

NALIVKINITE¹, Li₂NaFe₇²⁺Ti₂(Si₈O₂₄)O₂(OH)₄F, A NEW MINERAL OF THE ASTROPHYLLITE GROUP FROM THE DARAI-PIOZ MASSIF, TADJIKISTAN

Atali A. Agakhanov

Fersman Mineralogical Museum, RAS, Moscow, labfmm@rambler.ru

Leonid A. Pautov

Fersman Mineralogical Museum, RAS, Moscow, labfmm@rambler.ru

Yulia A. Uvarova

Queen's University, Kingston, Ontario, Canada

Elena Sokolova

University of Manitoba, Manitoba, Winnipeg, Canada

Frank C. Hawthorne

University of Manitoba, Manitoba, Winnipeg, Canada

Vladimir Y. Karpenko

Fersman Mineralogical Museum, RAS, Moscow, labfmm@rambler.ru

Nalivkinite, a new astrophyllite-group mineral, was discovered in the moraine of the Darai-Pioz alkaline massif located at the intersection of the Zeravshansky, Turkestansky and Alaisky Ridges, Tadjikistan. Nalivkinite occurs in the amphibole-quartz-feldspar rock in association with calcybeborosilite-(Y), bafertisite, jinshajiangite, zircon and thorite. Nalivkinite is brown with a bronze hue and a vitreous luster; in thin plates, it is transparent. Mohs hardness is 3, $D_{\text{meas.}} = 3.32(2) \text{ g/cm}^3$, $D_{\text{calc.}} = 3.315 \text{ g/cm}^3$. It is biaxial positive, $n_p = 1.703(2)$, $n_m = 1.716(2)$, $n_g = 1.745(2)$, $2V_{\text{meas.}} = +68(2)^\circ$, $2V_{\text{calc.}} = +68.6^\circ$. Nalivkinite is triclinic, space group $P-1$, $a = 5.3745(6) \text{ \AA}$; $b = 11.9299(15) \text{ \AA}$; $c = 11.6509(14) \text{ \AA}$; $\alpha = 113.325(3)^\circ$, $\beta = 94.524(2)^\circ$, $\gamma = 103.080(2)^\circ$, $V = 656.2(2) \text{ \AA}^3$, $Z = 1$. Cell dimensions refined from X-ray powder diffraction data are as follows: $a = 5.3707(2) \text{ \AA}$; $b = 11.9327(5) \text{ \AA}$; $c = 11.6546(4) \text{ \AA}$; $\alpha = 113.384(1)^\circ$, $\beta = 94.547(1)^\circ$, $103.047(1)^\circ$, $V = 655.85(2) \text{ \AA}^3$. The strongest reflections in the X-ray powder diffraction pattern are as follows: $[(d, \text{ \AA}), (I, \%), (hkl)]: 10.56 (100) (001), 3.50 (100) (003), 2.780 (80) (1-42), 2.648 (45) (-211), 2.578 (70) (130), 2.474 (15) (-212), 2.295 (30) (131), 2.106 (35) (-142), 1.760 (30) (133), 1.660 (15) (0-73)$. The infrared spectrum of nalivkinite is similar to that of astrophyllite, and the strongest lines are as follows (cm^{-1}): 3600, 1621, 1077(sh), 1056, 975, 929, 696, 649, 566, 441, 438. The chemical composition (electron microprobe, wt. %, Li₂O and Rb₂O by ICP OES, H₂O by the Penfield method): Al₂O₃ – 0.67, SiO₂ – 35.92, TiO₂ – 10.50, Nb₂O₅ – 1.68, CaO – 1.29, MgO – 0.09, MnO – 5.26, FeO – 32.76, Na₂O – 1.62, K₂O – 2.49, Li₂O – 3.76, Cs₂O – 1.40, Rb₂O – 0.85, H₂O – 3.13, F – 0.75, -O=F₂ – 0.32, total – 100.04. The empirical formula of nalivkinite is $(\text{Li}_{1.03}\text{K}_{0.69}\text{Cs}_{0.13}\text{Rb}_{0.12})_{1.97}(\text{Na}_{0.69}\text{Ca}_{0.30})_{0.99}(\text{Fe}_{5.97}^{2+}\text{Mn}_{0.97}\text{Mg}_{0.03}\text{Fe}_{0.97}(\text{Ti}_{1.72}\text{Nb}_{0.16}\text{Zr}_{0.08})_{1.96}[\text{Si}_{7.83}\text{Al}_{0.17}])_8\text{O}_{25.98}\text{OH}_{4.07}(\text{F}_{0.52}\text{OH}_{0.48})_{1.00}$ and the ideal formula is $\text{Li}_2\text{NaFe}_7^{2+}\text{Ti}_2(\text{Si}_8\text{O}_{24})\text{O}_2(\text{OH})_4\text{F}$. The crystal structure of nalivkinite was refined to an R₁ index of 6.26%. The name honors Dmitry Vasiljevich Nalivkin, a famous Russian geologist (1889–1982), author of numerous works on the geology, stratigraphy and paleontology of Central Asia. The holotype sample of nalivkinite is deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow.

3 tables, 3 figures, 12 references.

Keywords: nalivkinite, astrophyllite lithium analogue, Darai-Pioz alkaline massif.

Introduction

Minerals of the astrophyllite group have the general formula $\text{A}_2\text{BC}_7\text{D}_2\text{T}_8\text{O}_{26}(\text{OH})_4\text{X}_{0-1}$, where $^{[10]-[13]}\text{A} = \text{K}, \text{Cs}, \text{Rb}, \text{H}_2\text{O}, \text{H}_3\text{O}^+, \text{Li}, \text{Na}$ and \square ; $^{[10]}\text{B} = \text{Na}$ and Ca ; $^{[6]}\text{C} = \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mn}, \text{Na}, \text{Mg}$ and Zn ; $^{[6]}\text{D} = \text{Ti}, \text{Nb}$ and Zr ; $^{[4]}\text{T} = \text{Si}$ and Al ; $\text{X} = \text{F}, \text{OH}, \text{O}$ and \square (Piilonen *et al.*, 2003; Uvarova *et al.*, 2008).

The astrophyllite group includes nine mineral species: the structurally characterized species astrophyllite, magnesioastrophyllite, kupletskite (with two polytypes: kupletskite-1A and kupletskite-2M) and niobokupletskite, and the structurally uncharacterized species niobophyllite, cesium-kupletskite (recently renamed into a kupletskite-Cs) and zircophyllite. The minerals of the astrophyllite

¹ – Nalivkinite is recommended for the publication by the Commission on New Minerals and Mineral Names of the Russian Mineralogical Society, and was approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association on December 4, 2006.

group are commonly accessory minerals, but may be rock-forming minerals in alkaline rocks. There has been much work on the latter occurrence: a detailed review of the 19th and early 20th Century literature (including the original data on astrophyllite) are given by Bonshtedt (1931); later reviews and new data are given by Semenov (1972), Macdonald and Saunders (1973), Piilonen *et al.* (2003) and Uvarova *et al.* (2008).

Ganzeev *et al.* (1969) first drew attention to a deficiency of potassium and enrichment of lithium in astrophyllite from the Darai-Pioz massif: Li, % – 0.59; 0.59; 0.27, equivalent to 1.27; 1.27; 0.58 wt. % Li₂O. Higher contents of lithium (Li₂O – 1.30; 1.36 wt. %) in astrophyllite from Darai-Pioz were reported by Burova and Dusmatov (1971). Their work prompted re-investigation of this unusual astrophyllite from Darai-Pioz. Accordingly, the Li analogue of astrophyllite was discovered in rocks from the Upper Darai-Pioz massif, and was named nalivkinite in honour of Dmitry Vasiljevich Nalivkin (1889–1982), participant of the Pamiro-Tadjik expedition (1920–1930) and author of numerous works on the geology, stratigraphy and paleontology of Central Asia.

Occurrence

Nalivkinite was found in fenitized rocks of the Upper Darai-Pioz massif by the upper reaches of the Darai-Pioz river, started from the same glacier (Tadjikistan). In plan, the massif is slightly elongated in a northwesterly direction and adjoins the core of a large synclinal fold of C₂₋₃ slates, and the northern part of the massif an anticlinal fold of interbedded S_{1w}–S_{2ld} slates and limestones. The exposed part of the massif consists of granites, aegirine and quartz syenites, and cancrinite foyaites, and covers 18 km² (Dusmatov, 1971). A significant part of the massif is covered by glaciers and is completely inaccessible. In the last century, the glaciers of Central Asia have receded extensively, and the Darai-Pioz glacier is no exception. The receding glacier has left a steep-walled trough valley. Some parts of the massif can be seen but close examination is not possible without special equipment. As a result, knowledge of the massif is, in many respects, rather fragmentary in nature,

and the lion's share of mineralogical and petrographic work has been done on material collected from glacial debris. The vein rocks are even less accessible to observation in situ, particularly granitic pegmatites, subalkaline granitic pegmatites with rare-metal and rare-earth mineralization, reedmergnite pegmatites, carbonatites, pectolite-microcline-calcite veins, etc. Among the hydrothermally-altered rocks are albitites, aegirine-quartz-microcline-albite rocks with wollastonite, miserite, agrellite, as well as fenites. Detailed descriptions are given by Dusmatov (1968, 1971).

An important feature of rocks of the massif is their enrichment in Li. According to Dusmatov (1971), the following Li (ppm) contents were recorded: biotite granites – 135, quartz syenites – 45, aegirine syenites – 70, cancrinite syenites – 180, fenitized rocks – 250. There are sixteen Li minerals recorded from the Darai-Pioz massif, seven of which were discovered there. Indeed, Ganzeev *et al.* (1969) wrote: "Astrophyllite is a sensitive indicator of enrichment of Rb, Cs and Li in alkaline-rock massifs". These words prove to be true for the Darai-Pioz massif.

Nalivkinite occurs in boulders of the glacial moraine; in-place exposures have not been found. The samples consist of fine- to coarse-grained amphibole-quartz-feldspar rock of leucocratic appearance, with a patchy texture caused by aggregates of amphibole, bafertisite, calcybeborosilite-(Y) and nalivkinite. Microcline forms large grayish-yellow idiomorphic grains 1–8 cm in size, and the albite component does not exceed Ab₄₁, although intergrowths of virtually pure albite are observed. Quartz forms light grey, translucent, sometimes smoky, icy coarse-grained aggregates. Sodic amphibole occurs as prismatic crystals, frequently deformed, up to 3 cm long, in which relict aegirine can be observed. Fine-grained albite is common. The characteristic mineral of nalivkinite-bearing rocks is calcybeborosilite-(Y) which occurs as anhedral dark-grey-to-brown crystals up to 3 cm in size. There are thick lamellar aggregates of brown-red manganous bafertisite and jinshajiangite (fig.1), and rectangular pseudomorphs of fine-grained quartz-calcite-microcline up to 5–15 mm in size.

There are minor concentrations of dipyrimidililac crystals of zircon (1–3 mm), black octahedral crystals of uraniferous pyrochlore

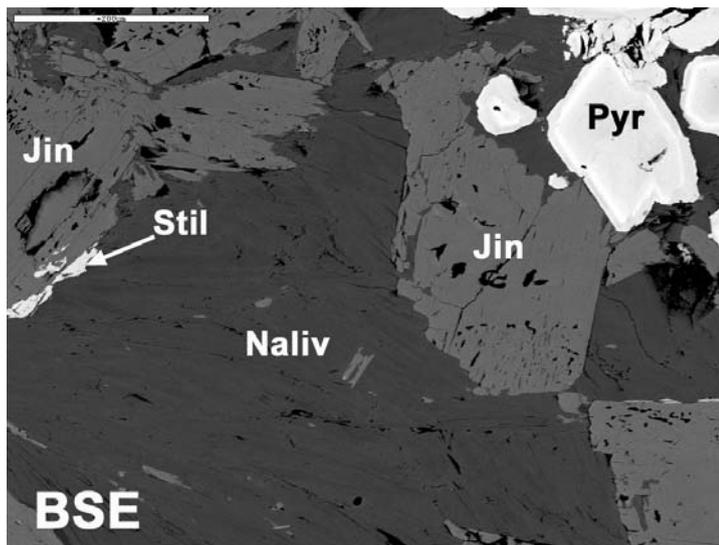
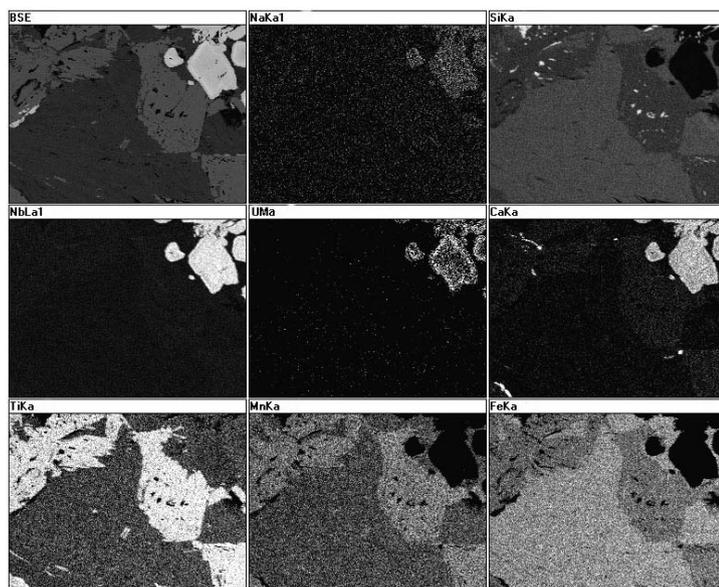


Fig. 1. Intergrowth of nalivkinite (Naliv) with jinshajiangite (Jin), pyrochlore (Pyr) and stillwellite-(Ce) (Stil). The BSE image of a polished section (top) and characteristic X-ray maps of the specified elements (bottom).



(0.5–2 mm), and pinkish-red prismatic crystals of stillwellite-(Ce) from 4 to 10 mm, grains of pale-violet fluorite up to 1 mm, crystals of pale-green thorite, yellow wedge-shaped crystals of Nb-bearing titanite ($\text{Nb}_2\text{O}_5 = 2.64$ wt. %, size <1 mm). Willemite, smithonite and barite occur in cavities caused by leaching of sphalerite.

Nalivkinite forms large gold-brown lamellar aggregates up to 4 x 5 cm (fig. 2) that are frequently deformed, shattered and penetrated by a network of quartz veinlets to 0.1–0.2 mm thick. The same veinlets also cut the lamellar aggregates of bafertisitite.

Physical properties

Appearance of nalivkinite is very similar to that of astrophyllite. In hand specimen, it is brown with a bronze hue; in thin plates, it is pale brown and transparent. Cleavage is perfect on (001), good on (010), and imperfect on (100). On breaking, lamellae and thin mica-like layers frequently occur. Nalivkinite is brittle with a pale-yellow streak and a vitreous lustre that is particularly prominent on cleavage fragments. In short-wave and long-wave UV-light, the mineral does not fluoresce. The Mohs hardness is 3. Micro-indentation VHN was determined with a 20g load on a PMT-3



Fig. 2. A general view of the amphibole-quartz-feldspar rock in which nalivekinite was discovered. Large platy aggregates of brownish-golden nalivekinite in microcline, intergrown with black anhedral crystals of sodic amphibole and pale-violet euhedral crystals of zircon. Size of sample: 5 x 4 x 1.5 cm

instrument standardized on NaCl; the mean value is 190 kg/mm^2 (average of 10 measurements in the range $170\text{--}218 \text{ kg/mm}^2$). A density of $3.32(2) \text{ g/cm}^3$ was determined by weighing grains in water-diluted Clerichi solution. The calculated densities for grains A and B are 3.315 g/cm^3 and 3.299 g/cm^3 , respectively.

Nalivekinite is biaxial positive; refractive indices were measured by spindle stage and are as follows: $n_p = 1,703(2)$; $n_m = 1,716(2)$; $n_g = 1,745(2)$ (for a wavelength of 589 nm). The optical-axial angle, measured on a Fedorov stage, is as follows: $2V_{\text{meas.}} = +68(2)^\circ$; $2V_{\text{calc.}} = +68.6^\circ$ (because of strong dispersion, it was necessary to make our measurements with Na light). Dispersion is strong, $r > v$. In the immersion liquids, practically all nalivekinite particles lay on the cleavage plane (001). Most grains resemble elongate parallelepipeds, and there are two discernable types of fragments: one has positive elongation and direct extinction $\text{Ng} \parallel a$, whereas the other less regular fragments with cross cleavage on (010) have negative elongation and inclined extinction $\text{Nm} : b = 3^\circ$. In convergent light, all fragments laying on (001) give an obtuse-bisectrix figure. The optic-axial plane is almost perpendicular to the (001) cleavage. Nalivekinite is pleochroic, $\text{Ng} =$ light yellowish-brown, $\text{Nm} =$ reddish brown, $\text{Np} =$ intensive brown, with absorption $\text{Np} > \text{Nm} > \text{Ng}$.

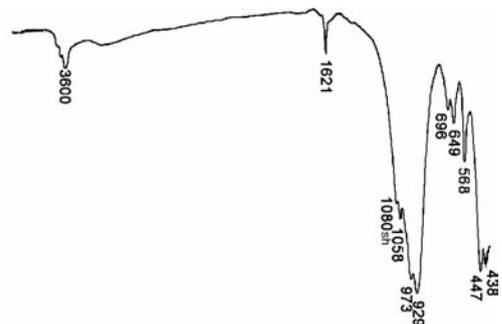
The infrared spectrum of nalivekinite (fig. 3) was measured on a Fourier-transform IR-spec-

trometer (Avatar, Thermo Nicolet, specimen: powder dispersed in KBr pellet). It has strong absorption bands as follows (cm^{-1}): 3600, 1621, 1077 (shoulder), 1058, 975, 929, 696, 649, 568, 447 and 438, and is very similar to that of astrophyllite. Presence of a narrow peak around 1620 cm^{-1} was noted by Morgunova et al. (2000) for potassium-poor astrophyllite and cesium-kupletskite from Darai-Pioz.

Chemical composition

The chemical composition of nalivekinite was determined primarily by electron-microprobe analysis in a polished section embedded in epoxy resin and prepared from sample No 5321. Grains for the determination of alka-

Fig. 3. IR spectrum of nalivekinite.



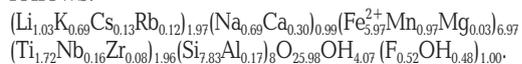
lis and H_2O content (and for determination of physical properties) were extracted from this sample. Grains were analyzed on a JEOL JXA-50A with an accelerating voltage of 20 kV and a current of 2 nA for energy-dispersive examination, and an accelerating voltage of 15 kV and a probe current of 25 nA for wavelength-dispersive analysis. Al, Si, Ti, Ca, Mg, Mn, Fe, Zr, Na, K, Cs, Ti and Nb were analysed with a Link EDS system, and F was measured by WDS. Standards used were as follows: microcline USNM 143966 (Al, Si, K), ilmenite USMN 96189 (Ti, Fe), anorthite USNM 137041 (Ca), LiNbO_3 (Nb), MgF_2 (Mg), Mn (Mn), omphacite USNM 110607 (Na), $\text{CsTbP}_4\text{O}_{12}$ (Cs) and MgF_2 (F). Data were reduced using the PAP program.

Concentrations of Li and Rb were measured by ISP OES. Carefully selected grains of nalivkinite were digested in heated polypropylene tubes with 40 % hydrofluoric acid (HF) and nitric acid (HNO_3). The resulting solution was evaporated twice with addition of HNO_3 to dissolve the dry residue. The solution was analysed with a Varian ICP-OES VISTA Pro. The content of H_2O was determined by the Penfield method using 40 mg of sample. The results of analysis are shown in table 1 (analyses 1 – 12). Lithium content and of some other components in nalivkinite were also determined by S.G. Simakin using secondary-ion mass spectrometry (SIMS) with a Cameca IMS-4F (Institute of Microelectronics and Information science, Russian Academy of Science). Concentrations of each element were calculated from the intensity relations of the ion current of an element normalized to 30 Si^+ using calibration constants from reference samples. For three points, the data are as follows (wt. %): Li_2O – 1.03, 1.23, 0.99; Rb_2O – 1.14, 0.92, 0.97; K_2O – 2.61, 2.37, 3.21; F – 0.74, 0.77, 0.89. Taking into account the precision of the SIMS method and the natural variability of these constituents in nalivkinite, these results are in good agreement with those obtained by electron-microprobe analysis and ICP OES. The composition of the nalivkinite grain on which the single-crystal X-ray data were collected (and the crystal structure was refined) is given in table 2 (column B). The FeO (i.e., Fe^{2+}) content was determined on the sample of grains from which the grain used for structural analysis was extracted. A weight of 10.32 mg was digested in a fluoroplastic crucible by boiling in 40% HF to which a known

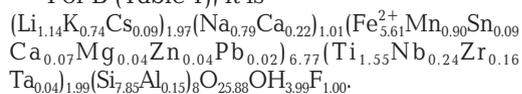
amount of the ammonium vanadate solution was added, the abundance of which was titrated with 0.01M Mohr's Salt solution (Sizykh et al., 1977). Two aliquots of diabase W-2a reference sample were analysed simultaneously to check for accuracy. The measured content of FeO in nalivkinite is 29.46 wt. %. This value is close to the amount of FeO measured by electron microprobe: 30.84 wt. %, indicating that there is negligible Fe_2O_3 in nalivkinite.

Inspection of the table of nalivkinite analyses shows that some variation in Fe, Mn, Nb, Cs, F and some other elements (that are not essential with regard to the nomenclature of the group). Some of these variations are shown in the BSE image in figure 2.

The chemical formula of nalivkinite, normalized on the basis of 8 (Si + Al) atoms using the average composition of A (Table 1) is as follows:



For B (Table 1), it is



The ideal formula of nalivkinite is: $\text{Li}_2\text{NaFe}_7^{2+}\text{Ti}_2(\text{Si}_8\text{O}_{24})\text{O}_2(\text{OH})_4\text{F}$.

The compatibility index, calculated for the average composition of A is as follows:

$$(1 - K_p/K_c) = 0.024 \text{ (excellent);}$$

that for B is $(1 - K_p/K_c) = 0.013$ (superior).

X-Ray powder diffraction data

X-ray powder diffraction data (tab. 2) were recorded with a RKU-114M camera (114.6 mm diameter), and with a DRON-2.0 X-ray diffractometer using quartz as an internal standard. The X-ray powder diffraction pattern of nalivkinite is similar to that of astrophyllite. The unit-cell parameters refined from the powder data are as follows: $a = 5.3707(2)$ Å, $b = 11.9327(5)$ Å, $c = 11.6546(4)$ Å, $\alpha = 113.384(1)^\circ$, $\beta = 94.547(1)^\circ$, $\gamma = 103.047(1)^\circ$, $V = 655.85(2)$ Å³, with $Z = 1$.

Crystal structure

The crystal structure of nalivkinite (Uvarova *et al.*, 2008) was refined to an R_1 index of 6.26% based on 2041 observed [$\text{Fo} > 4\sigma(\text{FI})$] unique reflections measured with $\text{MoK}\alpha$ X-radiation on a Bruker P4 diffractometer equipped with a Smart 4K CCD

Table 1. Chemical composition of nalivkinite, wt. %

| Compo- nents | A | | | | | | | | | | | | B | |
|--------------------------------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|-------|--------|--------|--------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | Avg | |
| SiO ₂ | 36.57 | 36.45 | 35.41 | 35.81 | 35.95 | 36.46 | 36.30 | 35.02 | 35.88 | 36.01 | 35.08 | 36.13 | 35.92 | 36.11 |
| Al ₂ O ₃ | 0.44 | 0.65 | 0.78 | 0.59 | 0.65 | 0.48 | 0.76 | 1.29 | 0.52 | 0.58 | 0.58 | 0.72 | 0.67 | 0.58 |
| TiO ₂ | 10.26 | 10.03 | 10.58 | 11.14 | 10.40 | 11.11 | 10.41 | 9.23 | 10.91 | 10.94 | 10.57 | 10.40 | 10.50 | 9.48 |
| Nb ₂ O ₅ | 1.39 | 1.60 | 1.74 | 1.07 | 1.90 | 1.81 | 1.49 | 3.35 | 1.16 | 1.13 | 1.19 | 1.93 | 1.65 | 2.40 |
| ZrO ₂ | 0.58 | 0.99 | 0.61 | 0.65 | 0.54 | 0.40 | 1.34 | 0.62 | 1.16 | 1.02 | 0.89 | 0.74 | 0.80 | 1.47 |
| MnO | 5.01 | 5.21 | 5.16 | 5.05 | 5.19 | 5.53 | 5.33 | 5.42 | 5.13 | 5.31 | 5.58 | 5.15 | 5.26 | 4.86 |
| FeO | 33.47 | 32.56 | 32.84 | 32.53 | 32.52 | 32.71 | 33.66 | 33.11 | 32.92 | 32.30 | 32.11 | 32.43 | 32.76 | 30.84 |
| CaO | 1.38 | 1.43 | 1.19 | 1.12 | 1.42 | 1.06 | 1.43 | 1.27 | 1.28 | 1.31 | 2.43 | 2.20 | 1.29 | 1.24 |
| MgO | 0.00 | 0.11 | 0.00 | 0.12 | 0.04 | 0.18 | 0.13 | 0.00 | 0.11 | 0.30 | 0.02 | 0.03 | 0.09 | 0.11 |
| Na ₂ O | 1.54 | 1.72 | 1.81 | 1.68 | 1.58 | 1.59 | 1.51 | 1.73 | 1.55 | 1.34 | 1.67 | 1.76 | 1.62 | 1.88 |
| K ₂ O | 2.62 | 2.35 | 2.58 | 2.31 | 2.48 | 2.49 | 2.56 | 3.12 | 2.37 | 2.32 | 2.43 | 2.20 | 2.49 | 2.68 |
| Cs ₂ O | 1.56 | 1.07 | 1.46 | 1.57 | 1.89 | 1.76 | 0.23 | 0.57 | 1.27 | 1.70 | 1.80 | 1.87 | 1.40 | 0.93 |
| Rb ₂ O* | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | 0.85 | |
| Li ₂ O* | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.18 | 1.30 |
| H ₂ O** | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 3.13 | 2.75 |
| F | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 0.75 | 1.45 |
| Total | 100.73 | 100.08 | 100.07 | 99.55 | 100.47 | 101.49 | 101.64 | 100.64 | 100.17 | 100.17 | 99.11 | 100.61 | 100.36 | 100.20 |
| -O=F ₂ | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.32 | 0.61 |
| Total | 100.41 | 99.76 | 99.75 | 99.23 | 100.15 | 101.17 | 101.32 | 100.32 | 99.85 | 99.85 | 98.79 | 100.29 | 100.04 | 99.59 |

A – analyses of grains from sample No 5321. Main components determined by electron microprobe JCSA-50A;

*Li₂O and Rb₂O determined by ICP OES;

**H₂O determined by the Penfield method; analysts: A.A. Agakhanov, L.A. Pautov.

B – analysis of the single crystal used for structure refinement of nalivkinite from the same sample. Main components determined by electron microprobe Cameca SX-100; Li₂O by ICP MS; H₂O was calculated from the crystal structure; total also includes SnO₂ – 0.89; Ta₂O₅ – 0.61; ZnO – 0.23; PbO – 0.39 wt. % (Uvarova et al., 2008).

detector. The cell parameters are as follows: $a = 5.3745(6)$ Å, $b = 11.9299(15)$ Å, $c = 11.6509(14)$ Å, $\alpha = 113.325(3)^\circ$, $\beta = 94.524(2)^\circ$, $\gamma = 103.080(2)^\circ$, $V = 656.2(2)$ Å³, space group $P-1$, $Z = 1$.

The structure of nalivkinite is similar to that of triclinic astrophyllite (Uvarova et al., 2008, Piiilonen et al., 2003). It consists of alternating heteropolyhedral sheets (H) of composition $[\text{TiSi}_4\text{O}_{12}]^{8-}$, with (SiO₄) tetrahedra and D (= Ti) octahedra, and octahedral sheets (O), with M (1), M (2), M (3) and M (4) octahedra connected by common edges. The H and O sheets are stacked along the c -axis, forming HOH layers that link through common vertices (F atoms) of D octahedra. The interlayer space contains the A (1) and B sites. There are four tetrahedrally coordinated T sites, five octahedrally coordinated M sites and two

interstitial A sites, A (1) and B in nalivkinite. The T sites, with $\langle T-O \rangle = 1.623$ Å, are occupied mainly by Si with minor Al. The occupancy of the octahedrally coordinated M sites is as follows: M (1) = $(\text{Fe}_{1.97}^{2+}\square_{0.03})$ with $\langle M(1)-O \rangle = 2.164$ Å; M (2) = $\text{Fe}_{2.00}^{2+}$ with $\langle M(2)-O \rangle = 2.146$ Å; M (3) = $(\text{Fe}_{1.03}^{2+}\text{Mn}_{0.97})$ with $\langle M(3)-O \rangle = 2.140$ Å; M (4) = $(\text{Fe}_{0.97}^{2+}\text{Mg}_{0.03})$ with $\langle M(4)-O \rangle = 2.140$ Å; $D = (\text{Ti}_{1.72}\text{Nb}_{0.16}\text{Zr}_{0.08})$ with $\langle D-O \rangle = 1.959$ Å. Of the two interstitial A (1) and B sites, A (1) splits into two half-occupied sites, A (1a) and A (1b), with A (1a) – A (1b) = $1.28(4)$ Å. The [5]-coordinated A (1b) site is occupied by $[\text{Li}_{1.00}\square_{0.00}]$ with $\langle A(1a)-O \rangle = 2.280$ Å, which gives 1.00 Li *apfu*; the [10]-coordinated A (1a) site is occupied by $(\text{K}_{0.75}\text{Li}_{0.14}\text{Cs}_{0.09}\text{Na}_{0.02}\square_{1.00})$ with $\langle A(1a)-O \rangle = 3.310$ Å, which gives $(\text{K}_{0.75}\text{Li}_{0.14}\text{Cs}_{0.09}\text{Na}_{0.02})$

apfu. The aggregate content of the A(1) site is $(\text{Li}_{1.14}\text{K}_{0.75}\text{Cs}_{0.09}\text{Na}_{0.02})_{2.00}$. The [10]-coordinated B site is occupied by $(\text{Na}_{0.78}\text{Ca}_{0.22})$ with $\langle\text{B}-\text{O}\rangle = 2.612 \text{ \AA}$. All site occupancies are reported in accord with Uvarova *et al.* (2008).

In nalivkinite, lithium is dominant at the A(1) site, which gives 2 *apfu*, and the end member is written as Li_2 , whereas in astrophyllite, K is dominant at this site. Thus, nalivkinite, $\text{Li}_2\text{NaFe}_7^{2+}\text{Ti}_2(\text{Si}_8\text{O}_{24})\text{O}_2(\text{OH})_4\text{F}$, is the Li analogue of astrophyllite, $\text{K}_2\text{NaFe}_7^{2+}\text{Ti}_2(\text{Si}_8\text{O}_{24})\text{O}_2(\text{OH})_4\text{F}$, and the first Li mineral in the astrophyllite group.

The properties of astrophyllite and nalivkinite are compared in table 3.

The origin of nalivkinite

The mineral association and observed paragenesis of nalivkinite show that it is associated with fenitization. It seems likely that nalivkinite crystallized directly in a lithium-rich environment. It is possible that nalivkinite formed later as a result of Li-K ion exchange in astrophyllite. According to the work of Chelishchev (1972), astrophyllite is a typical ion-exchange mineral, whose interlayer sites serve as active sites of ion exchange (the ion exchanges Rb-K and Cs-K were experimentally proven, but exchange of K by Li was not studied).

The holotype specimen of nalivkinite is deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow.

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This article is dedicated to V.D. Dusmatov's memory.

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Table 2. X-ray powder diffraction data of nalivkinite

| Camera | | Diffractometer | | Calculated | | <i>hkl</i> |
|-----------|--------------|----------------|--------------|------------|--------------|---------------|
| <i>I</i> | <i>d</i> | <i>I</i> | <i>D</i> | <i>I</i> | <i>d</i> | |
| | | 100 | 10.56 | 100 | 10.52 | 0 0 1 |
| | | 8 | 9.88 | 10 | 9.83 | 0 -1 1 |
| | | 2 | 5.80 | 4 | 5.79 | 0 -2 1 |
| | | 1 | 5.26 | 2 | 5.26 | 0 2 0 |
| | | 2 | 4.39 | 4 | 4.40 | -1 -1 1 |
| | | 2 | 4.31 | 3 | 4.33 | -1 2 0 |
| | | | | 2 | 4.31 | -1 2 0 |
| | | 1 | 4.05 | 2 | 4.06 | 0 2 1 |
| | | 2 | 3.76 | 3 | 3.76 | -1 2 1 |
| | | | | 1 | 3.75 | 1 -1 2 |
| 10 | 3.56 | 100 | 3.51 | 27 | 3.502 | 0 0 3 |
| | | 3 | 3.26 | 2 | 3.27 | 0 -3 3 |
| | | | | 6 | 3.25 | -1 -1 3 |
| | | 3 | 3.07 | 4 | 3.06 | -1 2 2 |
| | | 3 | 3.03 | 5 | 3.02 | 1 -2 3 |
| | | 2 | 2.965 | 1 | 2.966 | 0 3 1 |
| | | | | 2 | 2.965 | 0 1 3 |
| | | 3 | 2.855 | 5 | 2.853 | 1 1 2 |
| 10 | 2.79 | 80 | 2.780 | 20 | 2.780 | 1 -4 2 |
| | | | | 18 | 2.780 | -1 -3 1 |
| 7h | 2.64 | 45 | 2.638 | 18 | 2.650 | -2 1 1 |
| | | | | 12 | 2.627 | 0 0 4 |
| 10 | 2.57 | 70 | 2.578 | 20 | 2.578 | 1 3 0 |
| | | | | 21 | 2.575 | 1 -4 3 |
| 2 | 2.49 | 15 | 2.474 | 15 | 2.475 | -2 1 2 |
| 1 | 2.40 | 4 | 2.399 | 5 | 2.398 | -1 4 1 |
| 4 | 2.30 | 30 | 2.295 | 7 | 2.296 | 1 3 1 |
| 2 | 2.22 | 14 | 2.223 | 10 | 2.223 | -2 1 3 |
| 5 | 2.10 | 35 | 2.106 | 5 | 2.106 | -1 4 2 |
| 1 | 2.05 | 9 | 2.041 | 6 | 2.042 | 2 -1 3 |
| | | | 1.963 | 1 | 1.963 | -2 1 4 |
| | | | 1.930 | 1 | 1.930 | 0 -6 3 |
| 4 | 1.760 | 30 | 1.760 | 5 | 1.761 | 1 3 3 |
| | | | 1.757 | 5 | 1.758 | 1 -4 6 |
| 2 | 1.729 | 10 | 1.728 | 6 | 1.728 | -2 1 5 |
| 2 | 1.664 | 15 | 1.660 | 10 | 1.660 | 0 -7 3 |
| 2 | 1.622 | 11 | 1.620 | 2 | 1.619 | -1 4 4 |
| | | | 1.595 | 1 | 1.594 | -2 0 6 |
| 1 | 1.576 | 6 | 1.576 | 7 | 1.577 | 3 -5 1 |
| | | | | 7 | 1.576 | -3 -2 2 |
| 1 | 1.432 | 4 | 1.432 | 2 | 1.433 | -1 4 5 |
| | | | | 2 | 1.430 | -1 -3 8 |
| 1 | 1.407 | 2 | 1.407 | 2 | 1.408 | 2 -8 2 |
| | | | | 2 | 1.406 | -2 -6 4 |

Camera: *RKU 114M*, Fe-anode, Mn filter, *URS-501M*;

Diffractometer: *DRON-2.0*, Fe – anode, graphite monochromator, scan rate 1 deg/min, quartz as internal standard.

Analyst *A.A. Agakhanov*.

The most intense lines are shown in bold.

Table 3. Comparison of the properties of nalivkinite and astrophyllite

| | Nalivkinite | Astrophyllite |
|---|---------------------------------------|--|
| Formula | $K_2NaFe_7^{2+}Ti_2Si_8O_{26}(OH)_4F$ | $Li_2NaFe_7^{2+}Ti_2Si_8O_{26}(OH)_4F$ |
| Sp.group | <i>P</i> -1 | <i>P</i> -1 |
| <i>a</i> , Å | 5.3776(6) | 5.3745(6) |
| <i>b</i> , Å | 11.899(1) | 11.9299(15) |
| <i>c</i> , Å | 11.662(1) | 11.6509(14) |
| α , ° | 113.114(2) | 113.325(3) |
| β , ° | 94.630(2) | 94.524(2) |
| γ , ° | 103.090(2) | 103.080(2) |
| Z | 1 | 1 |
| Strong | 10.6 (100) | 10.56 (100) |
| lines of | 3.51 (80) | 3.50 (100) |
| X-ray - powder diffraction pattern | 2.648 (45) | 2.648 (45) |
| d_{obs} (Å) (<i>l</i>) | 2.578 (70) | 2.578 (70) |
| | 2.474 (15) | 2.474 (15) |
| | 2.295 (30) | 2.295 (30) |
| | 2.106 (35) | 2.106 (35) |
| | 1.760 (30) | 1.760 (30) |
| | 1.660 (15) | 1.660 (15) |
| Colour | Brownish-golden | Bronze-yellow, golden |
| Lustre | Pearly to vitreous | Pearly |
| Density _{meas.} (g/cm ³) | 3.3–3.4 | 3.32(2) |
| Density _{calc.} (g/cm ³) | 3.315 | |
| Mohs hardness | 3 | 3 |
| Optic sign | Biaxial (+) | Biaxial (+) |
| 2 <i>V</i> | 70–80° | 68° |
| n_p | 1.678 | 1.705 |
| n_m | 1.703 | 1.716 |
| n_g | 1.733 | 1.745 |

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