

Shirokshinite, $K(\text{NaMg}_2)\text{Si}_4\text{O}_{10}\text{F}_2$, a new mica with octahedral Na from Khibiny massif, Kola Peninsula: descriptive data and structural disorder

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Abstract: Shirokshinite, $K(\text{NaMg}_2)\text{Si}_4\text{O}_{10}\text{F}_2$, is the analogue of tainiolite, $K(\text{LiMg}_2)\text{Si}_4\text{O}_{10}\text{F}_2$, with the *M*1 octahedron fully occupied by Na instead of Li. It was found in the Kirovskii underground apatite mine (Kukisvumchorr Mountain, Khibiny massif, Kola Peninsula, Russia) as a late hydrothermal mineral in a small hyperalkaline pegmatite embedded in ristschorrite. Shirokshinite is associated with microcline, kupletskite, aegirine, natrolite, lorenzenite, calcite, remondite-(Ce), donnayite-(Y), mckelveyite-(Y) and galena. Crystals are usually skeletal and coarse hexagonal [001] prismatic. Shirokshinite is transparent to translucent, colourless to pale greyish, hardness Mohs' ~2.5; $D(\text{calc}) = 2.922 \text{ g/cm}^3$. Optically biaxial (-), $\alpha = 1.526(1)$, $\beta = 1.553(2)$, $\gamma = 1.553(2)$; $2V_{\text{meas}} = -5(5)^\circ$, $2V_{\text{calc}} = -0^\circ$; $Y = b$, $Z \sim a$, $X^\wedge c = 3(2)^\circ$. The IR spectrum of shirokshinite is unique even if close to that of tainiolite: in particular, the presence of Na^+ instead of Li^+ shifts some bands towards low-frequencies. Single-crystal diffraction data (MoK α -radiation) gave $a = 5.269(2)$, $b = 9.092(9)$, $c = 10.198(3) \text{ \AA}$, $\beta = 100.12(7)^\circ$, $Z = 2$, 1*M*-polytype, space group *C2/m*. Structure anisotropic refinement converged $R = 0.13$ for 715 observed reflections. Evidence of stacking faults in the structure is discussed and compared with the so called Đurovič effect. The very little ditrigonal distortion in spite of the large dimension of the Na octahedron is discussed in comparison with tainiolite. A critical revision of old published data indicating octahedral Na in micas shows that this hypothesis was biased by the low quality of the chemical analyses.

Key-words: shirokshinite, new mineral, sodium mica, Khibiny massif, Kola, structural disorder, octahedral Na.

Introduction

Mica group minerals show a stable crystal structure under a very wide range of chemical composition and almost forty species are now known: for an updated review of micas see Mottana *et al.* (2002). The chemical diversity of micas is favoured by cation and anion isomorphism in the structural sites shown in the general formula $IM_{2-3}\square_{1-0}T_4O_{10}A_2$ where *T*, *M* and *I* represent tetrahedral, octahedral and interlayer cations, respectively; *A* are additional anions. The following species-forming cations were known in micas: *T* = Si, Al, and rarely Fe^{3+} , Be, B; *M* = Al, Mg, Fe^{2+} , Li, and rarely Fe^{3+} , V^{3+} , Cr^{3+} , Mn^{2+} , Mn^{3+} , Zn; *I* = K, rarely Na, Ba, Ca, Cs, NH_4 ; *A* = OH, F, rarely O (Rieder *et al.*, 1998). The possibility of forming polytypes further increases the species variety in micas; *e.g.*, recently the theoretically possible but not yet structurally characterised 2*O*-polytype has been reported by Ferraris *et al.* (2001a). For an update review of mica structures and polytypes see Ferraris & Ivaldi (2002) and Nespolo & Đurovič (2002).

Because the crystal structures are solved for the majority of known natural and synthetic micas and the crystal chemistry of micas is widely studied, it was a surprise for us to discover a new natural mica with Na atoms dominant in an octahedral site and absent instead in the interlayer. This mica has formula $K(\text{NaMg}_2)\text{Si}_4\text{O}_{10}\text{F}_2$ and is the analogue of tainiolite, $K(\text{LiMg}_2)\text{Si}_4\text{O}_{10}\text{F}_2$, with the *M*1 octahedron fully occupied by Na instead of Li. The new trioctahedral mica was named shirokshinite in the memory of Russian geologist Nikolay Vasilievich Shirokshin (1809 – ?), a Captain of the Russian Mining Corps, who was the first researcher of Khibiny alkaline massif. He visited Khibiny Mountains for field observations in summer 1834 and published the first data on geology, petrology and geomorphology of Khibiny massif (Shirokshin, 1835).

The mineral species and name have been approved by the Commission on New Minerals and Mineral Names of the IMA (2001-063). A fragment of the holotype specimen is deposited in the Fersman Mineralogical Museum of the

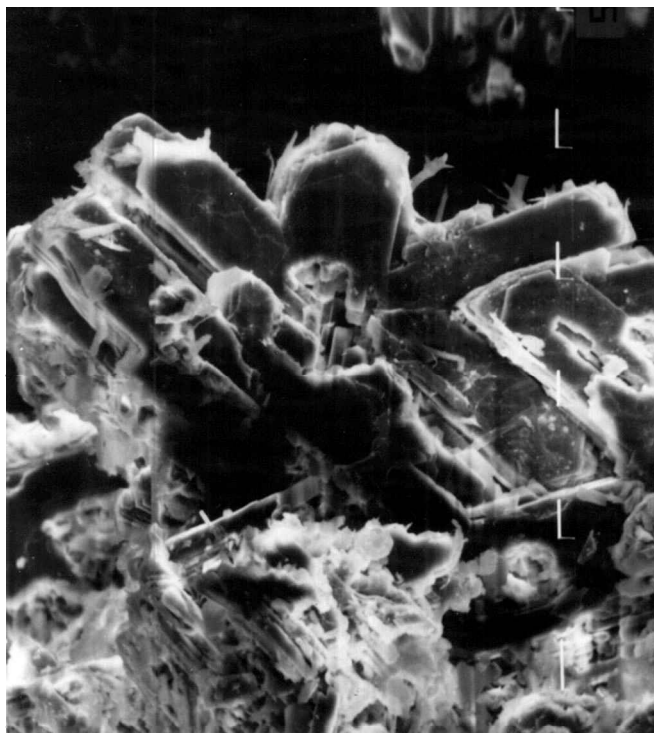


Fig. 1. SEM view of the skeletal morphology of shirokshinite. Width of the field of vision: 0.05 mm.

Table 1. Wavenumbers (cm^{-1}) of absorption bands in IR spectra of trioctahedral magnesian micas.

Shirokshinite	Tainiolite	Phlogopite	Band assignment
—	—	3660	ν (O-H)
<u>1130</u>	<u>1130</u>		
1060	1100sh	1070 sh	ν (Si-O-Si)
<u>945</u>	<u>966</u>	<u>1060</u>	ν (Si-O)
		970sh	
742		814	
<u>702</u>	<u>716</u>	<u>700</u>	δ (O-Si-O)
		680	
530sh	525sh	520sh	
493	500		δ (Si-O-Si);
471			ν (M-O)
<u>462</u>	<u>470</u>	<u>465</u>	
400			

ν = stretching vibrations, δ = bending vibrations; M = octahedral cation; sh = shoulder; most intense bands are underlined.

Russian Academy of Sciences, Moscow (registration record no. 2786/1).

Occurrence and general appearance

Shirokshinite was found in a specimen collected by amateur mineralogist A.S. Podlesnyi at level +252 m of Kirovskii underground apatite mine at Kukisvumchorr Mountain, southern part of Khibiny alkaline massif, Kola Peninsula,

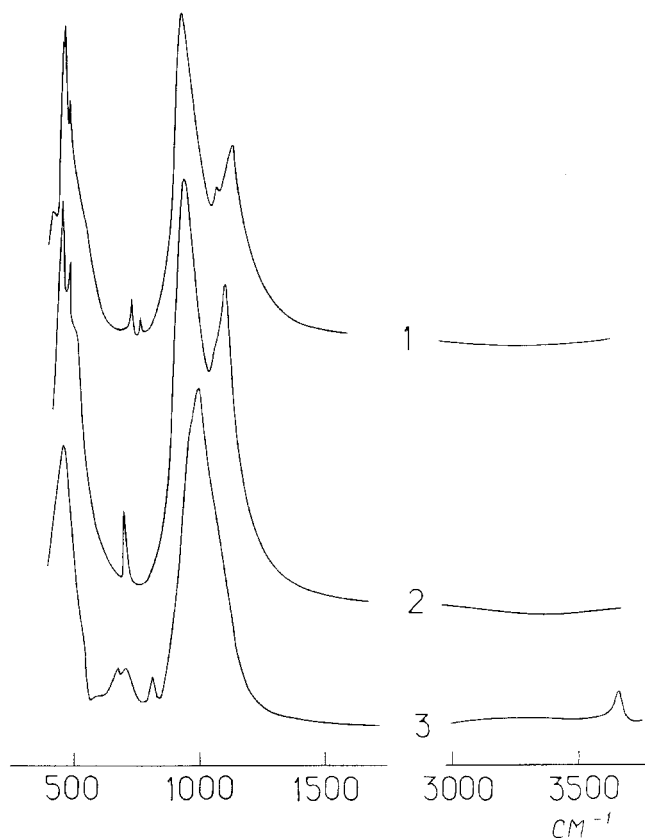


Fig. 2. IR spectra of shirokshinite (1), tainiolite from Lovozero massif, Kola (2), and phlogopite from Kovdor massif, Kola (3): see also Table 1.

Russia. It is a late hydrothermal mineral and occurs in a small hyperalkaline pegmatite embedded in ristschorrite near the contact with nepheline-apatite rock. Shirokshinite is associated with microcline, kupletskite, aegirine, natrolite, lorenzenite, calcite, remondite-(Ce), donnayite-(Y), mckelveyite-(Y) and galena.

The new mica occurs within small cavities of the pegmatite on the surface of microcline and kupletskite crystals. It forms coarse hexagonal [001] prismatic crystals up to 2.5 x 1 x 0.8 mm that are grouped in sheaf-like clusters up to 2.5 mm as maximum dimension. The crystals show usually a skeletal morphology; by analogy with other micas, possible crystal forms are {010}, {110} and {001}, maybe also {11-1}. The skeletons look like hollow "cases" and snowflakes; sometimes both morphologies have been observed together. Snowflakes and other kinds of skeletal textures consist of needle- or ruler-shaped individuals up to 0.06 mm in length forming angles of about 60° between them (Fig. 1). Non-skeletal crystals are rare; they are usually split and affected by a mosaic of tiny cavities. Their natural and cleavage {001} surfaces are often curved; lateral faces (probably {110} and {010}) are usually rough and corrugated.

After the 2O-polytype quoted above and biotite 3A₁ (Bortskiy *et al.*, 1987), shirokshinite represents the third peculiar mica found in the hyperalkaline Khibiny pluton.

Table 2. Chemical composition (wt. %) of shirokshinite and some other micas from alkaline pegmatites analysed in this work by electron microprobe.

	# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9
K ₂ O	10.18 (0.4)	11.19	10.97	10.35	10.53	9.63	11.08	9.84	11.03
Na ₂ O	7.01 (0.6)	7.36	0.30	0.95	0.21	0.57	0.09	0.08	0.05
Li ₂ O*	0.00	-	3.58	3.07	3.46	1.44	7.46	7.37	7.25
MgO	19.17 (0.9)	19.14	19.30	18.57	19.17	18.88	0.34	0.04	0.62
MnO	0.23 (0.05)	-	1.36	0.15	1.09	0.57	0.12	0.00	0.09
FeO **	1.54 (0.1)	-	0.69	4.13	0.67	6.24	1.05	0.13	0.22
ZnO	0.00	-	0.00	0.00	0.00	0.00	0.21	0.00	0.00
Al ₂ O ₃	0.24 (0.1)	-	1.21	1.88	0.69	11.02	11.17	12.69	13.57
TiO ₂	0.16 (0.05)	-	0.00	0.29	0.27	1.18	2.39	0.35	0.93
SiO ₂	57.64 (1.1)	57.08	59.85	56.49	58.59	45.27	61.07	61.85	59.80
H ₂ O*	0.00	-	0.07	0.86	0.53	2.68	0.00	0.00	0.00
F	9.19 (0.7)	9.03	9.45	7.47	8.22	3.24	10.14	10.62	10.25
-O=F ₂	-3.87	-3.80	-3.98	-3.14	-3.46	-1.36	-4.27	-4.47	-4.32
Total	101.49	100.00	102.80	101.55	99.97	99.36	100.86	98.50	99.49

Analyst N.N. Kononkova. ## 1, 3, 4, 5, 6, 9 are the mean of 3 point analyses each; ## 7, 8 are the mean of 2 point analyses each. Rb, Cs, Ca, Sr, Ba, V, Cr, Nb, Cl, S below detection limits. Formulae based on the 7 octahedral plus tetrahedral cations pfu and 22 negative charges; no O anions over 10 were added.

*Li and H₂O not analysed; Li has been calculated by constraining to 22 the sum of the cationic valences and to 7 the sum of octahedral plus tetrahedral cations pfu; the OH content has been obtained from charge balance.

** All Fe as Fe²⁺.

1 – Shirokshinite: Kirovskii Mine, Khibiny (estimated standard deviations are given in brackets):

$(\text{K}_{0.90}\text{Na}_{0.02})_{\Sigma 0.92}(\text{Na}_{0.92}\text{Mg}_{1.97}\text{Fe}_{0.09}\text{Mn}_{0.01}\text{Ti}_{0.01})_{\Sigma 3}(\text{Si}_{3.98}\text{Al}_{0.02})_{\Sigma 4}\text{O}_{9.995}\text{F}_{2.01}$.

2 – According to ideal formula $\text{KNaMg}_2\text{Si}_4\text{O}_{10}\text{F}_2$.

3 – Tainiolite, colourless and transparent: Narssarssuk, Greenland (specimen collected by G. Flink and obtained from Geological Museum of Copenhagen University; now no. 61149 in the systematic collection of Fersman Mineralogical Museum, Moscow):

$(\text{K}_{0.92}\text{Na}_{0.04})_{\Sigma 0.96}(\text{Mg}_{1.90}\text{Li}_{0.95}\text{Mn}_{0.08}\text{Fe}_{0.04}\text{Al}_{0.04})_{\Sigma 3.01}(\text{Si}_{3.95}\text{Al}_{0.05})_{\Sigma 4}\text{O}_{10}(\text{F}_{1.97}\text{OH}_{0.03})_{\Sigma 2}$.

4 – Tainiolite (“spodiophyllite”), pale coffee-coloured: Narssarssuk (specimen collected by O.B. Bøggild and obtained from Geological Museum of Copenhagen University, no. 205.1912, now no. 60270 in the systematic collection of Fersman Mineralogical Museum, Moscow):

$(\text{K}_{0.90}\text{Na}_{0.10})_{\Sigma 1}(\text{Mg}_{1.88}\text{Li}_{0.84}\text{Fe}_{0.23}\text{Na}_{0.03}\text{Mn}_{0.01}\text{Ti}_{0.01})_{\Sigma 3}(\text{Si}_{3.84}\text{Al}_{0.15})_{\Sigma 3.99}\text{O}_{10}(\text{F}_{1.61}\text{OH}_{0.39})_{\Sigma 2}$.

5 – Tainiolite, brownish: Lepkhe-Nelm Mt., Lovozero, Kola (specimen collected by I.V.P. from the same pegmatite as # 10 in Table 8):

$(\text{K}_{0.91}\text{Na}_{0.03})_{\Sigma 0.94}(\text{Mg}_{1.93}\text{Li}_{0.94}\text{Mn}_{0.06}\text{Al}_{0.01}\text{Fe}_{0.04}\text{Ti}_{0.01})_{\Sigma 2.99}(\text{Si}_{3.96}\text{Al}_{0.04})_{\Sigma 4}\text{O}_{10}(\text{F}_{1.76}\text{OH}_{0.24})_{\Sigma 2}$.

6 – Phlogopite (“spodiophyllite”), brown: Kuivchorr Mt., Lovozero (specimen collected by I.V.P. from the same pegmatite as # 8 in Table 8):

$(\text{K}_{0.87}\text{Na}_{0.08})_{\Sigma 0.95}(\text{Mg}_{1.99}\text{Li}_{0.41}\text{Fe}_{0.37}\text{Al}_{0.13}\text{Ti}_{0.06}\text{Mn}_{0.03})_{\Sigma 2.99}(\text{Si}_{3.21}\text{Al}_{0.79})_{\Sigma 4}\text{O}_{10}(\text{OH}_{1.27}\text{F}_{0.73})_{\Sigma 2}$.

7 – Polyolithionite, colourless: Narssarssuk (obtained from Geological Museum of Copenhagen University, collected by O.V. Petersen):

$(\text{K}_{0.92}\text{Na}_{0.01})_{\Sigma 0.93}(\text{Li}_{1.95}\text{Al}_{0.83}\text{Ti}_{0.12}\text{Fe}_{0.06}\text{Mg}_{0.03}\text{Mn}_{0.01}\text{Zn}_{0.01})_{\Sigma 3.01}(\text{Si}_{3.97}\text{Al}_{0.03})_{\Sigma 4}\text{O}_{9.96}\text{F}_{2.08}$.

8 – Polyolithionite, greenish: Qeqertaasaq Island, Kangerluarsuk, Ilímaussaq, Greenland (collected by I.V.P.):

$(\text{K}_{0.82}\text{Na}_{0.01})_{\Sigma 0.83}(\text{Li}_{1.94}\text{Al}_{0.98}\text{Ti}_{0.02}\text{Fe}_{0.01})_{\Sigma 2.95}\text{Si}_{4.05}\text{O}_{9.90}\text{F}_{2.20}$.

9 – Polyolithionite, brownish: Lepkhe-Nelm Mt., Lovozero (collected by I.V.P.):

$(\text{K}_{0.91}\text{Na}_{0.01})_{\Sigma 0.92}(\text{Li}_{1.91}\text{Al}_{0.97}\text{Mg}_{0.06}\text{Ti}_{0.05}\text{Fe}_{0.01})_{\Sigma 3}(\text{Si}_{3.92}\text{Al}_{0.08})_{\Sigma 4}\text{O}_{9.94}\text{F}_{2.12}$.

Experimental

Physical and optical properties

Shirokshinite is transparent to translucent, colourless to pale greyish, sometimes with greenish tint. Streak is white; lustre is pearly to vitreous. No fluorescence has been observed in UV light. Cleavage {001} perfect as usual for micas; fracture laminated. Leaf-like flexible, but almost not elastic; hardness Mohs' ~2.5. Density could not be satisfactorily measured because of the skeletal morphology; $D(\text{calc}) = 2.922 \text{ g/cm}^3$. As it is typical for micas, the two largest refractive indices are practically identical: optically biaxial (-), $\alpha = 1.526(1)$, $\beta = 1.553(2)$, $\gamma = 1.553(2)$; $2V_{\text{meas}} = -5(5)^\circ$, $2V_{\text{calc}} = -0^\circ$. Dispersion not observed; colourless, nonpleochroic. Orientation: $Y = b$, $Z \sim a$, $X^c = 3(2)^\circ$.

IR spectroscopy

A pellet of shirokshinite mixed with anhydrous KBr was analysed by a Specord 75 IR spectrometer (standards: polystyrol and NH₃; the precision of frequency measurement is $\pm 1 \text{ cm}^{-1}$). The IR spectrum of shirokshinite (Table 1, Fig. 2) is unique and its unusual features suggested the detailed study here presented. The overall aspect is relatively similar to that of the spectrum of tainiolite but the two spectra clearly differ in position and splitting of some absorption bands. In particular, the presence in shirokshinite of the heavier Na⁺ ion instead of Li⁺ causes significant shifts of some bands towards low-frequencies. The shift affects mainly the bands corresponding to the stretching (tainiolite: 1100 cm^{-1} ; shirokshinite: 1060 cm^{-1}) and bending (tainiolite: 500 cm^{-1} ; shirokshinite: 493 cm^{-1}) vibrations of the Si-O-Si bridge.

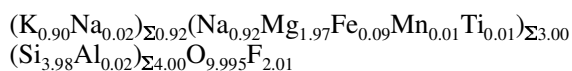
Table 3. X-ray powder data of shirokshinite.

I_{meas}	$d_{\text{meas}}(\text{\AA})$	I_{calc}^*	$d_{\text{calc}}(\text{\AA})$	hkl
70	10.0	100	10.02	001
10	4.98	17	5.011	002
40	4.52	23; 13	4.536; 4.504	020; 110
60	3.67	53	3.634	11-2
90	3.36	70; 72	3.363; 3.341	022; 003
50	3.16	72	3.123	112
50	2.92	48	2.901	11-3
20	2.68	33	2.690	023
90	2.59	20; 32;	2.625; 2.617;	20-1; 130;
		49; 87	2.594; 2.584	200; 13-1
30	2.50	8; 6;	2.508; 2.506;	113; 004;
		3	2.476	131
100	2.41	40; 82	2.412; 2.405	201; 13-2
30	2.27	13; 6;	2.272; 2.268;	22-1; 040;
		13	2.252	220
60	2.14	20; 46	2.156; 2.152	202; 13-3
10	2.10	5; 2	2.129; 2.066	221; 042
20	2.01	20	2.005	005
20	1.990	11	1.983	20-4
20	1.965	25	1.976	133
5	1.890	2; 2	1.895; 1.893	203; 13-4
10	1.825	3	1.817	22-4
5	1.755	3	1.749	223
5	1.723	2; 2	1.734; 1.724	134; 31-1
80	1.665	21; 46	1.663; 1.662	204; 13-5
5	1.635	6; 4	1.631; 1.630	31-3; 311
10	1.599	6; 6	1.596; 1.593	24-3; 152
10	1.560	4; 4	1.562; 1.561	242; 15-3
100	1.522	12; 21;	1.531; 1.527;	20-6; 135;
		41; 22	1.519; 1.512	33-1; 060
10	1.497	5; 4	1.501; 1.495	330; 061
10	1.447	1	1.451	22-6
10	1.433	3; 1	1.432; 1.428	007; 11-7
60	1.359	10; 21;	1.358; 1.354;	20-7; 136;
		3	1.345	046
50	1.314	4; 8;	1.316; 1.312;	40-1; 40-2;
		9	1.310	26-1
5	1.295	6	1.295	064
5	1.277	8	1.281	261
30	1.255	3; 6;	1.259; 1.254;	401; 26-3;
		4; 3	1.254; 1.253	226; 008
10	1.222	2; 1	1.224; 1.223	35-3; 351
10	1.205	2; 2	1.208; 1.207	172; 065
10	1.153	1; 1	1.161; 1.138	173; 44-1
10	1.095	1; 1	1.095; 1.093	20-9; 138
40	1.078	3; 8	1.078; 1.076	404; 26-6
20	1.058	5; 2	1.058; 1.058	13-9; 208

Shifts occur also for bands corresponding to the Si-O stretching vibrations (tainiolite: 966 cm^{-1} ; shirokshinite: 945 cm^{-1}). The presence of a triplet (471, 462 and 400 cm^{-1}) in the region of the M-O stretching vibrations of shirokshinite is apparently caused by the resonance between these vibrations and the bending vibrations of the Si-O-Si bridge. Absence of absorption bands in the 3000-3800 cm^{-1} region shows that shirokshinite does not contain OH-groups and water molecules; Be-O and B-O vibrations are also absent.

Chemical data

Electron microprobe analyses of shirokshinite and other samples (Table 2) were done on a Camebax Microbeam instrument using an operating voltage of 15 kV and an estimated beam current of 30 nA. Areas 10 x 10 μm^2 were scanned to minimise loss of F and Na. The following standards were used: orthoclase (K), albite (Na, Al), diopside (Ca, Mg), andradite (Fe, Si), MnTiO_3 (Mn, Ti), fluorapatite (F). Li was not analysed because of scarce substance; its absence in shirokshinite is supported both by the occurrence of sufficient octahedral cations and by the structure determination. H_2O was not determined because of the same reason; according to the IR spectrum it is absent and enough F is present for a full substitution $\text{F} \rightarrow \text{OH}$. The empirical formula of shirokshinite, based on 22 negative charge, is



and corresponds to an ideal formula $\text{KNaMg}_2\text{Si}_4\text{O}_{10}\text{F}_2$ which requires the composition given in Table 2. The compatibility index calculated from the Gladstone-Dale relationship (Mandarino, 1981) using $D(\text{calc})$ is 0.017 (superior).

X-ray crystallography

X-ray powder data for shirokshinite (Table 3) were obtained by Debye-Scherrer method ($\text{FeK}\alpha$ -radiation, camera RKD-57.3, internal standard Si). It is similar to that of tainiolite (Table 4, where other comparative data are reported) but some interplanar distances are larger as a result of substitution of Li^+ by larger Na^+ . Indexing has been done by considering also the corresponding pattern calculated from the parameters of the structure refinement (including the residual peaks; see below). Least-squares refined unit cell parameters are: $a = 5.269(2)$, $b = 9.071(2)$, $c = 10.178(4)$ \AA , $\beta = 100.03(3)^\circ$, $V = 479.0(4)$ \AA^3 ; $a : b : c = 0.5809 : 1 : 1.1220$.

Single-crystal diffraction data for shirokshinite were obtained on a Siemens P4 four-circle diffractometer using $\text{MoK}\alpha$ -radiation (Table 5). The following unit cell parameters have been obtained by least-squares refinement of 10 reflections ($2\theta \leq 21^\circ$): $a = 5.269(2)$, $b = 9.092(9)$, $c = 10.198(3)$ \AA , $\beta = 100.12(7)^\circ$, $V = 481(1)$ \AA^3 ; $Z = 2$ (1M-polytype).

Due to the skeletal morphology of shirokshinite, the best crystal available for single-crystal diffractometry showed still a widespread presence of broadening and streaking in the diffraction pattern (see below). The merging of the 2120 collected reflections ($h > 0$; $2\theta_{\text{max}} = 70^\circ$) gave a set of 715 independent observed reflections with $\text{Fo} > 4\sigma(\text{Fo})$. An anisotropic refinement (SHELXL97 package, Sheldrick 1997) converged to $R = 0.13$ in space group $C2/m$.

Discussion

Structural disorder

The presence of broadening and/or streaks in the diffraction pattern and of residual peaks in the difference electron den-

Table 4. Comparative characteristics of shirokshinite and tainiolite.

Mineral	Shirokshinite*	Tainiolite**
Formula	$K(\text{NaMg}_2)\text{Si}_4\text{O}_{10}\text{F}_2$	$K(\text{LiMg}_2)\text{Si}_4\text{O}_{10}\text{F}_2$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
Polytype	$1M$	$1M$
$a(\text{\AA})$	5.269	5.231
$b(\text{\AA})$	9.071	9.065
$c(\text{\AA})$	10.178	10.140
$\beta(^{\circ})$	100.03	99.52
$V(\text{\AA}^3)$	479.0	474.2
Z	2	2
Density (g/cm^3)	2.922 (calc)	2.81–2.87
α	1.526	1.520–1.540
β	1.553	1.546–1.570
γ	1.553	1.546–1.570
optic sign, $2V_{\text{meas}}$	-5°	$-0-5^{\circ}$
Strongest reflections of the X-ray	10.0–70–(001)	10.04–74–(001)
powder pattern:	3.67–60–(11-2)	5.01–44–(002)
$d(\text{\AA})-I-(hkl)$	3.36–90–(022, 003)	3.60–17–(11-2)
	2.59–90–(200, 13-1)	3.34–100–(003)
	2.41–100–(201, 13-2)	3.12–26–(112)
	2.14–60–(202, 13-3)	2.88–25–(11-3)
	1.665–80–(204, 13-5)	2.398–17–(202, 13-2)
	1.522–100–(135, 33-1)	1.999–35–(005)
	1.359–60–(20-7, 136)	1.655–17–(135, 006)

*This work; cell parameters from powder diffraction data. ** Toraya *et al.*, 1977; Minerals, 1992

Table 5. Miscellaneous data collection and structure refinement information for shirokshinite.

$a(\text{\AA})$	5.269(2)
$b(\text{\AA})$	9.092(11)
$c(\text{\AA})$	10.197(3)
$\beta(^{\circ})$	100.12(7)
$V(\text{\AA}^3)$	480.9(4)
Space-group	$C2/m$
Z	2
Abs. coef. (mm^{-1})	1.32
$F(000)$	420
$D_{\text{calc}}(\text{g/cm}^3)$	2.922
Crystal size (mm)	0.15x0.08x0.03
Radiation/monochrom.	$\text{MoK}\alpha$ / graphite
Scan mode	ω
2θ max($^{\circ}$)	70
$R(\text{int})$	0.19
Reflections collected	2120
Independ. reflections	1032
$ F_o > 4\sigma(F_o)$	715
Refinement method	Full-matrix LS on F^2
Weight [§]	$a = 0.1463, b = 10.91$
Goodness of fit on F^2	1.167
$R1$ [$ F_o > 4\sigma(F_o)$]	0.129
$R1$ (all data)	0.162
$WR2$	0.376

[§]weight = $1/[\sigma(F_o)^2 + (aP)^2 + bP]$; $P = [\max(F_o^2) + 2(F_c^2)]/3$

sity map clearly indicated the presence of stacking faults in the structure of shirokshinite. In particular, as discussed by Nespolo & Ferraris (2001), the occurrence of residual peaks

shifted by $\pm b/3$ from the positions of Si, K and basal oxygen atoms means one of the two following types of stacking faults related to $\pm b/3$ slips of half *TOT* layer (also known as 2:1 layer) at the level of the octahedral cations (for a more detailed analysis see the quoted paper).

Type (a) – The slip occurs on both (001) sides of the interlayer cation thus restoring the conditions for coordinating this cation, whose presence is thus not influenced, even locally. This type of planar defect is local and does not affect the bulk matrix. If the density of defects is low, crystallinity is not destroyed and only the so called non-family ($k \neq 3n$) reflections are affected by broadening and streaking. In this case the local shifts of atoms cannot be imagined by X-ray diffraction because the faults are dispersed in the matrix and do not diffract coherently. The residual peaks are consequent to a different scale between the diffracted intensities measured for the family reflections ($k = 3n$, unaffected) and the non-family reflections ($k \neq 3n$, affected); the so called Đurovič effect occurs (Nespolo & Ferraris, 2001).

Type (b) – The slip occurs only in the *TOT* layer on one (001) side of the interlayer cation, destroying the local coordination environment of this cations. The region (domain) adjacent to where the local slip occurred shows a relative shift of $\pm b/3$. If the fault is repeated, the matrix contains other domains with a relative shift. It can be shown that, if the structure is seen along [001] all the atoms belonging to shifted domains overlap equivalent atoms of the matrix except the basal oxygens, the interlayer cation, and 50% of the tetrahedral cation. If the density of faults is low, *i.e.* domains with a relative shift of $\pm b/3$ represent a minor part of the crystal, the overall periodicity is not destroyed, but the contribution to the total diffracted intensity from the domains can be substantial and influence the calculated electron density, which thus shows residual peaks in the positions of the shifted atoms. These peaks can be refined, but the combined presence of lower crystallinity and partially overlapped atoms reduces the quality of the structure refinement.

The occurrence of type (b) stacking faults in shirokshinite is proved by:

1. The residual peaks occurring at $\pm b/3$ from Si (~ 2 electrons), K (~ 1 electron) and basal oxygens (~ 0.6 electron from O1; smaller peaks correspond to O2 and O3), do not disappear (or at least reduce in height) by applying different scale factors to the family and non-family reflections.
2. The positions of the residual peaks can be refined and the R value is reduced from 0.16 to 0.13.
3. The analytical deficiency of interlayer cations [$0.90K + 0.02Na$ requiring 17.3 electrons (Table 1)] is confirmed by the refinement which shows 17.9(5) electrons (Table 6).

The crystal structure

In spite of the high R value, the refined number of electrons in the octahedral M sites (Table 6) shows that these sites cannot contain cations lighter than Na, in particular Li. According to the analytical formula reported above, the number of 36.6 electrons expected in the sites M reasonably compares with that of 38.3 ($11.7 + 2 \times 13.3$, Table 6) obtained from the

Table 6. Number of electrons per site (*el*, when refined), atom positions (*xyz*) and isotropic equivalent displacement factors (U_{eq}) ($\times 10^3$, Å²) for shirokshinite; *esd*'s in parentheses.

	<i>el</i>	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Si		0.0762(5)	0.1667(2)	0.2261(2)	15(1)
<i>M1</i>	11.7(5)	0	0	1/2	13(2)
<i>M2</i>	13.3(5)	0	0.3338(4)	1/2	19(1)
K	17.9(5)	0	1/2	0	35(2)
O1		0.048(2)	0	0.164(1)	24(2)
O2		0.308(1)	0.2471(9)	0.1636(7)	24(2)
O3		0.132(1)	0.1678(7)	0.3849(6)	19(1)
F		0.124(2)	1/2	0.3897(8)	39(2)

refinement. The number of refined electrons and the dimensions (Table 7) of *M1* (on the mirror plane), that are significantly larger than those of *M2* (on general position), clearly show that these two sites are occupied by Na and Mg, respectively. Thus, the ratio Mg/Na ~ 2 found by chemical analysis is confirmed by the structure refinement. According to the classification of the *TOT* layers, the structure of shirokshinite is based on a meso-octahedral *M1* layer (the origin of the *O* sheet, *i.e.* the site with different occupancy, is *M1*; *cf.* Ferraris & Ivaldi, 2002). The $\pm b/3$ shift discussed above transforms (Nespolo, 2001) a layer of type *M1* (origin at *M1*) into a layer of type *M2* [origin at *M2* or *M3*] which thus occurs as defect in the structure.

The ditrigonal distortion (rotation α) increases with the misfit between the octahedral (*O*) and tetrahedral (*T*) sheets in the *TOT* layer (*cf.* Ferraris & Ivaldi, 2002) and in trioctahedral micas is usually smaller than in the dioctahedral ones. Shirokshinite, as already tainiolite ($\alpha = 1.3^\circ$; Toraya *et al.*, 1977), with $\alpha = 1.26^\circ$ is among the trioctahedral micas with the smallest ditrigonal distortion (Table 7). In principle, being the Na octahedron larger ($\langle M1-O \rangle = 2.110$ Å) than that of Li in tainiolite ($\langle M1-O \rangle = 2.058$ Å), a worse *T/O* matching would be expected for shirokshinite. By comparing the parameters characterising the *TOT* layer of shirokshinite (Table 7) with the corresponding ones of tainiolite, it turns out that the larger dimensions of *M1* in the former mica is completely absorbed by an increase of the thickness of its *O* sheet (2.263 Å against 2.160 Å in tainiolite) and does not modify the dimensions of the same sheet in the (001) plane. The increase of the *O* thickness in shirokshinite is such that this sheet is thicker than the *T* sheet (Table 7); in tainiolite, instead, it is the contrary being the thickness of the *T* sheet 2.218 Å. Consequent to the small ditrigonal distortion, an almost regular dodecagonal prismatic coordination occurs for the interlayer cation (Table 7).

Octahedral Na

Many researchers (see details below) reported some more or less indirect evidences for Na in octahedral coordination in micas, but shirokshinite is the first reported mica with Na dominant in an octahedral site. Both octahedral and interlayer Na is instead quite common in the seidozerite-derivative layer titanosilicates which are based on mica-like layers where rows of Si-tetrahedra are replaced by rows of Ti-octa-

Table 7. Selected interatomic distances (Å) and deformation indicators (*di*) of shirokshinite; *esd*'s in parentheses. Symbols: thick = thickness of *T* and *O* sheets and of interlayer (*I*); α ditrigonal rotation; Δz tetrahedral tilting; τ tetrahedral elongation; Ψ octahedral flatterness; δ counter-rotation in the octahedra; ΔTM misfit between *T* and *O* sheets; *BLD* edge length distortion.

Bonds/di		Bonds/di		Bonds/di	
Si-O1	1.638(5)	<i>M1</i> -O3×2	2.115(6)	<i>M2</i> -O3×2	2.083(7)
Si-O2	1.647(7)	<i>M1</i> -F×2	2.100(11)	<i>M2</i> -O3×2	2.104(7)
Si-O2'	1.641(7)			<i>M2</i> -F×2	2.057(7)
Si-O3	1.594(6)				
<Si-O>	1.630(3)	< <i>M1</i> -O>	2.110(3)	< <i>M2</i> -O>	2.081(3)
K-O1×2	3.074(11)	K-O1×2	3.143(11)		
K-O2×4	3.073(8)	K-O2×4	3.123(8)		
<K-O> _{in}	3.073(4)	<K-O> _{out}	3.130(4)		
Thick _T (Å)	2.219	Δz (Å)	0.008	$\Psi(M1)$ (°)	57.3
Thick _O (Å)	2.263	ΔTM (Å)	0.207	$\Psi(M2)$ (°)	56.8
Thick _I (Å)	3.289	τ (°)	112.40	BLD(<i>M1</i>)	0.32
α (°)	1.26	$\delta M1$ (°)	0	BLD(<i>M2</i>)	0.78
		$\delta M2$ (°)	1.3		

hedra (*cf.* Ferraris *et al.*, 2001b). In the following some literature data showing possible octahedral Na in micas are critically analysed.

Hypotheses of octahedral Na are mainly based on the occurrence of mica analyses where $\Sigma(K + Na + Rb + Ca + Ba) > 1.0$ pfu. First data of this kind were reported by Boldyrev (1937) for muscovite and phlogopite. Serdyuchenko (1954, 1969) published three analyses of phlogopite and biotite from metamorphic rocks of Aldan Shield (Siberia) with $(K + Na + Ca) = 1.3$ –1.4 pfu and supposed that Na and Ca can occupy octahedral site in micas formed under high temperature. In their review, Weiss *et al.* (1985) assumed that Na can be octahedral in micas.

The largest values of $(K + Na)$ were reported in analyses of lithian micas. Na substitution for Li in octahedra was supposed by Ginzburg & Berkhin (1953), Ginzburg (1957) and Semenov (1959). Semenov's analyses of "spodiophyllite" from alkaline pegmatites of Narssarssuk, Greenland, and Lovozero, Kola Peninsula, seem especially interesting. "Spodiophyllite" from Narssarssuk was described as a new mineral "related to micas and chlorites" by Flink (1901) and was re-examined by Semenov (1959) who showed that instead it is a mica intermediate between phlogopite, $KMg_3(AlSi_3O_{10})(OH)_2$, and tainiolite, $K(LiMg_2)Si_4O_{10}F_2$, with formula (# 6 in Table 8):

$(K_{0.89}Na_{0.10}Ca_{0.01})_{\Sigma 1.00} [(Na_{0.49}Li_{0.40})_{\Sigma 0.89} (Mg_{1.47}Fe_{0.21}^{2+}Fe_{0.07}^{3+}Ti_{0.08}Mn_{0.01})_{\Sigma 1.84}]_{\Sigma 2.73} (Si_{3.56}Al_{0.40}Fe_{0.04}^{3+})_{\Sigma 4} O_{9.36}F_{1.70} OH_{0.94}$. The "spodiophyllite" of Narssarssuk can therefore be considered a lithium-enriched shirokshinite with some Fe and tetrahedral Al.

The analyses 5–11 in Table 8 support the existence of a solid solution phlogopite(biotite) – tainiolite – shirokshinite based on the following formal scheme of isomorphous substitutions:

$[Li^VI Si^IV F] + [Na^VI Si^IV F] \rightarrow [(Mg, Fe^{2+})^VI (Al, Fe^{3+})^IV (OH, F)]$. Analyses 1–4 allow to suppose a partial octahedral Na occupancy in polyolithionite, another lithian mica widespread in al-

Table 8. Chemical composition (wt.%) of Na-bearing lithian micas from published non-microprobe analyses.

	# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9	# 10	# 11
K ₂ O	11.05	5.37	11.13	9.12	7.80	10.20	9.50	8.03	11.5	11.38	11.07
Na ₂ O	1.61	7.63	2.06	5.14	8.55	4.50	3.11	3.86	1.8	1.22	2.01
Rb ₂ O	-	-	-	-	-	-	0.20	-	-	0.3	-
Li ₂ O	8.24	9.04	6.23	4.46	n.d.	1.45	0.47	0.64	3.8	2.44	3.21
CaO	-	-	0.73	0.20	-	0.20	0.32	0.54	-	-	-
MgO	-	-	0.24	0.09	10.16	14.50	19.04	16.41	19.1	17.42	19.26
MnO	0.31	-	0.12	Tr.	0.64	0.13	0.60	1.02	-	1.38	-
FeO	-	-	-	-	4.13	3.70	3.51	4.99	0.6	1.89	-
Fe ₂ O ₃	4.02	0.93	0.18	0.32	11.24	2.10	2.35	2.09	-	-	3.20
Al ₂ O ₃	10.24	12.57	13.11	18.38	4.27	5.00	4.84	11.13	2.7	tr.	-
TiO ₂	-	-	tr.	0.14	-	1.50	1.14	1.32	-	2.00	-
SiO ₂	58.68	59.25	60.83	57.22	53.61	52.30	49.20	45.75	52.2	52.88	53.40
F	8.16	7.32	4.50	4.58	n.d.	7.90	4.20	2.02	n.d.*	5.36	n.d.
H ₂ O ⁺	-	-	1.71	1.24	n.d.	-	2.66	2.70	n.d.	4.24	n.d.
H ₂ O ⁻	-	-	0.33	0.42	n.d.	-	-	-	n.d.	2.00	n.d.
I.o.i.	-	-	-	-	n.d.	-	-	-	8.3*	-	n.d.
-O=F ₂	-3.44	-3.08	-1.89	-1.93	-	-3.52	-1.77	-0.85	-	-2.25	-
Total	98.87	99.03	99.28	99.38	100.40	99.96	99.37	99.65	100.0	99.96	92.15

n.d. = not detected; tr. = trace.

Formulae based on (O,OH,F)₁₂ except for ## 5 and 11 which are based on 11 O atoms pfu because H₂O and F are not analysed.

1 – polyolithionite (Kangerluarsuk, Ilímaussaq, Greenland; Lorenzen, 1882):

 $(\text{K}_{0.95}\text{Na}_{0.21})\Sigma_{1.16}(\text{Li}_{2.23}\text{Al}_{0.76}\text{Fe}^{3+}_{0.20}\text{Mn}_{0.02})\Sigma_{3.21}(\text{Si}_{3.95}\text{Al}_{0.05})\Sigma_4\text{O}_{10}(\text{F}_{1.74}\text{O}_{0.26})\Sigma_2$ # 2 – polyolithionite (Ilímaussaq; Weidman, 1907): $(\text{Na}_{0.97}\text{K}_{0.45})\Sigma_{1.43}(\text{Li}_{2.39}\text{Al}_{0.87}\text{Fe}^{3+}_{0.05})\Sigma_{3.31}(\text{Si}_{3.90}\text{Al}_{0.10})\Sigma_4\text{O}_{10}(\text{F}_{1.52}\text{O}_{0.48})\Sigma_2$ # 3 – polyolithionite (Karnasurt Mt., Lovozero, Kola; Vlasov *et al.*, 1966): $(\text{K}_{0.94}\text{Ca}_{0.05}\text{Na}_{0.01})\Sigma_{1.00}(\text{Li}_{1.66}\text{Al}_{1.03}\text{Na}_{0.26}\text{Mg}_{0.02}\text{Fe}^{3+}_{0.01}\text{Mn}_{0.01})\Sigma_{2.99}\text{Si}_{4.04}\text{O}_{10}(\text{F}_{0.94}\text{OH}_{0.76}\text{O}_{0.30})\Sigma_2$

4 – “irvingite” (Wausau, Wisconsin, USA; Weidman, 1907):

 $(\text{K}_{0.78}\text{Na}_{0.21}\text{Ca}_{0.01})\Sigma_{1.00}(\text{Al}_{1.29}\text{Li}_{1.20}\text{Na}_{0.46}\text{Mg}_{0.01}\text{Ti}_{0.01})\Sigma_{3.00}(\text{Si}_{3.84}\text{Al}_{0.16})\Sigma_4\text{O}_{10}(\text{F}_{0.97}\text{OH}_{0.55}\text{O}_{0.48})\Sigma_2$

5 – “spodiophyllite” (Narssarsuk, Greenland; Flink, 1901):

 $(\text{K}_{0.68}\text{Na}_{0.32})\Sigma_{1.00}(\text{Mg}_{1.04}\text{Na}_{0.82}\text{Fe}^{3+}_{0.58}\text{Fe}^{2+}_{0.24}\text{Mn}_{0.04}\text{Al}_{0.04})\Sigma_{2.76}(\text{Si}_{3.69}\text{Al}_{0.31})\Sigma_4\text{O}_{10}(\text{OH},\text{F})_2$

6 = # 5, new analysis (Semenov, 1959):

 $(\text{K}_{0.89}\text{Na}_{0.10}\text{Ca}_{0.01})\Sigma_{1.00}(\text{Mg}_{1.47}\text{Na}_{0.49}\text{Li}_{0.40}\text{Fe}^{2+}_{0.21}\text{Fe}^{3+}_{0.07}\text{Ti}_{0.08}\text{Mn}_{0.01})\Sigma_{2.73}(\text{Si}_{3.56}\text{Al}_{0.40}\text{Fe}^{3+}_{0.04})\Sigma_4\text{O}_{9.36}\text{F}_{1.70}\text{OH}_{0.94}$

7 – “spodiophyllite” (Mannepakhk Mt., Lovozero; Semenov, 1959):

 $(\text{K}_{0.89}\text{Na}_{0.08}\text{Ca}_{0.02}\text{Rb}_{0.01})\Sigma_{1.00}(\text{Mg}_{2.04}\text{Na}_{0.35}\text{Fe}^{2+}_{0.20}\text{Li}_{0.14}\text{Fe}^{3+}_{0.07}\text{Ti}_{0.06}\text{Mn}_{0.04})\Sigma_{2.90}(\text{Si}_{3.53}\text{Al}_{0.41}\text{Fe}^{3+}_{0.06})\Sigma_4\text{O}_{10}(\text{F}_{0.99}\text{OH}_{0.95}\text{O}_{0.06})\Sigma_2$

8 – “spodiophyllite” (Kuivchorr Mt., Lovozero; Semenov, 1972):

 $(\text{K}_{0.73}\text{Na}_{0.23}\text{Ca}_{0.04})\Sigma_{1.00}(\text{Mg}_{1.75}\text{Fe}^{2+}_{0.30}\text{Na}_{0.21}\text{Li}_{0.18}\text{Fe}^{3+}_{0.11}\text{Ti}_{0.07}\text{Mn}_{0.06})\Sigma_{2.98}(\text{Si}_{3.27}\text{Al}_{0.73})\Sigma_4\text{O}_{10}(\text{OH}_{1.29}\text{F}_{0.46}\text{O}_{0.25})\Sigma_2$

9 – tainiolite (Narssarsuk; Flink, 1901); * I.o.i. = F, according to Bøggild (1953):

 $(\text{K}_{1.04}\text{Na}_{0.25})\Sigma_{1.29}(\text{Mg}_{2.01}\text{Li}_{1.09})\Sigma_{3.10}(\text{Si}_{3.71}\text{Al}_{0.23}\text{Fe}^{3+}_{0.04}\text{Mg}_{0.02})\Sigma_4\text{O}_{10}(\text{F}_{1.96}\text{O}_{0.04})\Sigma_2$

10 – tainiolite (Lepkhe-Nelm Mt., Lovozero; Semenov, 1959):

 $(\text{K}_{1.00}\text{Rb}_{0.01})\Sigma_{1.01}(\text{Mg}_{1.65}\text{Li}_{0.68}\text{Na}_{0.16}\text{Ti}_{0.10})\Sigma_{2.59}(\text{Si}_{3.66}\text{Mg}_{0.15}\text{Fe}^{2+}_{0.11}\text{Mn}_{0.08})\Sigma_4\text{O}_{8.87}\text{F}_{1.96}\text{OH}_{1.17}$ # 11 – tainiolite (Punkaruaiv Mt., Lovozero; Semenov, 1972): $\text{K}_{1.00}(\text{Mg}_{2.01}\text{Li}_{0.92}\text{Na}_{0.28})\Sigma_{3.21}(\text{Si}_{3.80}\text{Fe}^{3+}_{0.17}\text{Mg}_{0.03})\Sigma_4\text{O}_{10}(\text{OH},\text{F})_2$

kaline pegmatites and metasomatites. At the same time, however, numerous published analyses of lithian micas from granitic pegmatites and greisen deposits (Minerals, 1992) do not show high (K + Na) values.

Arkhipenko *et al.* (1965) published X-ray powder-diffraction and IR spectroscopy data on synthetic micas of the phlogopite – tainiolite series including Na-enriched phases. One sample has the formula:

$(\text{Na}_{0.63}\text{K}_{0.37})\Sigma_{1.00}(\text{Mg}_{2.34}\text{Na}_{0.22}\text{Al}_{0.08})\Sigma_{2.64}(\text{Si}_{3.97}\text{Al}_{0.03})\text{O}_{10.20}\text{F}_{1.80}$. The authors were not able to obtain convincing evidence of octahedral Na but supposed the existence of a sodic end-member with formula $\text{KMg}_2\text{NaSi}_4\text{O}_{10}\text{F}_2$.

The mentioned evidences of octahedral Na in micas must however be taken with great caution because they were obtained from wet chemical analyses where the possibility of having impurities in the large sample needed must be considered realistic. Note that some of the quoted analyses match

very badly the mica stoichiometry, as ## 1, 2, 9 and 11 in Table 8. Besides, among published electron probe data, we cannot find analyses with $(\text{K} + \text{Na} + \text{Ca}) > 1.1$ pfu. In this connection, we analysed by electron probe several samples of “spodiophyllite”, tainiolite and polyolithionite from Narssarsuk and Ilímaussaq (Greenland) and Lovozero (Kola Peninsula). In all these samples (Table 8) and also in other samples of tainiolite and polyolithionite from Khibiny massif not reported, the Na₂O content is less than 1 % wt. and (K + Na) never is over 1.0 pfu within standard deviations. In particular, we analysed samples of “spodiophyllite” and tainiolite from Narssarsuk collected by G. Flink and O.B. Bøggild and kindly provided by the Geological Museum of Copenhagen University. These samples (## 3 and 4 in Table 2) resulted ordinary tainiolite, as confirmed by IR spectra, and are now deposited in the Fersman Mineralogical Museum, Moscow. Micas from Lovozero were collected by one of the authors (I.V.P.) at the same pegmatites

of the specimens studied by Semenov (1959, 1972) and Vlasov *et al.* (1966) (## 3, 8 and 10 in Table 8). Admittedly we did not analyse the original samples, but (## 3-9, Table 2) the high Na contents reported by wet chemical methods are not confirmed by electron probe. The IR spectra of the samples 3-9 in Table 2 confirm the absence of octahedral Na.

Conclusions

A critical revision of published data indicating octahedral Na in micas shows that this hypothesis was biased by the low quality of the chemical analyses. Therefore, shirokshinite is the first studied mica where not only Na occurs in an octahedral site, but almost fills it. For sure, shirokshinite is an extremely rare mineral unlike tainiolite and polyolithionite that are widespread in alkaline pegmatites and metasomatites including hyper-sodic ones. Apparently a high Na and K content in the mineral-forming medium is an insufficient condition for octahedral occupancy of Na in micas. Presumably the formation of shirokshinite, the Na equivalent of tainiolite, is possible only under a strong deficiency of Li and Al.

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