fe3-O6	0.2115(5)	Si1-O17#4	0.1593(5)	K1-O22#6	0.2847(6)
Fe3-O5#2	0.2132(4)	Si1-O18	0.1592(6)	K1-O21#7	0.2939(5)
Fe3-O13#2	0.2137(3)	Si1-O19#2	0.1633(5)	K1-O31#2	0.3112(8)
Fe3-O12	0.2151(4)	Si1-O4	0.1638(4)	K1-O20#7	0.3389(6)
Fe3-O4	0.2173(4)	Si2- O20	0.1610(6)	K1-O26	0.3424(6)
Fe3-O11	0.196(5)	Si2-O19	0.1633(4)	K1-O20#6	0.3422(6)
Fe4-O6	0.2044(5)	Si2-O5	0.1653(4)	K1-O26#2	0.3431(6)
Fe4-O14	0.2083(4)	Si2-O18	0.1674(6)	K1-O18#6	0.3582(6)
Fe4-O13	0.2111(4)	Si3-O21	0.1596(6)	K1-O19#7	0.3630(7)
Fe4-O7	0.2167(5)	Si3-O22	0.1606(5)	K1-O25	0.3638(5)
Fe4-O5	0.2188(4)	Si3-O20	0.1621(5)	K2-O29#2	0.2761(5)
Fe4-O12	0.2258(5)	Si3-O7	0.1627(4)	K2-O30#9	0.2857(7)
Fe5-O7#2	0.2052(4)	Si4-O16	0.1581(5)	K2-O15#6	0.2916(6)
Fe5-O14	0.2108(4)	Si4-O15	0.1596(5)	K2-O16#7	0.2950(7)
Fe5-O8	0.2161(4)	Si4-O2	0.1616(4)	K2-O31#2	0.3092(8)
Fe5-O6	0.2162(4)	Si4-O17	0.1650(5)	K2-O23#2	0.3328(6)
Fe5-O1	0.2213(5)	Si5-O9#4	0.1569(4)	K2-O23	0.3406(6)
Fe5-O13#2	0.2248(5)	Si5-O26	0.1618(4)	K2-O17#6	0.3431(6)
Fe6-O1	0.2139(4)	Si5-O24#3	0.1626(5)	K2-O17#7	0.3440(6)
Fe6-O8#3	0.2151(4)	Si5-O25	0.1665(5)	K2-O24#1	0.3541(6)
Fe6-O9	0.2169(3)	Si6-O28	0.1595(5)	K2-O25#5	0.3647(6)
Fe6-O14	0.2202(5)	Si6-O27	0.1604(5)	K2-O19#8	0.3725(6)
Fe6-O2	0.2217(5)	Si6-O26	0.1612(5)		
Fe6-O7	0.2253(4)	Si6-O11	0.1642(4)		
Fe7-O3#1	0.2091(6)	Si7-O29	0.1592(6)		
Fe7-O2#2	0.2098(4)	Si7-O30	0.1593(5)		
Fe7-O10#5	0.2132(3)	Si7-O13	0.1608(4)		
Fe7-O9	0.2154(4)	Si7-O23#3	0.1631(5)		
Fe7-O8	0.2167(5)	Si8-O8	0.1592(4)		
Fe7-O1	0.2260(4)	Si8-O25#1	0.1609(5)		
		Si8-O23	0.1620(5)		
		Si8-O24#1	0.1652(4)		
	O3-H13	0.1002 (0.093)	O6-H26	0.0934 (0.103)	
	O10-H310	0.0968 (0.098)	O14-H414	0.1095 (0.095)	

Symmetry transformations used to generate equivalent atoms, #1 *x*, *y*, *z*+1; #2 *x*+1, *y*, *z*; #3 *x*–1, *y*, *z*; #4 *x*, *y*, *z*–1; #5 *x*+1, *y*, *z*+1; #6 *x*+1, *y*+1, *z*; #7 *x*+2, *y*+1, *z*; #8 *x*+2, *y*+1, *z*+1; #9 *x*+2, *y*, *z*; #10 *x*, *y*–1, *z*.

Na atoms are located in 10-fold polyhedra which can be described as a combination of tetragonal prism with tetragonal bipyramid. K atoms have irregular 12-fold coordination. According to the results of the structure determination, the chemical formula of astrophyllite can be written as

$$K_2Na(Fe, Mn, Mg, \square)_7[Ti_2(Si_4O_{12})_2|O_3](OH, F)_4.$$

Geometrical misfit between the octahedral and heterogeneous sheets forces arching of the former along [010] (fig. 1) and can be considered as a reason for symmetry reduction of the structure. Another specific feature of the structure is the direct contact between Ti-octahedra from H sheets which belong to neighbouring HOH layers. These contacts decrease the interlayer space of astrophyllite as compared with true layer silicates, namely with mica. Moreover it assumes some kind of skeleton character of astrophyllite, which leads to the increase of its structural stability and determines its wide distribution in alkaline rocks as a kind of accessory minerals. In contrast with astrophyllite, weaker bonds between 3-layered sheets in mica appear in the perfect cleavage parallel to the plane of the sheets.

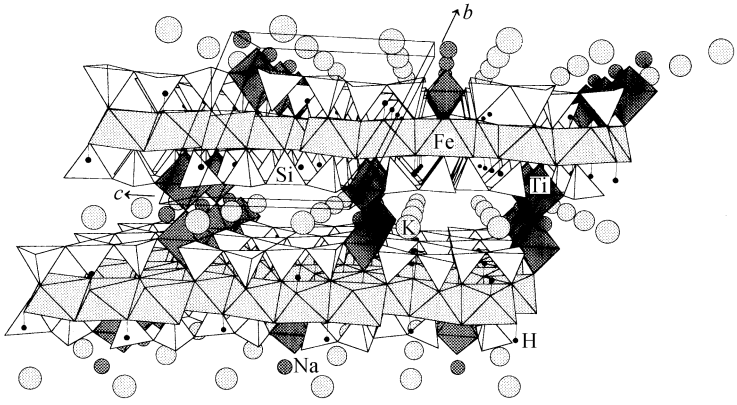

Fig. 1. Crystal structure of astrophyllite.

Astrophyllite group has also a close relationship with layered Ti-silicates, namely bafertisite and nafertisite[13]. All these structures are based on a 2∶1 HOH layer. Ferraris[14] emphasized that bafertisite, astrophyllite, nafertisite and other layer titanosilicates as well are members of a polysomatic series B_mM_n built up by B (bafertisite-like) and M (mica-like) modules. Because of its clear relationships with the phyllosilicates, the series has been called (Ferraris et al., 1996) heterophyllosilicate series to stress the extra (hetero) presence of Ti-polyhedra in the H sheet. For $m = 1$, the following cases have been reported: $n = 0$ —— bafertisite-type structure; $n = 1$ —— astrophyllite-type structure; $n = 2$ —— nafertisite; $n = \infty$ —— micas.

Apart from these general similarity, the octahedral sheets in bafertisite and astrophyllite comprise the small cations Fe, Mn and Mg in the octahedral sheets. In lamprophyllite and monoclinic astrophyllite Na^+ cations enter the octahedral sheets. It leads to the decrease to five of coordination number of Ti in the polyhedron which is shared with Na-octahedra in these structures. Thus Ti-O tetragonal pyramid participates in the formation of H sheets in lamprophyllite and

monoclinic astrophyllite.

Two main differences between triclinic and monoclinic astrophyllite can be summarised as in the following:

1) The octahedral sheets of monoclinic astrophyllite comprise the octahedra of a one valence large cation, although in astrophyllite the octahedral sheets are constituted only by octahedra of small cations (Fe, Mn, Mg and some others).

2) The heteropolyhedral sheets of astrophyllite and of monoclinic astrophyllite contain TiO_6 octahedra and tetragonal TiO_5 pyramids respectively.

Therefore, according to the structural and compositional differences the monoclinic astrophyllite and astrophyllite should be considered as two different mineral species and thus the monoclnic astrophyllite should be renamed.

Another interesting crystal chemical aspect of astrophyllite group is connected with topology of heteropyhedral sheets. In mica crystal structure the tetrahedral sheets contain the 6-membered rings formed by SiO_4 tetrahedra (fig. 2). In H sheets of astrophyllite one tetrahedron in the similar hexagonal ring is substituted by TiO_6 octahedron (fig. 3). This kind of crystal chemical phenomenon is different as compared with simple isomorphic substitution, which assumes that the type coordination polyhedron does not change. For example, Si-Al isomorphic replacement in tetrahedron occurs in sanidine, microcline and orthoclase. However, when the substitution occurs between the different types of polyhedra, the additional comment for this phenomenon is necessary.

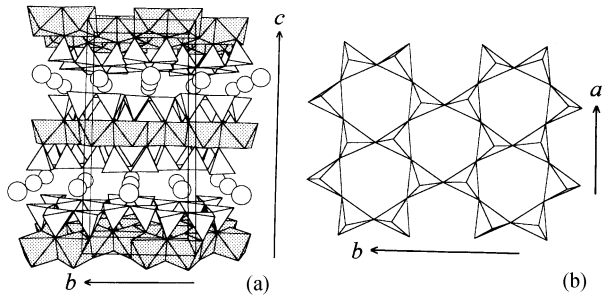

Fig. 2. Crystal structure of mica (a) and its tetrahedral sheet[Si_4O_{10}](b).

In this connection it is worthy to note that the functional group substitution is quite common in organic chemistry. For example, the substitution of methylene group CH_3 for hydrogen in benzene ring leads to the formation of toluene. In silicate crystal structure we can also find the similar functional substitution if we consider the replacement between polyhedra of different types. The substitution of TiO_5 tetragonal pyramids in monoclinic astrophyllite and TiO_6 octahedra in astrophyllite in their H sheets can be also considered as an example of functional substitution. According to this approach, the relationship between crystal chemical peculiarities of heterophyllotitanosilicates can be summarised as follows:

Astrophyllite, monoclinic astrophyllite, bafertisite and lamprophyllite contain heterogeneous sheets which topologically are related with Si, O sheets of mica where one or several SiO_4 tetra-

hedra are replaced for TiO_n polyhedra.

In astrophyllite only one SiO_4 tetrahedron within 6-membered ring of mica silicate sheet is substituted by TiO_6 octahedron (fig. 3).

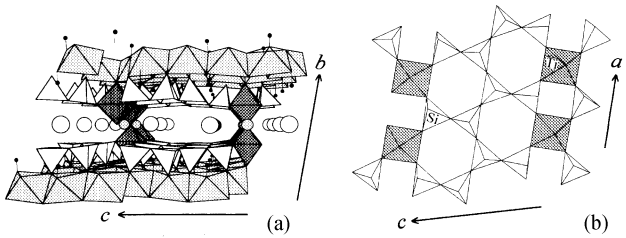

Fig. 3. Crystal structure of astrophyllite (a) and its complex anion net sheet $[Ti_2Si_8O_{24}| O_3]$ (b).

In monoclinic astrophyllite (fig. 4), only one SiO_4 tetrahedron within the same ring is also substituted by TiO_5 tetragonal pyramid.

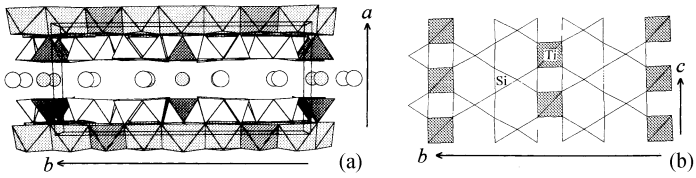

Fig. 4. Crystal structure of monoclinic astrophyllite (a) and its heterogeneous sheet $[Ti_2Si_8O_{24}| O_2]$ (b).

In bafertisite $BaFeFeTi[Si_2O_7]O(OH)_2$(fig. 5), two SiO_4 tetrahedra within the same ring are substituted by two TiO_6 octahedra and thus in heterogeneous sheet the Ti/O ratio = 1∶2.

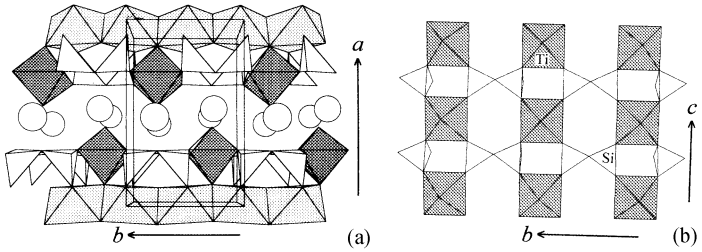

Fig. 5. Crystal structure of bafertisite (a) and its H sheet $[TiSi_2O_7| O_2]$ (b).

In lamprophyllite $(Ba, Sr, K)_2NaTi(NaFe^{2+})_2(Ti, Fe^{3+})_2[Si_2O_7]_2O_2(O, OH, F)_2$ (fig. 6), two SiO_4 tetrahedra are substituted by two TiO_5 tetragonal pyramids within 6-membered rings.

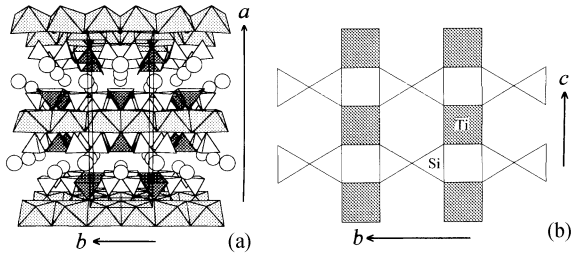

Fig. 6. Crystal structure of lamprophyllite (a) and its H sheet$[TiSi_2O_7| O]$ (b).

This kind of functional substitution between polyhedra of intermediate and small cations is a specific crystal chemical feature of heterophyllotitanosilicates. This phenomenon is obviously significant for the further development of crystal chemical classification of minerals and will be an object for the further studies.

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