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THE CRYSTAL STRUCTURE OF NALIVKINITE, A NEW LITHIUM MEMBER OF THE ASTROPHYLLITE GROUP

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ABSTRACT

The crystal structure of nalivkinite, ideally $Li_2\,Na\,Fe^{2+}{}_7\,Ti_2\,(Si_8\,O_{24})\,O_2\,(OH)_4\,F$, a new lithium member of the astrophyllite group, from the moraine of the Dara-i-Pioz glacier, the Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan, triclinic, *a* 5.3745(6), *b* 11.9299(15), *c* 11.6509(14) Å, α 113.325(3), β 94.524(2), γ 103.080(2)°, *V* 656.2(2) Å^3, space group $P\bar{1}$, $Z = 1$, $D_{calc.}$ 3.293 g/cm^3, has been refined to $R_1 = 6.3\%$ for 2041 unique ($F_0 > 4\sigma F$) reflections, collected on a Bruker single-crystal P4 diffractometer with a 4K CCD detector and Mo*K*α X-radiation. Electron-microprobe analysis gives SiO_2 36.11, Al_2O_3 0.58, Na_2O 1.88, K_2O 2.68, Cs_2O 0.93, CaO 1.24, MgO 0.11, FeO 30.84, MnO 4.86, ZnO 0.23, TiO_2 9.48, Nb_2O_5 2.40, Ta_2O_5 0.61, ZrO_2 1.47, SnO 0.89, PbO 0.39, F 1.45, $Li_2O_{ICP–MS}$ 1.30, $(H_2O)_{calc}$ 2.75, sum 100.2 wt.% (H_2O determined from crystal-structure analysis). The empirical formula based on 31 (O + OH + F) anions is $(Li_{1.14}\,K_{0.75}\,Cs_{0.09}\,Na_{0.02})_{\Sigma 2.00}\,(Na_{0.78}\,Ca_{0.22})_{\Sigma 1.00}\,(Fe^{2+}{}_{5.64}\,Mn_{0.90}\,Sn_{0.09}\,Ca_{0.07}\,Mg_{0.04}\,Zn_{0.04}\,Pb_{0.02}\square_{0.20})_{\Sigma 7.00}\,(Ti_{1.56}\,Nb_{0.24}\,Zr_{0.16}\,Ta_{0.04})_{\Sigma 2.00}\,[(Si_{7.89}\,Al_{0.15})_{8.04}\,O_{24}]\,O_2\,(OH)_4\,F$. The crystal structure of nalivkinite is topologically identical to that of triclinic astrophyllite. For nalivkinite, a general formula for the astrophyllite-group minerals, $A_2\,B\,C_7\,D_2\,(T_8\,O_{24})\,O_2\,(OH)_4\,X_{0–1}$, ideally has A = Li; B = $^{[10]}$Na; C = $^{[6]}Fe^{2+}$; D = $^{[6]}$Ti; T = $^{[4]}$Si and X = F. In the nalivkinite structure, four *T* sites are mainly occupied by Si with minor Al, with <*T*–O> = 1.623 Å. The *M*(1–4) sites are occupied by $(Fe^{2+}{}_{1.71}Ca_{0.07}Pb_{0.02}\square_{0.20})$, $Fe^{2+}{}_{2.00}$, $(Fe^{2+}{}_{1.10}\,Mn_{0.90})$ and $(Fe^{2+}{}_{0.83}\,Sn_{0.09}\,Zn_{0.04}\,Mg_{0.04})$, with <*M*(1–4)–O> = 2.164, 2.146, 2.140 and 2.140 Å, respectively. The *D* site is occupied by $(Ti_{1.56}\,Nb_{0.24}\,Zr_{0.16}Ta_{0.04})$, with <*D*–O> = 1.959 Å. There are two interstitial sites, *A* and *B*, ideally occupied by Li and Na. The *B* site is occupied by $(Na_{0.78}Ca_{0.22})$, with <*B*–O> = 2.612 Å. The *A* site splits into two half-occupied sites, *A*(1a) and *A*(1b), with *A*(1a)–*A*(1b) = 1.28(4) Å. The $^{[13]}A$(1a) site is occupied by K, Li, Cs and Na ($K_{0.75}Li_{0.14}Cs_{0.09}Na_{0.02}$ *apfu*), with <*A*(1a)–O> = 3.310 Å. The $^{[5]}A$(1b) site is occupied by Li (1.0 Li *apfu*), with <*A*(1b)–O> = 2.28 Å. The aggregate content of the *A* site is $(Li_{1.14}\,K_{0.75}\,Cs_{0.09}\,Na_{0.02})_{\Sigma 2.00}$ or, ideally, Li_2. In the structure, an O sheet of Fe^{2+} octahedra and two heteropolyhedral (H) sheets of (Si_4O_{12}) ribbons and Ti octahedra form an HOH block of composition $Fe^{2+}{}_7\,Ti_2\,(Si_4\,O_{12})_2\,O_2\,(OH)_4\,F$. The HOH blocks link *via* common vertices of Ti octahedra (F atoms) along [001] and contain interstitial cations at the *A* and *B* sites. Nalivkinite is a Li analogue of astrophyllite, and the two structures are related by the isovalent substitution Li (nalivkinite) ↔ K (astrophyllite) at the interstitial *A* site.

Keywords: nalivkinite, new Li mineral species, astrophyllite group, crystal structure, positional disorder.

SOMMAIRE

Nous avons établi la structure cristalline de la nalivkinite, de composition idéale $Li_2\,Na\,Fe^{2+}{}_7\,Ti_2\,(Si_8\,O_{24})\,O_2\,(OH)_4\,F$, nouveau membre riche en lithium du groupe de l'astrophyllite, provenant de la moraine du glacier Dara-i-Pioz, sur les flancs de l'arête Alai dans les montagnes Tien-Shan, dans le nord du Tajikistan. La structure est triclinique, *a* 5.3745(6), *b* 11.9299(15), *c* 11.6509(14) Å, α 113.325(3), β 94.524(2), γ 103.080(2)°, *V* 656.2(2) Å^3, groupe spatial $P\bar{1}$, $Z = 1$, $D_{calc.}$ 3.293 g/cm^3; nous l'avons affiné jusqu'à un résidu R_1 de 6.3% en utilisant 2041 réflexions uniques ($F_0 > 4\sigma F$) prélevées avec un diffractomètre Bruker P4 pour monocristaux muni d'un détecteur 4K de type CCD et avec rayonnement Mo*K*α. Une analyse à la microsonde électronique a donné: SiO_2 36.11, Al_2O_3 0.58, Na_2O 1.88, K_2O 2.68, Cs_2O 0.93, CaO 1.24, MgO 0.11, FeO 30.84, MnO 4.86, ZnO 0.23, TiO_2 9.48, Nb_2O_5 2.40, Ta_2O_5 0.61, ZrO_2 1.47, SnO 0.89, PbO 0.39, F 1.45, $Li_2O_{ICP–MS}$ 1.30, $(H_2O)_{calc}$ 2.75, pour un total de 100.2% (par poids; la quantité de H_2O a été déterminée à partir de l'ébauche de la structure). La formule empirique, fondée sur 31 anions (O + OH + F) est $(Li_{1.14}\,K_{0.75}\,Cs_{0.09}\,Na_{0.02})_{\Sigma 2.00}\,(Na_{0.78}\,Ca_{0.22})_{\Sigma 1.00}\,(Fe^{2+}{}_{5.64}\,Mn_{0.90}\,Sn_{0.09}\,Ca_{0.07}\,Mg_{0.04}\,Zn_{0.04}\,Pb_{0.02}\square_{0.20})_{\Sigma 7.00}\,(Ti_{1.56}\,Nb_{0.24}\,Zr_{0.16}\,Ta_{0.04})_{\Sigma 2.00}\,[(Si_{7.89}\,Al_{0.15})_{8.04}\,O_{24}]\,O_2(OH)_4\,F$. La structure cristalline de la nalivkinite est topologiquement identique à celle de l'astrophyllite triclinique. Dans le cas de la nalivkinite, la formule générale des minéraux

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de ce groupe, $A_2\,B\,C_7\,D_2\,(T_8\,O_{24})\,O_2\,(OH)_4\,X_{0–1}$, se traduit idéalement par A = Li; B = $^{[10]}$Na; C = $^{[6]}Fe^{2+}$; D = $^{[6]}$Ti; T = $^{[4]}$Si et X = F. Dans la structure de la nalivkinite, quatre sites T sont surtout des sites Si, avec Al accessoire; $<T–O>$ = 1.623 Å. Les sites $M(1–4)$ sont peuplés par $(Fe^{2+}_{1.71}Ca_{0.07}Pb_{0.02}\square_{0.20})$, $Fe^{2+}_{2.00}$, $(Fe^{2+}_{1.10}\,Mn_{0.90})$ et $(Fe^{2+}_{0.83}\,Sn_{0.09}\,Zn_{0.04}\,Mg_{0.04})$, avec $<M(1–4)–O>$ = 2.164, 2.146, 2.140 et 2.140 Å, respectivement. Le site D contient $(Ti_{1.56}\,Nb_{0.24}\,Zr_{0.16}Ta_{0.04})$, avec $<D–O>$ = 1.959 Å. Il y a deux sites interstitiels, A et B, idéalement remplis par Li et Na. Le site B contient $(Na_{0.78}Ca_{0.22})$, avec $<B–O>$ = 2.612 Å. Le site A est subdivisé en deux sous-sites à moitié occupés, A(1a) et A(1b), avec A(1a)–A(1b) = 1.28(4) Å. Le site $^{[13]}A$(1a) contient K, Li, Cs et Na, $(K_{0.75}Li_{0.14}Cs_{0.09}Na_{0.02})$ *apfu*, avec $<A(1a)–O>$ = 3.310 Å. Le site $^{[5]}A$(1b) contient le lithium, 1.0 Li *apfu*, avec $<A(1b)–O>$ = 2.28 Å. Le contenu global du site A est $(Li_{1.14}\,K_{0.75}\,Cs_{0.09}\,Na_{0.02})_{\Sigma 2.00}$ ou, de façon idéale, Li_2. Dans la structure, un feuillet d'octaèdres contenant Fe^{2+} et deux feuillets hétéropolyédriques (H) de rubans (Si_4O_{12}) et des octaèdres Ti forment un bloc HOH de composition $Fe^{2+}_7\,Ti_2\,(Si_4\,O_{12})_2\,O_2\,(OH)_4\,F$. Ces blocs HOH sont liés grâce aux coins communs des octaèdres Ti (les atomes F) le long de [001]; ils contiennent des cations interstitiels aux sites A et B. La nalivkinite est l'analogue lithinifère de l'astrophyllite, et les deux structures sont reliées par la substitution isovalente Li (nalivkinite) ↔ K (astrophyllite) au site interstitiel A.

(Traduit par la Rédaction)

Mots-clés: nalivkinite, nouvelle espèce minérale à Li, groupe de l'astrophyllite, structure cristalline, désordre de position.

INTRODUCTION

Nalivkinite, ideally $Li_2\,Na\,Fe^{2+}_7\,Ti_2\,O_2\,(Si_8\,O_{24})\,(OH)_4\,F$, was described from the moraine of the Dara-i-Pioz glacier, the Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan (Agakhanov *et al.* 2008). In that moraine, nalivkinite occurs in a coarse-grained quartzofeldspathic rock in association with quartz, microcline, calcybeborosilite-(Y) (up to 3 cm long), bafertisite (up to 5 cm), green thorite (up to 0.3 cm long), fluorite, aegirine and polylithionite. Nalivkinite is a new lithium-dominant member of the astrophyllite group. The presence of Li in astrophyllite-group minerals is unique. Piilonen *et al.* (2003a) analyzed 15 samples from Mont Saint-Hilaire using inductively coupled plasma – atomic emission spectrometry (ICP–AES); reported lithium contents were in the range from 42.7 to 453.3 ppm. In nalivkinite, the A site is dominated by Li. The morraine of the Dara-i-Pioz glacier is well known for its great diversity of rare minerals of Cs, B, the rare-earth elements (REE), Zr, Ba, Be and Li. Quite a few lithium minerals occur at the Dara-i-Pioz massif: milarite-group minerals (sogdianite, dusmatovite, darapiozite, berezanskite), neptunite, zektzerite, baratovite, sokolovaite and faizievite. Here, we report the crystal structure and crystal chemistry of nalivkinite, and adopt the notation of Piilonen *et al.* (2003b).

PREVIOUS WORK

Astrophyllite-group minerals are alkali-rich titanosilicates that can be divided into two main subgroups, Fe^{2+}- and Mn^{2+}-dominant species. Astrophyllite, a Fe^{2+}-dominant member, was first described as a new mineral species by Weibye (1848). A hundred years later, kupletskite, a Mn-dominant member, was described as a new mineral species (Semenov 1956). There has been extensive work on the astrophyllite group of minerals, both in mineralogy and crystallography. Piilonen *et al.* (2003a, b) summarized previous work, performed additional experimental analyses (X-ray single-crystal diffraction, electron-microprobe analysis and Mössbauer spectroscopy), and generalized the crystal chemistry of the astrophyllite-group minerals. Piilonen *et al.* (2003a, b) wrote the general formula as $A_2\,B\,C_7\,D_2\,T_8\,O_{26}\,(OH)_4\,X_{0–1}$, where A = $^{[10]–[13]}$(K, Rb, Cs, Na, H_3O^+, H_2O or $\square$); B = $^{[10]}$(Na or Ca); C = $^{[6]}(Fe^{2+}$, Mn, Fe^{3+}, Na, Mg or Zn); D = $^{[6]}$(Ti, Nb, Zr); T = Si, Al and X = F, OH, O, $\square$. In the crystal structure of astrophyllite-group minerals, a sheet of close-packed M octahedra (O sheet) and two heteropolyhedral (H) sheets of (Si_4O_{12}) ribbons and D (= Ti, Nb) octahedra form an HOH block [the HOH notation of Ferraris (1997)] of composition $C_7\,D_2\,(Si_4\,O_{12})_2\,O_2\,(OH)_4\,X_{0–1}$. The HOH blocks link along [001] *via* common vertices of D octahedra (F atoms) and have interstitial cations at the A and B sites. Currently, there are nine minerals in the astrophyllite group, including two polytypes of kupletskite, one of monoclinic (2M) and one of triclinic (1A) symmetry (Piilonen *et al.* 2001). In Table 1, we present ideal formulae and references covering descriptions and structure work on newly defined astrophyllite-group minerals.

CHEMICAL COMPOSITION

The crystal of nalivkinite used for X-ray diffraction was mounted on a Perspex disc, ground, polished, carbon-coated and analyzed with a Cameca SX 100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of 15 keV, a specimen current of 20 nA, a beam size of 10 μm, and count times on peak and background of 20 and 10 s, respectively. The following standards were used for K and L X-ray lines: Si, Ca: diopside; Al: andalusite; Na: albite; K: orthoclase; F: topaz; Mg: pyrope; Ti: titanite; Mn: spessartine; Fe: fayalite; Zn: gahnite; Nb: $BaNaNbO_4$; Ta: tantalite-(Mn); Sn: SnO_2; Cs: pollucite; Zr: zircon; Pb: galena. Data were reduced using the X-PHI procedure (Merlet 1992). The amount of H_2O was calculated from the structure refinement. The single crystal of nalivkinite was analyzed by inductively coupled plasma – mass spectrometry (ICP–MS). The amount of Li determined is 6040 ppm, which corresponds to 1.30 wt.% Li_2O. In Table 2, we give the chemical composition and empirical formula unit based on 31 (O + OH + F) anions: $(Li_{1.14}K_{0.75}Cs_{0.09}Na_{0.02})_{\Sigma 2.00}(Na_{0.78}Ca_{0.22})_{\Sigma 1.00}(Fe^{2+}_{5.64}Mn_{0.90}Sn_{0.09}Ca_{0.07}Mg_{0.04}Zn_{0.04}Pb_{0.02}\square_{0.20})_{\Sigma 7.00}(Ti_{1.56}Nb_{0.24}Zr_{0.16}Ta_{0.04})_{\Sigma 2.00}[(Si_{7.89}Al_{0.15})_{\Sigma 8.04}O_{24}]O_2(OH)_4F$, $Z = 1$.

X-RAY DATA COLLECTION AND STRUCTURE REFINEMENT

X-ray-diffraction data were collected with a Bruker *P*4 diffractometer equipped with a 4K CCD detector (Mo*K*α radiation) from a single-crystal of nalivkinite with dimensions 0.24 × 0.12 × 0.01 mm. The intensities of 6447 reflections with $-7 < h < 7$, $-15 < k < 15$, $-16 < l < 16$ were collected to 59.99°2θ using 45 s per 0.3° frame: an empirical absorption correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters were obtained from 4340 reflections with $I > 20\sigma I$. During the refinement stage, the data were truncated at 49.98° because there was no significant intensity of diffracted beams beyond $2\theta = 50°$. Using atom coordinates from Piilonen *et al.* (2000), the crystal structure of nalivkinite was refined to $R_1 = 0.063$ and a Go*F* value of 1.101 for 2041 independent reflections (251 refined parameters including extinction) with the Bruker SHELXTL version 5.1 system of programs (Sheldrick 1997). Hydrogen atoms were included at the last stages of refinement, and both H positions were softly constrained by setting the O–H distances equal to 0.98 Å. Site occupancies were refined for the *M* (occupied primarily by Fe), *D* (occupied primarily by Ti), *B* (occupied by Na) and *A*(1a) and *A*(1b) sites (occupied by Li, K, Na and Cs). Details of data collection and structure refinement are given in Table 3, final atom parameters are given in Table 4, selected interatomic distances in Table 5, refined site-scattering values and assigned populations for selected cation sites are given in Table 6, and bond-valence values in Table 7. A table of structure factors may be obtained from the Depository of Unpublished Data, on the MAC website [document Nalivkinite CM46_651].

DESCRIPTION OF THE STRUCTURE

Topology of the structure

The crystal structure of nalivkinite is topologically identical to that of (triclinic) astrophyllite (Piilonen *et al.* 2003b). In this structure, (SiO_4) tetrahedra link *via* common vertices to form astrophyllite ribbons (Si_4O_{12}) along [100]. The astrophyllite ribbons and Ti octahedra

TABLE 1. IDEAL FORMULAE AND UNIT-CELL PARAMETERS OF THE ASTROPHYLLITE-GROUP MINERALS

Mineral	Ideal formula**	*a* (Å) α (°)	*b* (Å) β (°)	*c* (Å) γ (°)	Space group	*Z*	Ref.
nalivkinite	$Li_2NaFe^{2+}_7Ti_2(Si_8O_{24})O_2(OH)_4F$	5.3745 94.524	11.930 103.080	11.651 113.325	$P\overline{1}$	1	(1)
astrophyllite (RUS8)***	$K_2NaFe^{2+}_7Ti_2(Si_8O_{24})O_2(OH)_4F$	5.3754 113.133	11.8970 94.638	11.6634 103.081	$P\overline{1}$	1	(2)
magnesioastrophyllite	$K_2Na(Fe^{2+}_4Mg_2Na)Ti_2(Si_8O_{24})O_2(OH)_4$	5.322	23.129 99.55	10.370	*C*2	2	(3)
niobophyllite*	$K_2NaFe^{2+}_{6.5}\square_{0.5}Nb_2(Si_8O_{24})O_2(OH)_4O$	5.391 113.1	11.88 94.5	11.66 103.1	*P*1 or $P\overline{1}$		(4)
hydroastrophyllite*	$(H_3O,K)_2Ca(Fe^{2+},Mn)_{5-6}Ti_2(Si_8O_{24})O_2(OH)_4F$	5.42 112.2	11.98 95.15	11.86 103.42	n.d.		(5)
kupletskite-1*A* (NOR17)***	$K_2NaMn_7Ti_2(Si_8O_{24})O_2(OH)_4F$	5.3784 112.964	11.9085 94.697	11.7236 103.112	$P\overline{1}$	1	(6)
kupletskite-2*M* (RUS9)***	$K_2NaMn_7Ti_2(Si_8O_{24})O_2(OH)_4F$	5.4022	23.226 95.246	21.1782	*C*2/*c*	4	(7)
niobokupletskite	$K_2NaMn_7(NbTi)(Si_8O_{24})O_2(OH)_4O$	5.4303 112.927	11.924 94.750	11.747 103.175	$P\overline{1}$	1	(8)
kupletskite-(Cs)*	$Cs_2NaMn_7Ti_2(Si_8O_{24})O_2(OH)_4F$	5.41 89	11.74 90	21.16 102.38	n.d.	2	(9)
zircophyllite*	$K_2NaMn_7Zr_2(Si_8O_{24})O_2(OH)_4F$		n.d.		n.d.	n.d.	(10)

* No structural data are available; n.d.: not determined. ** revised formulae are taken from Piilonen *et al.* (2003b) and modified in accord with the end-member criteria except for hydroastrophyllite; *** name of sample from Piilonen *et al.* (2001,2003b).
References (the latest and the first references on structure are the first and second entries in the numbered list of references,respectively): (1) this work; (2) Piilonen *et al.* (2003b), Woodrow (1967); (3) Shi *et al.* (1998); (4) Nickel *et al.* (1964); (5) Hubei Geologic College (1974); (6) Piilonen *et al.* (2003b), P'eng & Ma (1964); (7) Piilonen *et al.* (2001); (8)Piilonen *et al.* (2000); (9) Yefimov *et al.* (1971); (10) Kapustin (1973).

share common vertices in the heteropolyhedral (H) sheet of composition $(TiSi_4O_{12})^{4-}$. The *M*(1), *M*(2), *M*(3) and *M*(4) octahedra form a sheet of close-packed octahedra (O) of ideal composition $(Fe^{2+}{}_7O_{14})$. An O sheet and two adjacent H sheets link through common vertices of (SiO_4) tetrahedra, Ti-octahedra and *M*-octahedra to form an HOH block parallel to (001). Along [001], HOH blocks link through common vertices of Ti octahedra,

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) OF NALIVKINITE

SiO_2	36.11	Si	7.89	Na	0.78
Al_2O_3	0.58	Al	0.15	Ca	0.22
FeO	30.84	Σ*T*	8.04	Σ*B*	1.00
MnO	4.86				
SnO	0.89	Fe^{2+}	5.64	Li	1.14
ZnO	0.23	Mn	0.90	K	0.75
MgO	0.11	Sn	0.09	Cs	0.09
PbO	0.39	Zn	0.04	Na	0.02
TiO_2	9.48	Mg	0.04	Σ*A*	2.00
Nb_2O_5	2.40	Pb	0.02		
ZrO_2	1.47	Ca	0.07	F	1.00
Ta_2O_5	0.61	Σ*C*	6.80	OH	4.00
Na_2O	1.88				
CaO	1.24	Ti	1.56		
Li_2O*	1.30	Nb	0.24		
K_2O	2.68	Zr	0.16		
Cs_2O	0.93	Ta	0.04		
F	1.45	Σ*D*	2.00		
H_2O**	2.75				
F=O	–0.61				
Total	99.59				

* Determined by ICP–MS, ** calculated from crystal-structure analysis.

TABLE 3. MISCELLANEOUS REFINEMENT-DATA FOR NALIVKINITE

a (Å)	5.3745(6)	Absorption coefficient (mm^{-1})	5.11
b	11.9299(15)	*F*(000)	629.6
c	11.6509(14)	$D_{calc.}$ (g/cm^3)	3.293
α (°)	113.325(3)	Crystal size (mm)	0.24 × 0.12
β	94.524(2)		0.01
γ	103.080(2)	Radiation/ filter	Mo*K*α/graphite
V ($Å^3$)	656.2(2)	2θ range for data collection	49.98
Space group	$P\bar{1}$	*R*(int) (%)	2.10
Z	1		
Reflections collected		6447	
Unique reflections		5211	
Independent reflections		2317	
$F_o > 4\sigma F$		2041	
Refinement method		Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F_o^2$	
Goodness of fit on $F^2$1.101			
Final $R_{(obs)}$ (%) [$F_o > 4\sigma F$]		R_1 = 6.26	
R indices (all data) (%)		R_1 = 6.86	
		wR_2 = 17.47	
		Goo*F* = 1.101	

TABLE 4. FINAL COORDINATES AND DISPLACEMENT PARAMETERS ($Å^2$) OF ATOMS IN NALIVKINITE

	x	*y*	*z*	U_{eq}*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M(1)	0.8490(2)	0.2053(1)	0.4796(1)	0.0081(5)	0.0078(7)	0.0065(7)	0.0125(8)	0.0058(5)	0.0032(5)	0.0029(5)
M(2)	0.2804(2)	0.06734(9)	0.4895(1)	0.0075(5)	0.0066(7)	0.0065(7)	0.0127(7)	0.0068(5)	0.0035(4)	0.0028(5)
M(3)	0.4225(2)	0.35177(9)	0.4848(1)	0.0076(5)	0.0072(7)	0.0055(7)	0.0135(7)	0.0061(5)	0.0038(5)	0.0035(5)
M(4)	0	½	½	0.0073(6)	0.0059(9)	0.0047(9)	0.0131(10)	0.0052(7)	0.0024(6)	0.0023(6)
D	0.0781(2)	0.0856(1)	0.1976(1)	0.0105(4)	0.0066(6)	0.0087(6)	0.0191(7)	0.0074(5)	0.0038(4)	0.0043(4)
T(1)	0.6767(4)	0.2703(2)	0.2308(2)	0.0077(5)	0.0059(10)	0.0104(10)	0.0121(11)	0.0091(9)	0.0035(8)	0.0037(8)
T(2)	0.8144(4)	0.5467(2)	0.2564(2)	0.0081(5)	0.0081(10)	0.0060(10)	0.0127(11)	0.0061(9)	0.0021(8)	0.0024(8)
T(3)	0.3802(4)	0.6767(2)	0.2584(2)	0.0059(5)	0.0061(10)	0.0041(10)	0.0094(11)	0.0046(8)	0.0017(8)	0.0019(8)
T(4)	0.5049(4)	0.9309(2)	0.2347(2)	0.0074(5)	0.0078(10)	0.0060(10)	0.0113(11)	0.0061(8)	0.0019(8)	0.0029(8)
A(1a)	0.1464(7)	0.2860(4)	0.9977(3)	0.0290(10)	0.0186(18)	0.0589(28)	0.0000(15)	0.0028(16)	0.0008(13)	0.0117(18)
A(1b)	0.087(6)	0.177(4)	–0.000(3)	0.0290(10)	0.0186(18)	0.0589(28)	0.0000(15)	0.0028(16)	0.0008(13)	0.0117(18)
B	½	0	0	0.0074(13)	0.0119(20)	0.0082(21)	0.0037(20)	0.0036(15)	0.0013(14)	0.0041(15)
O(1)	0.7252(10)	0.3158(5)	0.3840(5)	0.0074(11)	0.0092(25)	0.0092(26)	0.0067(26)	0.0058(21)	0.0020(20)	0.0037(21)
O(2)	0.1462(10)	0.1600(5)	0.3723(5)	0.0076(11)	0.0105(26)	0.0063(26)	0.0053(25)	0.0015(21)	0.0008(20)	0.0029(21)
O(3)	0.1261(10)	0.3895(5)	0.5902(5)	0.0073(11)	0.0049(24)	0.0046(25)	0.0136(28)	0.0049(21)	0.0016(20)	0.0013(20)
O(4)	0.2998(10)	0.4626(5)	0.4003(5)	0.0093(11)	0.0125(27)	0.0065(26)	0.0121(28)	0.0059(22)	0.0029(21)	0.0048(21)
O(5)	0.9913(10)	0.1171(5)	0.5917(5)	0.0093(11)	0.0096(26)	0.0085(26)	0.0137(28)	0.0071(22)	0.0050(21)	0.0044(21)
O(6)	0.5571(10)	0.2554(5)	0.5872(5)	0.0070(11)	0.0064(25)	0.0090(26)	0.0100(27)	0.0076(22)	0.0029(20)	0.0035(20)
O(7)	0.5730(10)	0.0162(5)	0.3885(5)	0.0080(11)	0.0090(25)	0.0060(25)	0.0115(27)	0.0057(22)	0.0019(20)	0.0030(20)
O(8)	0.0749(10)	0.5898(5)	0.2025(5)	0.0159(12)	0.0132(28)	0.0177(30)	0.0149(30)	0.0067(24)	0.0043(23)	0.0010(23)
O(9)	0.2491(11)	0.0421(6)	0.8303(6)	0.0226(14)	0.0183(30)	0.0219(32)	0.0184(32)	0.0041(26)	0.0080(25)	–0.0048(25)
O(10)	0.4273(10)	0.4131(5)	0.7972(5)	0.0147(12)	0.0169(28)	0.0173(29)	0.0126(29)	0.0059(24)	0.0029(23)	0.0107(24)
O(11)	0.1266(12)	0.8075(6)	0.8317(6)	0.0230(14)	0.0297(33)	0.0312(35)	0.0206(33)	0.0140(28)	0.0105(27)	0.0243(29)
O(12)	0.2610(12)	0.9557(6)	0.1696(6)	0.0221(14)	0.0286(33)	0.0204(31)	0.0167(31)	0.0021(25)	–0.0029(25)	0.0191(27)
O(13)	0.2706(11)	0.6062(5)	0.8033(6)	0.0180(13)	0.0278(32)	0.0099(28)	0.0186(31)	0.0086(24)	0.0042(25)	0.0048(24)
O(14)	0.5742(12)	0.2211(5)	0.8002(6)	0.0188(13)	0.0312(33)	0.0105(28)	0.0176(31)	0.0093(24)	0.0041(25)	0.0050(25)
O(15)	0.3820(11)	0.1889(6)	0.1664(5)	0.0206(13)	0.0135(28)	0.0305(34)	0.0123(30)	0.0123(26)	–0.0028(23)	–0.0081(25)
F	0	0	0	0.0174(14)	0.0177(33)	0.0149(33)	0.0211(37)	0.0091(29)	0.0022(27)	0.0052(27)
H(1)	0.21(2)	0.416(7)	0.309(3)	0.0112						
H(2)	0.05(2)	0.167(7)	0.686(2)	0.0112						

* $U_{eq} = (⅓)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

which are F atoms. The interlayer space contains the *A* and *B* sites (Fig. 1).

Cation sites

There are four tetrahedrally coordinated *T* sites in the crystal structure of nalivkinite, with <*T*–O> = 1.623 Å (Table 4), occupied primarily by Si with minor Al. There are five octahedrally coordinated sites. Four Fe^{2+}-dominant sites occur in the O sheet (Fig. 1). The *M*(1) site is occupied by $(Fe^{2+}_{1.71}Ca_{0.07}Pb_{0.02}\square_{0.20})$ and coordinated by five O atoms and one OH group with <*M*(1)–O,OH> = 2.164 Å. The *M*(2–4) sites are coordinated by four O atoms and two OH groups; the *M*(2) site is occupied by $Fe^{2+}_{2.00}$ with <*M*(2)–O,OH> = 2.146 Å; the *M*(3) site is occupied by $(Fe^{2+}_{1.10}Mn_{0.90})$ with <*M*(3)–O,OH> = 2.140 Å; the *M*(4) site is occupied by $(Fe^{2+}_{0.83}Sn_{0.09}Zn_{0.04}Mg_{0.04})$ with <*M*(4)–O,OH> = 2.140 Å. The *D* site occurs in the H sheet; it is occupied by $(Ti_{1.56}Nb_{0.24}Zr_{0.16}Ta_{0.04})$ and is coordinated by five O atoms and one F atom, with <*D*–O,F> = 1.959 Å.

Interstitial sites

In the structure of astrophyllite-group minerals, there are two interstitial sites, *A* and *B*. The [10]-coordinated *B* site is occupied by $(Na_{0.78}Ca_{0.22})$ with <*B*–O> = 2.612 Å, and this in accord with the pattern in astrophyllite-group minerals (Piilonen *et al.* 2003b). The *A* site is usually [13]-coordinated, both in the triclinic and monoclinic structures (Fig. 2a) (in the monoclinic structure, there are two *A* sites, both of which are [13]-coordinated). In several triclinic structures, the *A* site splits into two sites, *A*(1a) and *A*(1b) (notation of Piilonen *et al.* 2003b). Originally, positional disorder at the *A* site was documented for kupletskite-1*A* by Christiansen *et al.* (1998) and later found in three structures: two kupletskite-1*A* (Piilonen *et al.* 2001, 2003b) and niobokupletskite (Piilonen *et al.* 2000; Table 8). In

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN NALIVKINITE

M(1)–O(1)	2.205(5)	*M*(2)–O(2)	2.238(5)
M(1)–O(2)	2.140(5)	*M*(2)–O(5)*	2.081(5)
M(1)–O(3)	2.164(5)	*M*(2)–O(5)a*	2.133(5)
M(1)–O(5)*	2.166(5)	*M*(2)–O(6)	2.177(5)
M(1)–O(6)	2.129(5)	*M*(2)–O(7)	2.095(5)
M(1)–O(7)	2.181(5)	*M*(2)–O(7)a	2.222(5)
<*M*(1)–O,OH>	2.164	*M*(2)–O,OH>	2.158
M(3)–O(1)	2.104(5)	*M*(4)–O(1) ×2	2.168(5)
M(3)–O(2)	2.222(5)	*M*(4)–O(3) ×2	2.166(5)
M(3)–O(3)	2.108(5)	*M*(4)–O(4)* ×2	2.087(5)
M(3)–O(4)*	2.115(5)	<*M*(4)–O,OH>	2.140
M(3)–O(4)b*	2.183(5)		
M(3)–O(6)	2.144(5)		
<*M*(3)–O,OH>	2.146		
T(1)–O(1)	1.626(5)	*T*(2)–O(3)	1.612(6)
T(1)–O(11)	1.594(6)	*T*(2)–O(8)	1.639(5)
T(1)–O(13)	1.644(6)	*T*(2)–O(10)	1.643(5)
T(1)–O(15)	1.599(6)	*T*(2)–O(13)	1.608(5)
<*T*(1)–O>	1.616	<*T*(2)–O>	1.626
T(3)–O(6)	1.623(5)	*T*(4)–O(7)	1.632(6)
T(3)–O(8)	1.649(5)	*T*(4)–O(9)	1.606(6)
T(3)–O(10)	1.642(5)	*T*(4)–O(12)	1.606(6)
T(3)–O(14)	1.601(6)	*T*(4)–O(14)	1.636(6)
<*T*(3)–O>	1.629	<*T*(4)–O>	1.620
T(1)–O(13)–*T*(2)	144.4(4)	*D*–O(2)	1.835(5)
T(2)–O(8)–*T*(3)	138.9(4)	*D*–O(9)	1.956(6)
T(2)–O(10)–*T*(3)	139.1(4)	*D*–O(11)	1.968(6)
T(3)–O(14)–*T*(4)	144.4(4)	*D*–O(12)	1.952(5)
		D–O(15)	1.964(6)
		D–F	2.076(1)
		<*D*–O,F>	1.959
B–O(9) ×2	2.581(6)	*A*(1a)–O(8)	3.486(7)
B–O(11) ×2	2.622(7)	*A*(1a)–O(8)c	3.593(7)
B–O(12) ×2	2.598(6)	*A*(1a)–O(9)	2.996(7)
B–O(15) ×2	2.573(6)	*A*(1a)–O(10)	3.516(7)
B–F ×2	2.687(1)	*A*(1a)–O(10)d	3.531(7)
<*B*–O,F>	2.612	*A*(1a)–O(11)	2.971(7)
		A(1a)–O(12)	2.988(7)
A(1b)–O(9)	2.38(3)	*A*(1a)–O(13)	3.394(7)
A(1b)–O(11)	2.31(3)	*A*(1a)–O(13)e	3.438(7)
A(1b)–O(12)	2.34(3)	*A*(1a)–O(14)	3.377(7)
A(1b)–O(15)	2.34 (3)	*A*(1a)–O(14)f	3.428(7)
A(1b)–F	2.05(3)	*A*(1a)–O(15)	2.980(7)
<*A*(1b)–O,F>	2.28	*A*(1a)–F	3.335(5)
		<*A*(1a)–O,F>	3.310

a: −*x* + 1, −*y*, −*z* + 1; b: −*x* + 1, −*y* + 1, −*z* + 1; c: *x*, *y*, *z* + 1; d: −*x* + 1, −*y* + 1, −*z* + 2; e: −*x*, −*y* + 1, −*z* + 2; f: *x* − 1, *y*, *z*. * (OH) group.

TABLE 6. REFINED SITE-SCATTERING (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR NALIVKINITE

	Refined site-scattering	Site population	Calculated site-scattering	$<X–\varphi>_{calc}$ * (Å)	$<X–\varphi>_{obs}$ (Å)
M(1)	49.7(4)	1.71 Fe^{2+} + 0.07 Ca + 0.02 Pb + 0.2 □	47.5	2.173	2.164
M(2)	52.0(4)	2.00 Fe^{2+}	52.0	2.160	2.158
M(3)	51.5(4)	1.10 Fe^{2+} + 0.90 Mn	51.1	2.183	2.146
M(4)	26.2(2)	0.83 Fe^{2+} + 0.09 Sn + 0.04 Mg + 0.04 Zn	27.8	2.148	2.140
D	52.6(4)	1.56 Ti + 0.24 Nb + 0.16 Zr + 0.04 Ta	53.5	1.991	1.959
A(1a)	19.8(3)	0.75 K + 0.14 Li + 0.09 Cs + 0.02 Na + 1.00 □	19.8	**	3.310
A(1b)	3.0(3)	1.00 Li + 1.00 □	3.00	**	2.280
B	12.4(2)	0.78 Na + 0.22 Ca	13.0	2.608	2.612

* Calculated by summing constituent ionic radii; values from Shannon (1976), φ = O, F.
** As these sites are only partly occupied, the cation–anion distances could not be calculated.

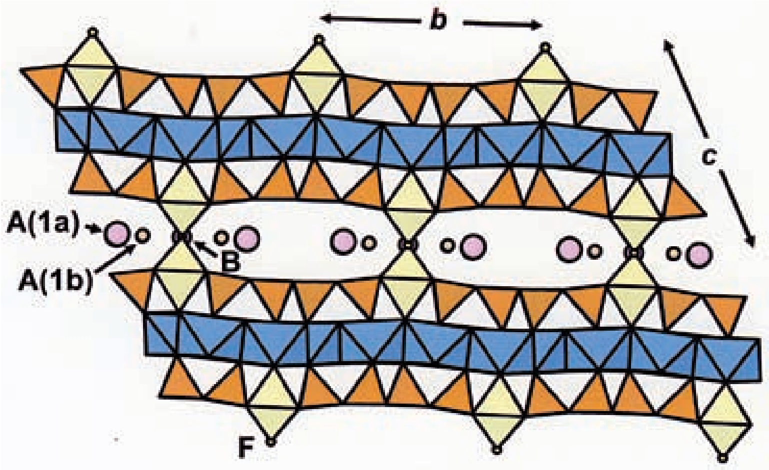

FIG. 1. General view of the crystal structure of nalivkinite. (SiO_4) tetrahedra are orange, Fe^{2+}-dominant *M*(1,2,3,4) octahedra are blue, Ti-dominant *D* octahedra are yellow; A(1a) = K, A(1b) = Li and *B* = Na atoms are shown as mauve, orange and purple circles, respectively. The F atoms are shown as small yellow circles.

TABLE 7. BOND-VALENCE* TABLE FOR NALIVKINITE

	M(1)	*M*(2)	*M*(3)	*M*(4)	*D*	*T*(1)	*T*(2)	*T*(3)	*T*(4)	*A*(1a)	*A*(1b)	*B*	H(1)	H(2)	Σ
O(1)	0.27		0.40	$0.32^{\times 2 \rightarrow}$		1.00									1.99
O(2)	0.32	0.26	0.29		1.01										1.88
O(3)	0.30		0.39	$0.33^{\times 2 \rightarrow}$			1.03								2.05
O(4)***			0.38 0.32	$0.40^{\times 2 \rightarrow}$									0.91		2.01
O(5)***	0.30	0.39 0.34												0.89	1.92
O(6)	0.33	0.30	0.35					1.00							1.98
O(7)	0.28	0.38 0.27							0.98						1.91
O(8)							0.96	0.94		0.01 0.01					1.92
O(9)					0.73				1.05	0.05	0.04	$0.14_{2\downarrow}$			2.01
O(10)							0.95	0.95		0.01 0.01					1.92
O(11)					0.71	1.08				0.05	0.05	$0.12_{2\downarrow}$	0.05		2.06
O(12)					0.74				1.05	0.05	0.05	$0.13_{2\downarrow}$			2.02
O(13)						0.95	1.04			0.01 0.01			0.04		2.05
O(14)								1.06	0.97	0.01 0.01				0.11	2.20
O(15)					0.72	1.07				0.05	0.05	$0.14_{2\downarrow}$			2.03
F**					$0.35^{\times 2 \rightarrow}$					$0.03^{\times 2 \rightarrow}$	$0.08^{\times 2 \rightarrow}$	$0.10_{2\downarrow}^{2 \rightarrow}$			1.12
Total	1.80	1.94	2.13	2.10	4.26	4.10	3.98	3.95	4.05	0.31	0.27	1.26	1.00	1.00	
Aggregate charge	1.80	2.00	2.00	2.00	4.14	4.00	4.00	4.00	4.00	0.50	0.50	1.22	1.00	1.00	

* bond-valence parameters (*vu*) from Brown & Altermatt (1985); ** bond-valence parameters (*vu*) from Brown (1981). *** (OH) group.

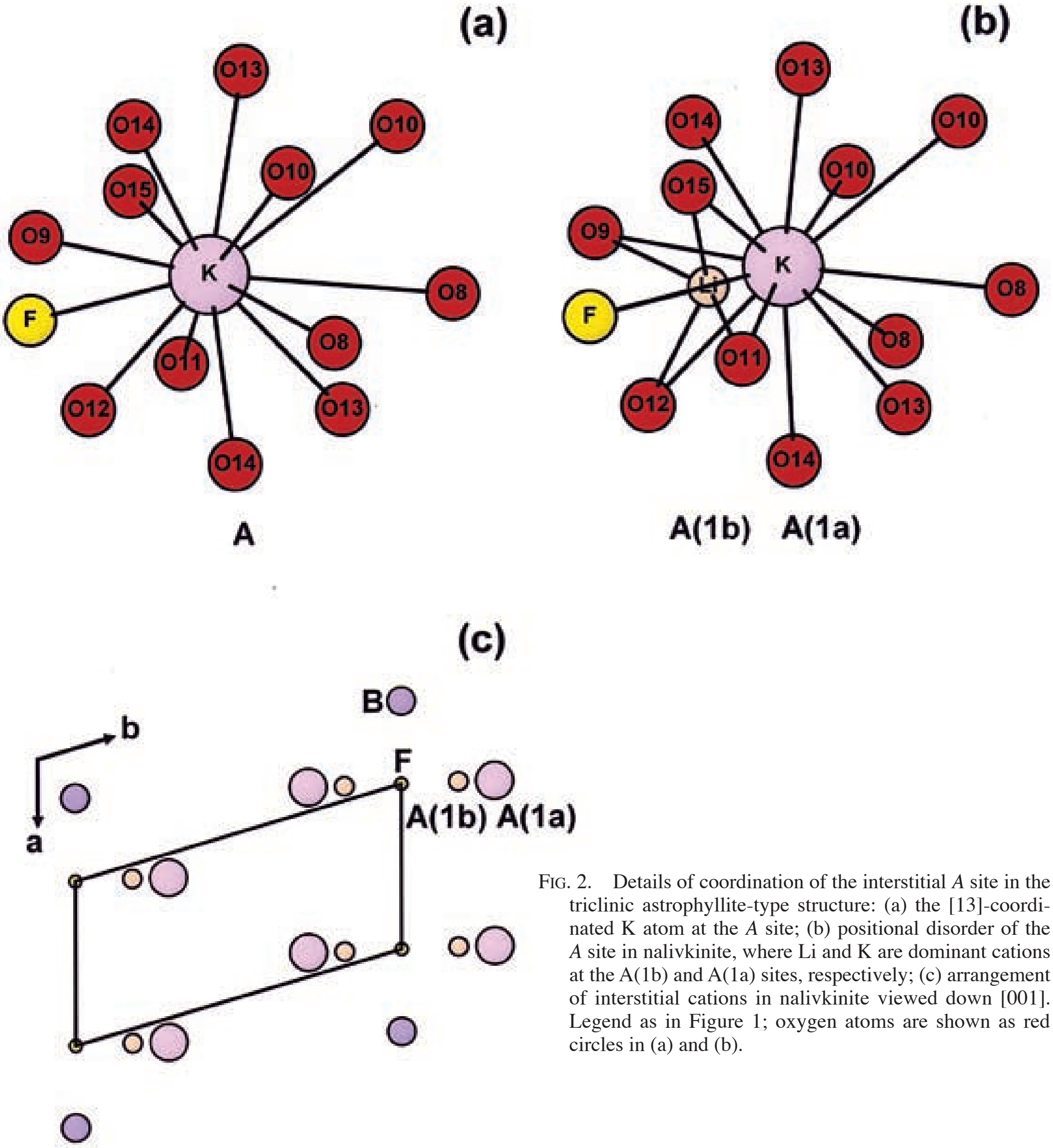

FIG. 2. Details of coordination of the interstitial *A* site in the triclinic astrophyllite-type structure: (a) the [13]-coordinated K atom at the *A* site; (b) positional disorder of the *A* site in nalivkinite, where Li and K are dominant cations at the A(1b) and A(1a) sites, respectively; (c) arrangement of interstitial cations in nalivkinite viewed down [001]. Legend as in Figure 1; oxygen atoms are shown as red circles in (a) and (b).

nalivkinite, the *A* site, which gives 2 *apfu*, splits into two sites, *A*(1a) and *A*(1b), with a short *A*(1a)–*A*(1b) distance = 1.28(4) Å (Tables 6, 8, Figs. 2b, 2c). Therefore, the *A*(1b) and *A*(1a) sites can be only partially occupied. The [13]-coordinated *A*(1a) site is occupied mainly by K [$^{[13]}$r = 1.68 Å (Shannon 1976)], with subordinate Li, Cs and Na, which gives ($K_{0.75}$ $Li_{0.14}$ $Cs_{0.09}$ $Na_{0.02}$$\square_{1.00}$) *apfu*, and it is coordinated by twelve O atoms and one F atom, with <*A*(1a)–O,F> = 3.310 Å. The [5]-coordinated *A*(1b) site is half-occupied by Li ($^{[5]}$r = 0.68 Å) with <*A*(1b)–O> = 2.28 Å, which gives 1.0 Li *apfu*. The *A*(1b) site is coordinated by 4 O atoms and one F atom. The <*A*(1b)–O> bond length (2.28 Å) is longer than the mean <Li–O> bond length for [5]-coordinated Li, which is 2.10(6) Å (Wenger & Armbruster 1991). This observation can be explained by partial occupation of the *A*(1b) site: the Li–O distance increases as the occupation factor decreases (Shannon 1976). The aggregate content of the *A* site is ($Li_{1.14}$ $K_{0.75}$ $Cs_{0.09}$ $Na_{0.02}$)$_{Σ2.00}$. Note that prior to the discovery of nalivkinite, positional disorder

TABLE 8. POSITIONAL DISORDER OF THE *A* SITE IN ASTROPHYLLITE-GROUP MINERALS§

Mineral	Composition of the *A* site (*apfu*)		CN *		<*A*(1a,1b)–φ> **(Å)		*A*(1a)–*A*(1b) (Å)	Ref.
	A(1a)	*A*(1b)	*A*(1a)	*A*(1b)	*A*(1a)	*A*(1b)		
nalivkinite	$K_{0.75}Li_{0.14}Cs_{0.09}Na_{0.02}\square_{1.00}$	$Li_{1.00}\square_{1.00}$	13	5	3.310	2.28	1.28	(1)
niobokupletskite	$K_{0.96}Rb_{0.13}\square_{0.91}$	$\square_{1.18}K_{0.82}$	13	13	3.32	3.32	0.37	(2)
kupletskite-1*A*	$K_{1.89}\square_{0.11}$	$\square_{1.86}Na_{0.14}$	12	5	3.33	2.40	0.86	(3)
kupletskite-1*A* (RUS8)***	$K_{1.77}\square_{0.23}$	$\square_{1.77}K_{0.23}$	12	5	3.265	2.407	0.92	(4)
kupletskite-1*A* (NOR17)***	$K_{1.74}\square_{0.26}$	$\square_{1.74}Na_{0.26}$	12	5	3.270	2.380	0.85	(5)

* coordination number; ** φ – O,F; A(1a) – φ ≤ 3.8 Å; *** name of sample from Piilonen *et al.* (2001, 2003b). References: (1) this work, (2) Piilonen *et al.* (2000), (3) Christiansen *et al.* (1998), (4) Piilonen *et al.* (2001), (5) Piilonen *et al.* (2003b). § space group $P\bar{1}$.

TABLE 9. HYDROGEN BONDING IN THE CRYSTAL STRUCTURE OF NALIVKINITE

D–H...A	D–A (Å)	D–H (Å)	H...A (Å)	∠D–H...A (°)
O(4)–H(1)–O(11) *	3.426(8)	0.990(1)	2.585(7)	143(5)
O(4)–H(1)–O(13) *	3.448(8)	0.990(1)	2.654(7)	137(5)
O(5)–H(2)–O(14)	3.496(8)	0.981(1)	2.615(7)	150(5)

* bifurcated bond.

of the *A* site was documented only for Mn-dominant members of the astrophyllite group, in three samples of kupletskite and niobokupletskite (Table 8). Details of positional disorder of the *A* site in nalivkinite correlate well with those of kupletskite-1*A* (Christiansen *et al.* 1998 and NOR17 from Piilonen *et al.* 2003b), where [12]-coordinated *A*(1a) and [5]-coordinated *A*(1b) sites are occupied by a large K atom ($^{[12]}r$ = 1.64 Å) and a smaller Na atom ($^{[5]}r$ = 1.00 Å), respectively.

Hydrogen bonding

Details of hydrogen bonding in nalivkinite are given in Table 9. Hydrogen bonds occur between OH groups of the O sheet and apical O atoms of (SiO_4) tetrahedra. There is very weak hydrogen bonding in nalivkinite. Brown (1976) has examined the issue of very weak hydrogen bonds in inorganic structures. He showed that significant hydrogen bonds occur in perchloric acid hydrates in the range H…O between 2.3 and 3.1 Å. The H…O distances in nalivkinite are in the range 2.58–2.65 Å, well within the range given by Brown (1976), indicating that these interactions are significant. The H(1) atom of the (OH) group at the O(4) site is involved in a bifurcated hydrogen-bond with D–H...A angles of 143 and 137°, respectively.

SUMMARY

Nalivkinite, ideally $Li_2 Na Fe^{2+}_7 Ti_2 (Si_8 O_{24}) O_2 (OH)_4 F$, is a new lithium-dominant member of the astrophyllite group. It is a Li-analogue of astrophyllite, and the two structures are related by the isovalent substitution Li (nalivkinite) ↔ K (astrophyllite) at the interstitial *A* site.

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