RESEARCH PAPERS

Structure Refinement of Monoclinic Astrophyllite

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Abstract

The crystal structure of monoclinic magnesium astrophyllite has been redetermined. The samples were from Khibina alkaline massifs, Russia. $K_2NaNa(Fe,Mn)_4Mg_2Ti_2[Si_4O_{12}]_2(OH)_4(OH,F)_2$, M_r = 1202.31, monoclinic, $A2$, a = 10.370 (3), b = 23.129 (5), c = 5.322 (1) Å, β = 99.55 (2)°, V = 1258.8 (5) Å^3, Z = 2, D_x = 3.173 Mg m^{-3}, Mo $K\alpha$, λ = 0.71069 Å, μ = 3.74 mm^{-1}, $F(000)$ = 1179, T = room temperature, R = 0.057 for 1720 reflections. The determination indicated that the coordination number of Ti is five. In tetrahedra of astrophyllite the open-branched Si—O chain connected with Ti—O semi-octahedra by corner-sharing formed a continuous sheet. Na atoms have two types of coordination. Their coordination numbers are eight and six. The Na atoms with coordination number eight are situated between layers. Other types of Na atoms are situated within the layers and form Na—O octahedra with partial occupancies.

1. Introduction

Astrophyllite is one of a large group of silicate minerals that occur as accessory or pegmatite minerals in alkaline igneous rocks. These minerals are characterized chemically by the presence of large amounts of sodium, titanium or zirconium and often manganese, and the almost complete absence of aluminium and magnesium. The well known occurrence of astrophyllite was discovered at the eastern locality, Kraemers Island, East Greenland. Layne *et al.* (1982) reported its western locality (East Greenland), where the astrophyllite occurs in elongated prisms. Abdel-Rahman (1992) reported the mineral chemistry and paragenesis of astrophyllite from Egypt. 18 chemical analyses of astrophyllite indicated that substitution in the astrophyllite unit cell involves fluorine, calcium, manganese, zinc, magnesium, niobium, zirconium, tin and aluminium. Unusually high niobium contents (up to 5 wt% Nb_2O_5) characterize the Egyptian astrophyllite.

The first determination of the structure of astrophyllite was made by Peng & Ma (1963) at the X-ray

Laboratory of China University of Geosciences. These results led to the formula $K_2Na_2(Fe^{2+},Mn)_2(Fe^{2+},Fe^{2+})_3Mg_2Ti_2[Si_4O_{12}]_2(O,OH)_3(OH,F)_4$ with Z = 2. The structural model was obtained in the space group $A2/m$ and was based on the localization of 19 atoms in a (001) projection. The most specific feature of this structure was a new type of silicate chain $[Si_4O_{12}]_\infty^{8\infty-}$, which was later termed a branched tetrahedral chain (Liebau, 1985). In 1964 Peng & Ma (1964), also published as X-ray Laboratory (1974), studied triclinic manganese astrophyllite. A structural model based on two-dimensional coordinates was suggested. In 1974 they gave the results in detail. The factors which control the isomorphism and the polymorphism of the astrophyllite group minerals were discussed. The crystal chemistry of sheet titanium silicates was considered and the two functions of titanium polyhedra in crystal structures were emphasized. Zvyagin & Vrublevskaya (1976) derived polytypic forms of astrophyllite. They considered that the formation of the astrophyllite structure from its characteristic (Si, Ti) and (Fe, Mn, Mg) structural elements is far from unambiguous.

In 1967 Woodrow (1967) published the crystal structure of triclinic astrophyllite. Its unit cell is different compared with monoclinic astrophyllite. The crystal data of monoclinic and triclinic astrophyllite are given in Table 1.

Although there is a definite difference in the values of the lattice parameters and in the space groups between monoclinic and triclinic astrophyllite, both minerals contain the same type of open-branched (Si_4O_{12}) chains. The difference in chemical composition, however, has produced a different stacking arrangement and symmetry.

In this study we realized the structure refinement of the monoclinic astrophyllite, using the sample kindly provided by A. Khomyakov from the Khibina alkaline massifs, Kala Peninsula, Russia (sample no. 3086). The translucent astrophyllite crystals are rice-straw-yellow in colour and have a vitreous lustre. The crystal form is a prism with size 0.12 × 0.12 × 0.21 mm. They have a Mohs hardness of 3.5–4.0 and a calculated specific gravity of 3.172 Mg m^{-3} (as V = 1258.5 Å^3). The

Table 1. *Experimental details*

Crystal data	
Chemical formula	$Fe_4H_4K_2Mg_2Na_2O_{30}Si_8Ti_2$
Chemical formula weight	1202.31
Cell setting	Monoclinic
Space group	$A2$
a (Å)	10.370 (3)
b (Å)	23.129 (5)
c (Å)	5.322 (1)
β (°)	99.55 (2)
V (Å^3)	1258.8 (5)
Z	2
D_x (Mg m^{-3})	3.173
D_m (Mg m^{-3})	3.35
Density measured by	Density bottle method
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71069
No. of reflections for cell parameters	14
θ range (°)	14–24
μ (mm^{-1})	3.78
Temperature (K)	298
Crystal form	Prism
Crystal size (mm)	0.21 × 0.12 × 0.12
Crystal colour	Yellow
Data collection	
Diffractometer	Rigaku RASA-IIS
Data collection method	$2\theta/\omega$ scans
Absorption correction	Refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min}	0.808
T_{max}	0.904
No. of measured reflections	5308
No. of independent reflections	2473
No. of observed reflections	1720
Criterion for observed reflections	$F^2 > 4\sigma(F^2)$
R_{int}	0.0687
θ_{max} (°)	35
Range of h, k, l	$-16 \rightarrow h \rightarrow 18$
	$0 \rightarrow k \rightarrow 19$
	$-18 \rightarrow l \rightarrow 18$
No. of standard reflections	3
Frequency of standard reflections	Every 100 reflections
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.057
$wR(F^2)$	0.1540
S	0.819
No. of reflections used in refinement	1804
No. of parameters used	252
H-atom treatment	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F^2) + (0.1532P)^2 + 0.04P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.767
$\Delta\rho_{max}$ (e Å^{-3})	2.470
$\Delta\rho_{min}$ (e Å^{-3})	-1.850
Extinction method	None
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 2. *Fractional atomic coordinates and occupancies*

	x	y	z	Occupancies
Na1	0.0	0.0047 (6)	0.0	1.0248 (50)
Fe1	0.0	-0.07000 (8)	1/2	0.9382 (31)
Fe2	0.0	0.07849 (6)	1/2	0.9582 (33)
Fe3	0.0	-0.13960 (9)	0.0	0.8304 (31)
Fe4	0.0	0.14983 (9)	0.0	0.7492 (32)
Mg1	0.0	-0.20778 (11)	1/2	1.4544 (63)
Mg2	0.0	0.21977 (10)	1/2	1.5740 (69)
Ti	0.28802 (9)	0.00415 (17)	0.43713 (17)	1.0000 (33)
Si1	0.2641 (2)	-0.21274 (9)	-0.0782 (4)	1.0
Si2	0.2649 (2)	0.22238 (9)	0.0797 (5)	1.0
Si3	0.2710 (2)	-0.08085 (10)	-0.0704 (5)	1.0
Si4	-0.2713 (2)	0.09007 (11)	0.0790 (5)	1.0
K1	1/2	-0.13404 (16)	1/2	0.96294 (53)
K2	1/2	0.14335 (16)	1/2	1.0000 (58)
Na2	1/2	0.0048 (6)	1.0	1.0354 (52)
O1	0.1168 (4)	0.0027 (5)	0.4037 (8)	1.0
O2	0.1146 (5)	-0.0776 (3)	-0.1285 (11)	1.0
O3	-0.1142 (6)	0.0860 (3)	0.1447 (13)	1.0
O4	0.3419 (6)	-0.0525 (3)	0.7037 (13)	1.0
O5	0.3366 (6)	0.0625 (3)	0.6981 (13)	1.0
O6	0.3293 (5)	-0.0542 (3)	0.1987 (12)	1.0
O7	0.3296 (8)	0.0605 (4)	0.1946 (15)	1.0
O8	0.3200 (5)	-0.1477 (3)	-0.0420 (13)	1.0
O9	-0.3272 (6)	0.1587 (3)	0.0671 (14)	1.0
O10	0.1041 (6)	-0.2147 (3)	-0.1266 (11)	1.0
O11	-0.1097 (5)	0.2207 (3)	0.1314 (12)	1.0
O12	0.3235 (5)	-0.2465 (3)	0.6924 (11)	1.0
O13	0.3205 (6)	-0.2496 (3)	0.1801 (12)	1.0
O14	0.1058 (5)	-0.1418 (2)	0.3643 (11)	1.0
O15	-0.1010 (6)	0.1535 (4)	0.6323 (13)	1.0

with the composition plane {100}. On the basis of O + OH = 30, analyses by electron microprobe of this material (the data was provided by Khomyakov, sample no. 3086) yield the formula: $(K_{1.750}Ca_{0.032})_{1.782}Na_{2.015}$-$(Fe^{2+}_{2.604},Mn_{1.077})_{3.681}Mg_{1.851}Ti_{1.812}[(Si_{3.919},Al_{0.076})_{3.995}$-$O_{12}]_2[(OH)_{5.980},F_{0.072})]_{6.052}$, which can be simplified as $K_2NaNa(Fe,Mn)_4Mg_2Ti_2[Si_4O_{12}]_2(OH)_4(OH,F)_2$.

A DTA analysis of astrophyllite was carried out to determine the presence of H_2O and OH groups. At 323 K an endothermic event was recorded, but was very weak. At 582 K the second endothermic event was recorded. This probably reflects the exclusion of non-essential H_2O from the crystal defect regions and channels. At 929–948 K an exothermic peak was recorded. This probably reflects a type of phase transition. The endothermic event at 1080–1089 K can be explained owing to the loss of structural OH, which led to the destruction of the crystal structure. Probably, the final endothermic event at 1180 K indicates the melting of astrophyllite.

2. Experimental

X-ray data from a single crystal of astrophyllite from Khibina alkaline massifs (sample no. 3086) were measured using an automated Rigaku RASA-IIS diffractometer and graphite-monochromated Mo $K\alpha$ radiation. The unit-cell parameters were obtained by

material exhibits a perfect {100} cleavage. Optically, the crystals are biaxial negative with $2V = 75°$. Refractive indices are $\alpha = 1.660$ (2), $\beta = 1.702$ (2) and $\gamma = 1.725$ (2)°, $c \wedge \gamma = 5°$, $\beta = b$. Some crystals are twinned,

Table 3. *Anisotropic displacement parameters for monoclinic magnesium astrophyllite*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U^{eq}
Na 1	0.0173 (13)	0.0188 (14)	0.0107 (13)	0.00000	0.0033 (10)	0.00000	0.0155 (7)
Fe1	0.0212 (8)	0.0185 (9)	0.0203 (9)	0.00000	0.0063 (7)	0.00000	0.0197 (5)
Fe2	0.0125 (7)	0.0103 (7)	0.0048 (6)	0.00000	−0.0029 (5)	0.00000	0.0097 (4)
Fe3	0.0191 (9)	0.0186 (9)	0.0122 (8)	0.00000	−0.0026 (7)	0.00000	0.0172 (5)
Fe4	0.0104 (8)	0.0096 (9)	0.0134 (9)	0.00000	0.0092 (7)	0.00000	0.0103 (5)
Mg1	0.0142 (11)	0.0097 (10)	0.0135 (12)	0.00000	0.0045 (9)	0.00000	0.0122 (6)
Mg2	0.0101 (10)	0.0080 (10)	0.0027 (9)	0.00000	−0.0005 (7)	0.00000	0.0071 (5)
Ti	0.0120 (3)	0.0113 (3)	0.0098 (3)	−0.0008 (11)	0.0024 (3)	−0.0004 (11)	0.0110 (2)
Si1	0.0120 (8)	0.0149 (9)	0.0076 (8)	−0.0005 (7)	0.0012 (7)	−0.0024 (7)	0.0116 (5)
Si2	0.0133 (9)	0.0067 (8)	0.0151 (10)	0.0011 (7)	0.0053 (8)	0.0005 (7)	0.0114 (5)
Si3	0.0140 (8)	0.0084 (7)	0.0164 (9)	−0.0020 (8)	−0.0001 (7)	0.0015 (7)	0.0132 (5)
Si4	0.0096 (8)	0.0167 (10)	0.0089 (8)	0.0002 (8)	0.0054 (7)	−0.0015 (8)	0.0113 (5)
K1	0.0281 (15)	0.0274 (14)	0.0375 (19)	0.00000	−0.0019 (13)	0.00000	0.0319 (9)
K2	0.0237 (14)	0.0305 (17)	0.0372 (17)	0.00000	0.0152 (12)	0.00000	0.0293 (9)
Na	0.0136 (13)	0.0192 (14)	0.0244 (17)	0.00000	−0.0007 (12)	0.00000	0.0195 (8)
O1	0.0112 (13)	0.0173 (17)	0.0174 (17)	−0.0094 (33)	−0.0017 (13)	0.0083 (31)	0.0158 (8)
O2	0.0172 (20)	0.0126 (20)	0.0159 (21)	0.0031 (19)	0.0155 (18)	0.0002 (18)	0.0138 (11)
O3	0.0083 (21)	0.0212 (28)	0.0201 (27)	0.0028 (24)	−0.0095 (20)	−0.0028 (21)	0.0179 (14)
O4	0.0116 (21)	0.0179 (25)	0.0240 (29)	−0.0011 (23)	−0.0004 (21)	−0.0018 (19)	0.0182 (14)
O5	0.0180 (26)	0.0340 (35)	0.0165 (27)	−0.0153 (25)	0.0140 (21)	−0.0050 (25)	0.0216 (15)
O6	0.0145 (19)	0.0270 (28)	0.0213 (24)	−0.0013 (23)	0.0166 (18)	0.0110 (20)	0.0194 (13)
O7	0.0281 (34)	0.0377 (39)	0.0226 (32)	0.0195 (30)	−0.0125 (27)	0.0017 (31)	0.0314 (19)
O8	0.0083 (19)	0.0177 (24)	0.0271 (29)	−0.0107 (21)	0.0032 (20)	−0.0024 (17)	0.0177 (13)
O9	0.0225 (27)	0.0057 (22)	0.0280 (31)	0.0082 (21)	0.0010 (24)	0.0027 (20)	0.0191 (14)
O10	0.0246 (26)	0.0175 (26)	0.0089 (23)	0.0004 (10)	−0.0031 (21)	−0.0014 (21)	0.0177 (14)
O11	0.0006 (16)	0.0076 (20)	0.0215 (26)	−0.0012 (20)	0.0071 (17)	0.0001 (15)	0.0093 (11)
O12	0.0122 (19)	0.0231 (26)	0.0148 (23)	0.0016 (21)	0.0064 (18)	0.0000 (19)	0.0162 (12)
O13	0.0125 (22)	0.0218 (27)	0.0143 (25)	0.0105 (22)	−0.0026 (20)	0.0018 (21)	0.0168 (13)
O14	0.0118 (20)	0.0043 (18)	0.0134 (22)	−0.0103 (16)	0.0006 (18)	−0.0021 (15)	0.0100 (11)
O15	0.0131 (25)	0.0392 (41)	0.0162 (270	0.0073 (29)	0.0054 (22)	0.0032 (28)	0.0225 (17)
H1							0.067
H2							0.032

least-squares refinement using 14 reflections, collected in the interval $2\theta = 28–48°$. The values determined were $a = 10.370\,(3)$, $b = 23.129\,(5)$, $c = 5.322\,(1)\,\text{Å}$, $\beta = 99.55\,(2)°$. The intensity data were measured using the $2\theta/\omega$ scan mode. The 2θ width was adjusted for dispersion by the equation $\theta = A + B\,\tan\theta$, where $A = 1.728$, $B = 0.5$. Three standard peaks were measured every 100 reflections and no significant change in their intensities was observed during data collection.

3. Structure determination

The structure of astrophyllite was determined using *SHELXS*86 (Sheldrick, 1985) and refined using *SHELXL*93 (Sheldrick, 1993). Considering $A2/m$, $A2$ and Am as possible space groups for astrophyllite, these three space groups have been tried in the present investigation. During the refinement in space group $A2/m$ and Am, none of the results were satisfactory and the $R(F^2)$ factors cannot reduce below 0.15, although $A2$ agreed better with the experimental results. According to space group $A2$, Fe atoms occupy five octahedral sites; Mg atoms, two octahedral sites; Ti atoms, one semi-octahedral site; K atoms were localized in two crystal chemical sites, which are situated between two layers. According to chemical analyses and the

feature of atomic positions, Na atoms should be located in two crystal chemical sites. One should be between the layers. How about the other crystal chemical site of the Na atom? We noticed that the interatomic distances of an octahedron, which was arranged previously with Fe atoms, were longer than the usual Fe−O bonds, so we anticipated that another Na atom was arranged at this site (Na1). The refinement of the structure confirmed that this suggestion was reasonable.

During the structure analyses, we discovered that one oxygen in a special position with $x = \frac{1}{2}$, which forms one of two apical vertices in [TiO_6] octahedra, is absent. This result was shown in a Fourier map section ($\frac{1}{2}$, y, z). This fact indicated that the coordination number of Ti is five rather than six. The Ti−O coordination polyhedron is a semi-octahedron in which four vertices are shared with Si−O tetrahedra and the fifth is shared with a Na1−O octahedron.

The atomic coordinates and occupancies are listed in Table 2 and displacement parameters in Table 3. The interatomic distances are given in Table 4. The F_o and F_c data have been deposited.† The H atoms were

Table 4. *Bond distances (Å) of monoclinic astrophyllite*

Fe1—O octahedron		Si1—O13	1.640 (7)
2 × Fe1—O2	2.138 (6)	Si2—O tetrahedron	
2 × Fe1—O14	2.178 (6)	Si2—O9	1.605 (7)
2 × Fe1—O1	2.183 (9)	Si2—O11	1.588 (5)
Fe2—O octahedron		Si2—O12	1.640 (6)
2 × Fe2—O3	2.066 (6)	Si2—O13	1.623 (7)
2 × Fe2—O15	2.202 (8)	Si3—O tetrahedron	
2 × Fe2—O1	2.238 (8)	Si3—O6	1.584 (7)
Fe3—O octahedron		Si3—O4	1.646 (7)
2 × Fe3—O2	2.051 (6)	Si3—O2	1.602 (6)
2 × Fe3—O14	2.064 (5)	Si3—O8	1.626 (6)
2 × Fe3—O10	2.208 (7)	Si4—O tetrahedron	
Fe4—O octahedron		Si4—O3	1.611 (6)
2 × Fe4—O15	2.062 (7)	Si4—O5	1.593 (7)
2 × Fe4—O3	2.116 (7)	Si4—O9	1.688 (7)
2 × Fe4—O11	1.175 (6)	Si4—O7	1.631 (8)
Mg1—O octahedron		Ti—O semi-octahedron	
2 × Mg1—O14	2.078 (6)	Ti—O1	1.755 (4)
2 × Mg1—O10	2.104 (6)	Ti—O4	1.943 (7)
2 × Mg1—O11	1.187 (6)	Ti—O5	1.942 (7)
Mg2—O octahedron		Ti—O6	1.948 (7)
2 × Mg2—O15	2.045 (8)	Ti—O7	1.923 (9)
2 × Mg2—O11	2.098 (6)	All other Ti—O distances	
2 × Mg2—O10	2.040 (7)	≥ 3.622 Å	
Na1—O octahedron		K1—polyhedron	
2 × Na1—O1	2.285 (4)	2 × K1—O4	2.831 (7)
2 × Na1—O3	2.416 (12)	2 × K1—O6	2.859 (7)
2 × Na1—O2	2.402 (12)	2 × K1—O8	3.181 (6)
Na2—polyhedron		2 × K1—O8	3.322 (7)
2 × Na2—O4	2.464 (10)	2 × K1—O12	3.433 (7)
2 × N2—O5	2.516 (10)	K2—polyhedron	
2 × Na2—O6	2.594 (10)	2 × K2—O5	2.841 (8)
2 × Na2—O7	2.543 (11)	2 × K2—O7	2.912 (9)
Si1—O tetrahedron		2 × K2—O9	3.165 (8)
Si1—O8	1.612 (6)	2 × K2—O9	3.263 (7)
Si1—O10	1.637 (7)	2 × K2—O12	3.395 (7)
Si1—O12	1.653 (7)	2 × K2—O13	3.333 (8)

located by calculating the difference electron density. Only isotropic thermal parameters of H atoms were refined.

3.1. *Description*

The coordination polyhedra of the crystal structure in monoclinic magnesium astrophyllite are shown in Figs. 1 and 2. Similarly, with mica the structure of astrophyllite contains three-layered sheets. Two external sheets are formed by the branched (Si,O) chains, connected by Ti—O semi-octahedra, whereas the internal sheet is formed by Fe—O, Mg—O and Na1—O octahedra. The interlayer space is filled by large K and Na2 cations (Fig. 1). The height of the three-layered sheet is 3.529 Å.

Fig. 2 shows astrophyllite-type branched single Si—O chains. According to the crystal chemical classification of silicates (Liebau, 1985), this type of silicate chain belongs to an open-branched zweier single chain $\{oB, 1^1_\infty\}[^2Si_4O_{12}]_2$. The branches of tetrahedra are connected with Ti—O semi-octahedra by corner-sharing and thus the continuous mixed sheets (100) are formed.

Na atoms occupy two crystal chemical sites. One is characterized by an eightfold coordination and is situated between the layers. Another Na atom is located inside an octahedron and is situated within the layer. The ranges of their bonds are 2.464–2.594 and 2.285–2.402 Å, respectively. The refinement indicated that the occupancies of Mg are larger than $\frac{1}{2}$, probably as a result of Fe entrance in the same crystal chemical sites.

4. Discussion

In the structure of monoclinic astrophyllite the Ti atoms have fivefold coordination rather than the more usual octahedral coordination, which was found, for example, in the structure of triclinic astrophyllite (Woodrow, 1967). The crystal chemistry of Ti silicates has been discussed in previous publications devoted to the structure determination of astrophyllite and lamprophyllite (Peng & Ma, 1963; Peng et al., 1984; Woodrow, 1967). Usually, titanium has octahedral coordination in silicates. In astrophyllite titanium plays a role similar to silicon and is situated between adjacent branched chains making up planar Ti—Si—O mixed layers (Fig. 2). This case is similar to lamprophyllite, apart from different Ti coordination: semi-octahedral in astrophyllite and octahedral in lamprophyllite. The semi-octahedra of astrophyllite are formed by the following crystal chemical environment: four terminal O atoms are contributed by branches from two Si—O chains plus O1, which is provided by Fe—O polyhedra. The distances between titanium and oxygen which are situated in the base of the semi-octahedron are within the interval 1.923–1.948 Å. These distances are similar to Ti—O bond lengths in Ti—O polyhedra. However, the distance between Ti and an apical semi-octahedral vertex is shorter, 1.755 Å, and is comparable to the Si—O bond length. This investigation indicated that the existence of Ti semi-octahedra as a kind of intermediate coordination polyhedron is reasonable in titanium silicates.

The crystal structure of astrophyllite is similar to bafertisite and lamprophyllite structure, because they contain similar three-layered sheets. Besides, their (Si,O) tetrahedral complexes can be considered as a result of the partial replacement of some of the Si—O polyhedra in mica-like tetrahedral layers by Ti—O polyhedra: in monoclinic astrophyllite Ti—O semi-octahedra substitute one Si—O polyhedron in each six-membered ring, since in bafertisite and lamprophyllite two tetrahedra in each hexagonal ring are replaced by Ti—O polyhedra. In astrophyllite the edges of Si—O polyhedra are approximated by the edges of Mg—O polyhedra. Therefore, the central axis of the astrophyllitic Si—O chain is fixed at the Mg—O polyhedron and produces a twofold symmetrical axis. As a result, the monoclinic structure appears. Thus, this investigation revealed the structural and chemical differences

between monoclinic magnesium astrophyllite and triclinic astrophyllite, as well as the similarity between astrophyllite from one side and lamprophyllite and bafertisite from the other.

Zvyagin and Vrublevskaya derived two group astrophyllites, each containing seven polytypic structures differing with regard to symmetry and the ordering period of the layers. Obviously, monoclinic astrophyllite belongs to a type of centred orthogonal cell ($C2/m$ symmetry). The appearance of the space group $A2$ was caused by a deviation of atomic position in the symmetric centre. Zvyagin and Vrublevskaya
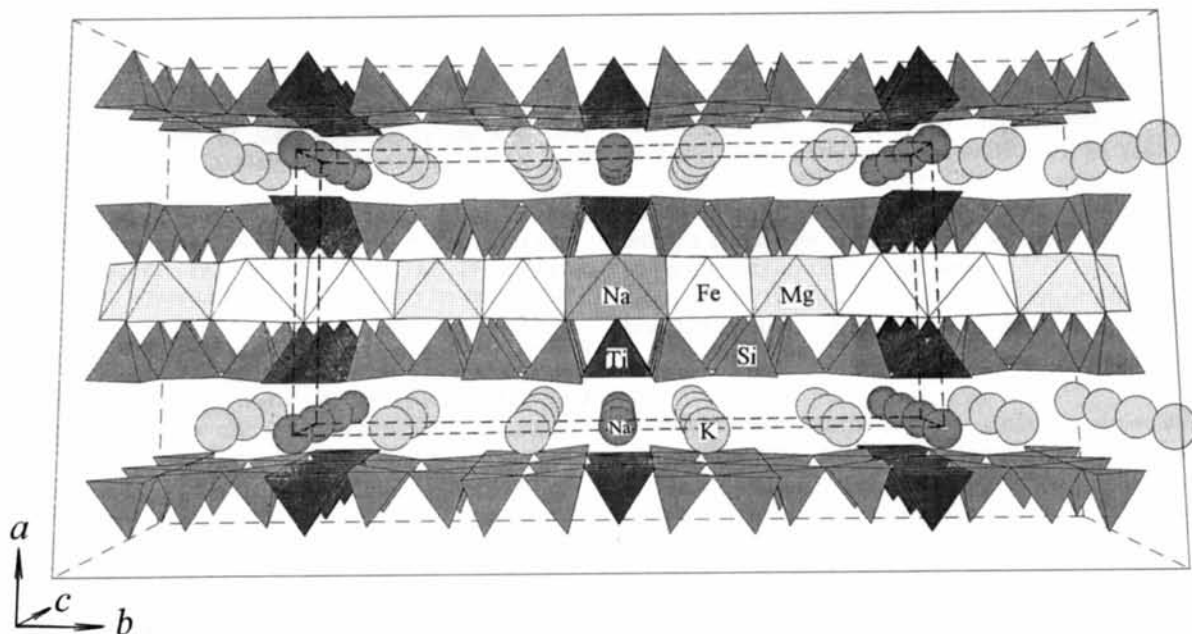
Fig. 1. The description of monoclinic magnesium astrophyllite crystal structure by polyhedra along the c axis.
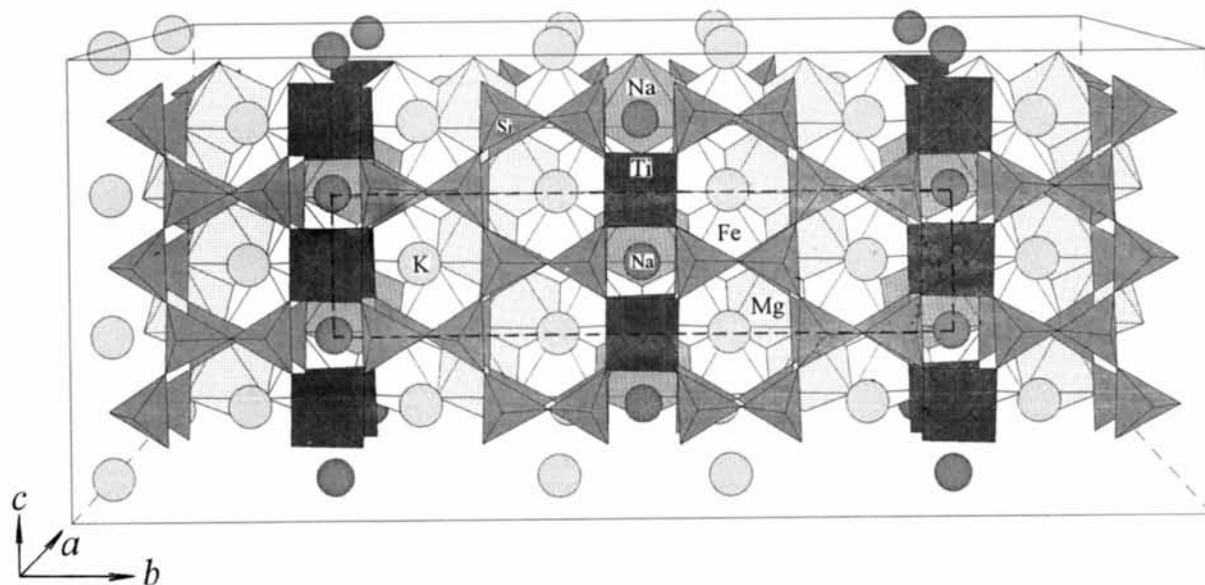

Fig. 2. The connection between the tetrahedra and semi-octahedra of Ti in the Si—O tetrahedral sheet along the a axis in monoclinic magnesium astrophyllite.

considered this feature of natural astrophyllite (Peng & Ma, 1963; Woodrow, 1967).

Besides bafertisite and lamprophyllite, triclinic astrophyllite also has a close relationship with nafertisite $(Na,K)_3(Fe^{2+},Fe^{3+},\square\square)_{10}[Ti_2(Si,Fe^{3+},Al)_{12}O_{37}](OH,O)_6$, recently studied by Ferraris *et al.* (1996). Both structures are characterized by the direct contacts of mica-like three-layered sheets through the *trans*-vertices of Ti—O octahedra, which are inserted between (Si,O) complexes. The substitution of Ti—O octahedra by Ti—O semi-octahedra in the monoclinic astrophyllite excludes such direct contacts between mica-like layers. Moreover, the tetrahedral complex of nafertisite $[Si_{12}O_{34}]$ differs from that of monoclinic astrophyllite $[Si_4O_{12}]$ and in terms of Liebau's (1985) classification must be considered as an open-branched zweier double chain. However, the presence of mixed mica-like layers and the similar role of Ti^{4+} cations allow both modifications of astrophyllite to be considered as members of the polysomatic series, which also includes bafertisite and nafertisite (Ferraris *et al.*, 1996).

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