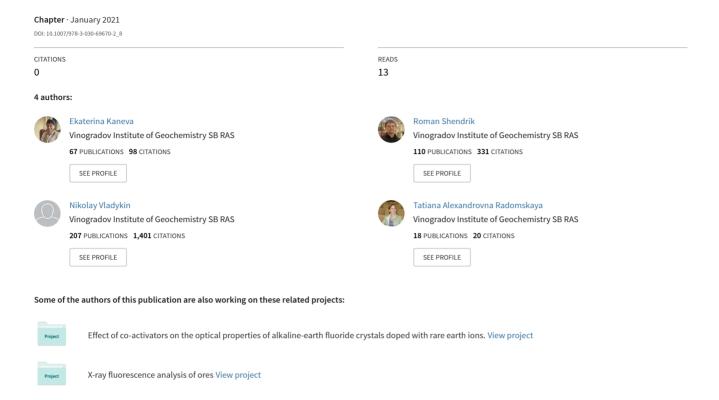
# Crystal-Chemical Features of Rare and Complex Silicates from Charoite Rocks of the Malyy Murun Volcano-Plutonic Alkaline Complex





# Crystal-Chemical Features of Rare and Complex Silicates from Charoite Rocks of the Malyy Murun Volcano-Plutonic Alkaline Complex

E. V. Kaneva, R. Y. Shendrik, N. V. Vladykin, and T. A. Radomskaya

#### **Abstract**

The article summarizes the available crystal-chemical data and presents new results of structural and spectroscopic studies of a number of rare and complex silicates found out in the rocks of the Malyy Murun massif—the eastern part of the Murun volcano-plutonic alkaline complex. Murun complex is the world's largest massif of potassium-carbonated alkaline rocks; it is located on the southwestern edge of the Aldan Shield, on the border of Yakutia and Irkutsk region. The work presents descriptions of crystal-chemical and spectroscopic features of tinaksite and tokkoite—silicates with hybrid tetrahedral radical in the crystal structure, agrellite and frankamenite containing tubular silica-oxygen anions, fedorite, and a new mineral in the Murun massif—fluorcarletonite with double tetrahedral layers.

#### **Keywords**

Murun massif · Crystal chemistry · Infrared spectroscopy · Tinaksite · Tokkoite · Agrellite · Frankamenite · Fluorcarletonite · Fedorite

Irkutsk Scientific Center of Siberian Branch of Russian, 134 Lermontov St., 664033 Irkutsk, Russia

E. V. Kaneva (⋈) · R. Y. Shendrik · N. V. Vladykin · T. A. Radomskaya Vinogradov Institute of Geochemistry SB RAS, 1A Favorsky Str., 664033 Irkutsk, Russia e-mail: kev604@mail.ru

N. V. Vladykin

# 1 Introduction

Starting from the 1960s, a number of new minerals with unusual composition and crystal structure were discovered at the Murun massif. The Murun massif's specific geographical location and difficult accessibility do not allow for a comprehensive and systematic study of its mineralization. There are still many open questions related to structural properties and correlations between structural features and chemical compositions of minerals. The choice of a group of rare and complex silicates of the Little Murun alkaline rocks as the object of crystal-chemical study is dictated by the fact that, although the structures of many of these mineral species have already been determined, previous studies were conducted on samples from other deposits and/or did not include complete data based on modern knowledge and technology.

This paper provides an overview of crystal-chemical features of some rare and complex silicates in the light of new data obtained by the authors.

According to the type and complexity of [SiO<sub>4</sub>]-tetrahedra in the crystal structure, the minerals considered here can be divided into the following groups: (1) silicates with hybrid tetrahedral radical, (2) silicates with tubular tetrahedral radicals, and (3) silicates with double tetrahedral layers.

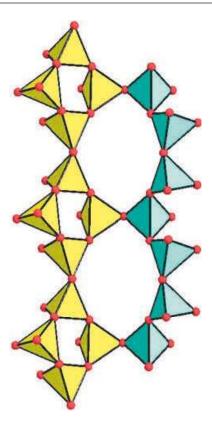
Infrared (IR) spectroscopy is a rather convenient method to detect some structural features of complex silicates.

# 2 Silicates with Hybrid Tetrahedral Radical

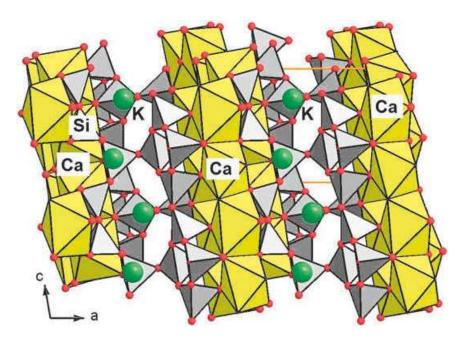
**Tinaksite**, K<sub>2</sub>Ca<sub>2</sub>NaTi(Si<sub>7</sub>O<sub>18</sub>OH)O, and **tokkoite**, K<sub>2</sub>Ca<sub>4</sub>(Si<sub>7</sub>O<sub>18</sub>OH)(OH,F), are found in the charoitites of the Murun massif. Tinaksite often forms radially radiant aggregates or rosette-like clusters. It is associated with potassium feldspar, aegirine, quartz, frankamenite, xonotlite, and a number of rare minerals. The color of the mineral is bright brown to red–orange. The mineral was firstly described in 1965 by Rogov et al. [1]. Von Bissert [2] has been determined, and Rozhdestvenskaya et al. [3] have been refined the crystal structure of tinaksite from the Murun massif. Tinaskite was also discovered in the Rosvumchorr deposit (Khibiny massif), where it is found in pegmatites occurring in rischorrites and urtites [4].

Tokkoite has a light-brown, silver-brown or yellowish color; it crystallizes in the form of radial aggregates in association with charoite, tinaksite, miserite, aegirine, and K-feldspar. The mineral was first described by Lazebnik et al. [5], and the crystal structure was determined in 1989 by Rozhdestvenskaya et al. [6].

A description of the crystal-chemical features of the isostructural tokkoite and tinaksite should be started with the chains of wollastonite ( $[Si_3O_9]$ ) and vlasovite ( $[Si_4O_{11}]$ ) types. Their condensation leads to a special arrangement of tetrahedra along the c axis with the formation of four- and eight-membered rings (Fig. 1). Such a radical is called hybrid and has the composition  $[Si_7O_{18}OH]^{9-}$ . One of the positions of the potassium atoms located in the structural cavities in both minerals is



**Fig. 1** Hybrid tetrahedral radical (3) in the structure of tinaksite and tokkoite as a result of condensation of wollastonite (cyan) and vlasovite (yellow) chains



**Fig. 2** Tokkoite crystal structure. Si tetrahedra are shown in grey, Ca-octahedra are yellow, and potassium atoms are green spheres

split into several different positions. Ribbons of cation-centered polyhedra are connected through common vertices, forming layers. Silicate radicals and layers of polyhedra combine to form a heterogeneous framework of the structure of minerals (Fig. 2).

Recent detailed studies [7] provided new insights into the crystal-chemistry of tinaksite and tokkoite. A comparison of geometric parameters shows significant similarities between the two structures. Average unit cell parameters for tinaksite (sp. gr. P): are:  $a \approx 10.373$ ,  $b \approx 12.176$ ,  $c \approx 7.057$  Å,  $\alpha \approx 90.82^{\circ}$ ,  $\beta \approx 99.22^{\circ}$ ,  $\gamma \approx 92.80^{\circ}$ ,  $V \approx 878.5$  Å<sup>3</sup>; for tokkoite (P):  $a \approx 10.423$ ,  $b \approx 12.477$ ,  $c \approx 7.112$  Å,  $\alpha \approx 89.92$ ,  $\beta \approx 99.68^{\circ}$ ,  $\gamma \approx 92.97^{\circ}$ ,  $V \approx 910.5$  Å<sup>3</sup> [7].

The derivation of structural formulas for tokkoite and tinaksite is difficult because of the presence of several atoms occupying different cationic positions, atoms with variable charge and coordination number (Fe, Ti), and a small amount of rare-earth elements. The 6- and 7-coordinated atomic positions have a rather diverse chemical composition. The formulas were determined on the basis of Si = 7atoms per formula unit by combining the results of electron microprobe analysis, Mössbauer data, and crystal structure refinements. Focusing on the octahedral sites, it was assumed that, due to the greater chemical heterogeneity in the tokkoite, Fe, in addition to two oxidation states, can have several structural positions. Thus, it also has a more complex Mössbauer spectrum with respect to tinaksite. The results of the Mossbauer analysis showed that Fe<sup>2+</sup> is the main state of iron oxidation in both minerals (Fe<sup>2+</sup> = 60.0(6)% in tokkoite and 87.2(4)% in tinaksite). The spectra indicate the presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> in octahedral coordination, while two different local Fe<sup>2+</sup> environments were found in tokkoite. The Ca atoms in the tokkoite are distributed over all available octahedral sites, while in the tinaksite, Ca atoms occupy only the M3 and M4 octahedra.

The structural formulas of tokkoite and tinaksite,  $K_{1.95}(Ca_{0.39}Ti_{0.22}Fe^{2+}_{\phantom{2}0.11}Fe^{3+}_{\phantom{3}0.10}$  $Mg_{0.17})(Ca_{0.77}Na_{0.23})(Ca_{0.96}Fe^{2+}_{0.04})(Ca_{0.94}Mn_{0.06})(F_{0.72}O_{0.24}(OH)_{0.04})[Si_7O_{18}(OH)]$ and  $K_{2.01}(Ti_{0.81}Fe^{2+}_{0.12}Fe^{3+}_{0.02}Mg_{0.05}Mn_{0.01})(Na_{0.86}Ca_{0.14})(Ca_{0.97}Mg_{0.03})(Ca_{0.92}Mn_{0.09})$ (O<sub>0.81</sub>OH<sub>0.19</sub>)[Si<sub>7</sub>O<sub>18</sub>(OH)], respectively, differ mainly in the composition of the anionic positions M1, M2 and position O20. Based on the ideal tokkoite formula, K<sub>2</sub>Ca<sub>4</sub>  $(Si_7O_{18}OH)(OH,F)$ , the substitution reaction  $2Ca^{2+}_{(M1+M2)} + (F,OH)^{-}_{(O20)} \leftrightarrow Ti^{4+}_{(M1)}$ +  $Na^{+}_{(M2)}$  +  $O^{2-}_{(O20)}$  leads to the ideal tinaksite formula,  $K_2Ca_2NaTi(Si_7O_{18}OH)O$ , as previously was reported by Rozhdestvenskaya and Nikishova [8]. Geometrical features, the difference in the parameters of the unit cells and the distortion parameters of the polyhedra, indicate local stress in the structure, mainly with respect to the M1 position. In particular, the substitution of Ti atoms by Ca atoms in M1 implies the expansion of the polyhedral layer, which affects the distance between the cations and the deformation of the bond angle. It leads to an increase in the unit cell parameters, mainly along the b axis. In conclusion, the chemical composition of M1 and O20 can affect strong geometric distortions without causing damage to the structure. Therefore, M1 and O20 play a major role in crystal chemistry and, possibly, introducing restrictions on the existence of a solid solution between tinaksite and tokkoite [7].

# 3 Silicates with Tubular Tetrahedral Radicals

**Agrellite**, NaCa<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>F, is a rare mineral, first discovered as a rock-forming mineral in the province of Quebec (Canada) in regional metamorphic alkaline rocks [9]. Later, the agrellite was found at the southeastern periphery of the Murun massif, Russia [10]. The following minerals can be found in paragenesis with agrellite: aegirine, K-feldspar, albite, quartz, and alkaline amphibole. Sometimes fluorite, pectolite, miserite, fedorite, eudialyte, wadeite may prevail; calcite, dolomite, sphene, apatite, zircon, narsarsukite, rosenbuschite, strontianite, pyrite, galena, sphalerite, thorosteenstrupine can also be associated with it.

Agrellite is also noted as a rare find on Mount Karnasurt of the Lovozero Massif, Russia [11], and in the pluton Woso, Wisconsin, USA [12]. In addition, the presence of agrellite on the Dara-i-Pioz massif (Tajikistan) was briefly reported in the literature [13, 14].

The symmetry, space group and approximate unit cell parameters were firstly published by Gittins et al. [9], who applied the photographic method to study the Canadian sample. The crystal structure was solved in 1979 using a mineral from Quebec [15]. Rozhdestvenskaya et al. in 1998 published the results of powder X-ray diffraction of strontium agrellite from the Yakutian charoitite (Murun massif) [16], and at about the same time the data of a single-crystal X-ray study were published [17]. Agrellite found on the Murun massif can be described as elongated grayish-white crystals up to 5 cm in size. According to the results of the investigation, it differs from the Murun agrellite described earlier in literature [10, 17]. The formula of the studied mineral, calculated on the basis of 4 silicon atoms per formula unit, is  $(Na_{0.99}K_{0.01})(Ca_{1.94}Sr_{0.03}Na_{0.02}(Mn,Fe)_{0.01})[Si_4O_{10}](F_{0.96}OH_{0.04})$  [18]. Thus, a simplified formula of the investigated aggrellite is:  $NaCa_2[Si_4O_{10}]F$ . The mineral is triclinic. The unit cell parameters are: a = 7.7628(1), b = 18.9505 (4), c = 6.9847(1) Å,  $\alpha = 89.774(1)^\circ$ ,  $\beta = 116.581(1)^\circ$ ,  $\gamma = 94.311(1)^\circ$ , V = 915.80

Silicate tubes consist of two centrosymmetrically connected single silicate chains. Individual chain is formed by four-membered tetrahedral rings similar to the vlasovite chain of the composition  $[Si_4O_{11}]$  [19]. These rings through their vertices are combined into chains elongated along the c axis. Two adjacent chains are connected via an oxygen atom, resulting in the formation of a silicate tube of the composition  $[Si_8O_{20}]$ . Each tube contains two different eight-membered tetrahedral rings, which have four common tetrahedral. Its diameter is determined by a six-membered ring. The eightfold ring joins the calcium polyhedra.

(3)  $Å^3$  [18].

The crystal structure of the Murun agrellite sample studied by the authors [18, 20] corresponds to the model proposed by Ghose and Wan in 1979 [15] for the structure of REE-agrellite.

An EPR signal at room temperature and at 77 K was observed in the agrellite samples and referred to  $Mn^{2+}$  ions (I = 5/2). In the crystal structure of agrellite, Mn replaces calcium in a position surrounded by two fluorine ions [18].

Frankamenite, K<sub>3</sub>Na<sub>3</sub>Ca<sub>5</sub>Si<sub>12</sub>O<sub>30</sub>F<sub>3</sub>(OH)·H<sub>2</sub>O, is associated with charoite, pectolite, microcline, aegirine, tinaksite, and quartz [21]. The mineral forms flattened, rosette-like, or radially radiant aggregates and may have different coloring: from gray, bluish- and lilacky-grey to greenish and brown colors. In 1992, Nikishova and co-authors presented the results of the study of the mineral, calling it triclinic canasite [22]. The structure of this variety was refined in the space group *P1*. The crystal structure and interatomic distances only slightly differ from similar characteristics of monoclinic canasite from the Khibiny massif. In 1995, triclinic canasite was approved by the Commission on New Minerals, Nomenclature, and Classification as a new mineral frankamenite [23]. It was named after the Russian mineralogist and crystallographer, Professor of St. Petersburg State University V.A. Frank-Kamenetsky. Frankamenite has the following average crystal-chemical formula: K<sub>2,93</sub>(Na<sub>2,93</sub>Ca<sub>5,05</sub>Mn<sub>0,07</sub>)Si<sub>12</sub>O<sub>30</sub>[F<sub>2,83</sub>(OH)<sub>1,35</sub>]·0.79H<sub>2</sub>O [22].

The parameters of the unit cell of the Murun frankamenite: a = 10.094(3), b = 12.691(3), c = 7.240(1) Å,  $\alpha = 90.00(2)^{\circ}$ ,  $\beta = 111.02(2)^{\circ}$ ,  $\gamma = 110.20(2)^{\circ}$ , V = 804.5(7) Å<sup>3</sup> (according to [24]).

The crystal structures of Khibiny canasite and Murun frankamenite consist of tubular radical  $[Si_{12}O_{30}]^{12^-}$  with octagonal section and zigzag walls of octahedra populated with calcium and sodium. In the structure of the canasite Na and Ca cations are usually ordered by different octahedra positions: two positions are occupied by Na<sup>+</sup> ions, the remaining two are filled by Ca<sup>2+</sup>. In the triclinic structure of frankamenite only one of eight octahedral positions is fully occupied by the Na<sup>+</sup> ion, one position is occupied by Ca<sup>2+</sup> ion, and the remaining six ones are mixed (Ca, Na)-positions [24]. In contrast to canasite, the H<sub>2</sub>O molecule is localized between potassium atoms in the center of the silicate tube of the frankamenite structure [22, 24].

According to Nikishova et al. [22], a high degree of order in monoclinic canasite suggests slower growth of its crystals in the pegmatites of Khibiny. The manifestation of a high degree of ordering of most octahedral positions in frankamenite indicates other conditions of its crystallization.

# 4 Silicates with Double Tetrahedral Layers

**Fedorite**, (Na,K)<sub>2–3</sub>Ca<sub>4</sub>Na<sub>3</sub>(Si<sub>16</sub>O<sub>38</sub>)F<sub>2</sub>·3.5H<sub>2</sub>O is a rare and complex silicate, firstly discovered in the phenytized rocks adjacent to the alkaline complex of the Turiy Peninsula, Kola Peninsula, Russia [25]. In 1968, the mineral was approved and named after mathematician, crystallographer, and mineralogist Evgraf Stepanovich Fedorov. Subsequently, the second discovery of the mineral in charoite rocks of the Malyy Murun complex was reported [26]. Fedorite has a modular structure [27] and it is part of a group of silicates that consist of modules of tetrahedral and octahedral layers. The structure of the fedorite was solved by Sokolova et al. [28] and later refined by Joswig et al. [29]. However, the remaining uncertainties in the positions of

interstitial atoms and the order of cations occupying octahedral and tetrahedral positions were clarified in 2001 by Mitchell and Burns [30].

Crystal-chemical formula of Murun fedorite:  $(K_{2.17}Na_{0.12}Ba_{0.01})$   $(Ca_{4.31}Na_{2.61}Mn_{0.07}Fe_{0.01})(Si_{15.98}Al_{0.02})(O_{37.68}OH_{0.32})(F_2OH_{0.40}Cl_{0.03})\cdot 0.7H_2O$  [31]. The mineral is crystallized in triclinic symmetry (space group P). Parameters of the unit cell:  $a\approx 9.64, b\approx 9.65, c\approx 12.62$  Å,  $\alpha\approx 102.46^{\circ}, \beta\approx 96.24^{\circ}, \gamma\approx 119.93^{\circ}, V\approx 960$  Å<sup>3</sup> (according to [31]).

The crystal structure of the fedorite consists of layers of [8]-coordinated cations associated with a double layer of Si–O-tetrahedra. Tetrahedral layers consist of hexagonal rings but contain tetrahedra of two orientations. The layer of octahedra (O-layer) consists of edge-shared (Ca,Na)-octahedra. Tetrahedral nets of adjacent modules are connected through inverted tetrahedra. H<sub>2</sub>O molecules, K, and Na atoms are placed between the layers. Fedorite is one of the simplest of the modular structures because it consists only of O (octahedra) and T (tetrahedra) structural units in a  $OT_2\overline{T}_2O$  sequence of stacking. In this scheme, identical sheets linked by a center of symmetry are marked with a "strip" symbol.

In 2020, Kaneva et al. [31] obtained for the first time spectra of EPR, optical absorption, and emission of Mn<sup>2+</sup> ions for fedorite. Some samples of the mineral containing Mn and Ce have bright raspberry coloring due to the presence of Mn<sup>4+</sup> ions [31].

**Fluorcarletonite**, KNa<sub>4</sub>Ca<sub>4</sub>Si<sub>8</sub>O<sub>18</sub>(CO<sub>3</sub>)<sub>4</sub>F·H<sub>2</sub>O, a rare mineral belonging to the group of phyllosilicates, is an F-analog of carletonite named after Carleton University [32]. The mineral was discovered in 2019 by Kaneva et al. [33] in charoitites of the Murun massif. Blue fluorcarletonite forms close intergrowths with apophyllite, which indicates their joint crystallization, and it is also associated with pectolite and charoite.

The study of the crystal structure of carletonite was published by Chao in 1972 [34]. At present, it is almost impossible to find samples of carletonite in the Poudrette quarry, Mont Saint-Hilaire, Canada—the only known mineral deposit in the world—because the area where the mineral was found was flooded [35].

The crystal-chemical formula of fluorcarletonite was calculated on the basis of (Si + Al) = 8 atoms per formula unit, while the  $H_2O$  content is consistent with the refined occupancies of the positions of water molecules in the crystal structure. The average formula of Murun fluorcarletonite:

 $K_{1.04}Na_{3.89}Ca_{3.87}Ti_{0.01}(Si_{7.99}Al_{0.01}O_{18})(CO_3)_{3.86}(F_{0.72}OH_{0.28})\cdot 1.11H_2O\ [33].$ 

It is noteworthy that Al is almost absent, and Ti concentration is lower in Murun fluorcarletonite compared to carletonite from the Mont Saint-Hilaire (Canada).

The parameters of the fluorocarletonite unit cell (space group P4/mbm) refined in TOPAS 4 [36]: a = 13.219(1) Å, c = 16.707(2) Å, V = 2919.4(6) Å3 [33].

The crystal structure of the mineral consists of silicate layers, layers of Na- and Ca-centered polyhedra, as well as  $K^+$  cations occupying cavities inside the eight-membered silicate rings.  $H_2O$  molecules are located in the pores of silicate double layers. Finally, the isolated triangles of the  $CO_3$  group are bonded to layers

of Na and Ca polyhedra. Silicate layer with composition  $[Si_8O_{18}]^{4-}$  in carletonite and fluorcarletonite is the result of condensation of two branched single layers.

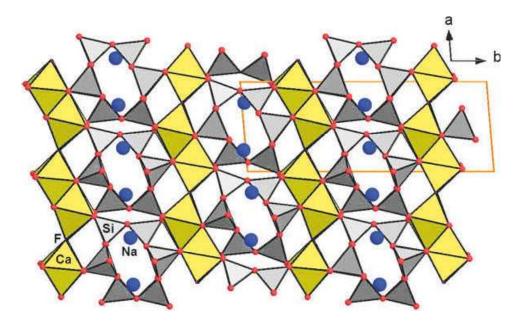
### 5 Discussion and Conclusion

On the infrared spectra of the minerals (Figs. 7, 8 and 9) the Si–O stretching vibrational modes are appeared in the region from 900 to 1200 cm<sup>-1</sup>: Si–O vibrations with the participation of non-bridging oxygen atoms ( $\sim 900-1000 \text{ cm}^{-1}$ ) and bridging Si–O–Si ( $\sim 1000-1200 \text{ cm}^{-1}$ ). Si–O–Si bending vibrations, mixed silicon-oxygen rings vibrations and stretching vibrational modes of different cations are characterized by the spectrum region from 500 to 700 cm<sup>-1</sup>.

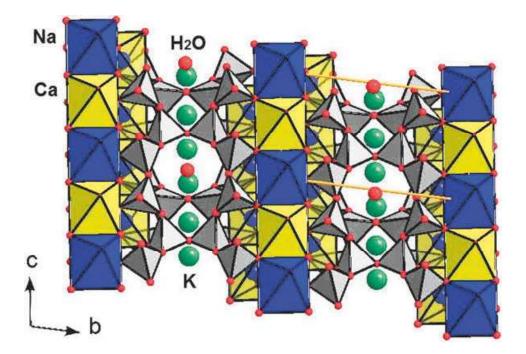
**Table 1** Band positions (cm<sup>-1</sup>) in IR spectra of some rare silicates of Murun massif

	<u> </u>	
	Tinaksite (Fig. 7 line 1)	Tokkoite (Fig. 7 line 2)
ν(ΟΗ)	3366w, 3469	3374, 3479w
δ(H–O–H)	1640	1634
v(Si–O–Si)	1111, 1090, 1076, 1025w	1109, 1095, 1047
v(Si–O)	994sh, 965, 940	995, 940, 955, 922sh
δ(Si–O-Si) and Si–O ring	784w, 727, 699, 654, 644, 635, 543, 508	786w, 733, 698, 656, 637sh, 550, 522
v(Ti-O)	681	683w
	Agrellite (Fig. 8 line 3)	Frankamenite (Fig. 8 line 4)
v(OH)	3564w	3559
ν(H–O–H)	3065w, 3470w	3518w, 3609
δ(Η–Ο-Η)	1636w	1598, 1701
v(Si–O–Si)	1141, 1092, 1063, 1041, 1036, 1005	1124, 1091, 1023
v(Si–O)	963	953
δ(Si–O–Si) and Si–O ring	781, 715w, 689, 654, 612, 590	798, 768, 698, 677, 648, 623w, 516
	Fedorite (Fig. 9 line 5)	Fluorcarletonite (Fig. 9 line 6)
v(OH)	3562, 3639	3655
ν(H–O–H)	3157, 3433	3564, 3587
δ(H–O–H)	1635	1770
v(Si–O-Si)	1129, 1041	1197, 1166w, 1148w, 1072sh, 1051
δ(Si–O–Si) and Si–O ring	798, 621, 516	785, 592, 524, 502, 488
ν(C–O)		1396, 1451, 1480, 1527
δ(C-O)		662, 693, 728, 874

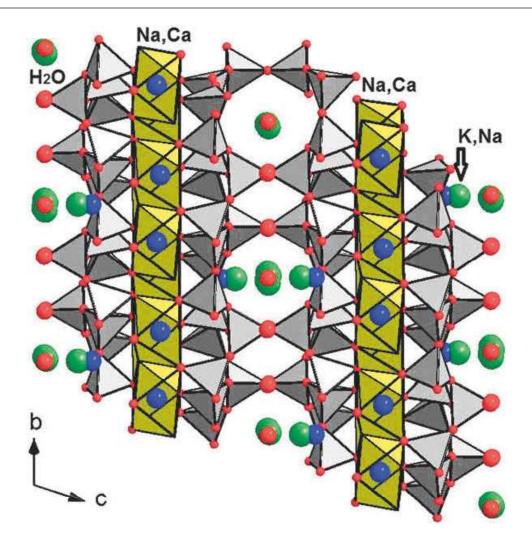
Note ν—stretching vibrations, δ—bending vibrations, w—weak band, sh—shoulder



**Fig. 3** Crystal structure of agrellite [18]. Si tetrahedra are shown in gray, Ca octahedra are yellow, and sodium atoms are blue spheres



**Fig. 4** Crystal structure of frankamenite (by [24]). Si-tetrahedra are shown in gray, Ca-octahedra are yellow, Na-octahedra are blue, potassium atoms are green spheres, oxygen atoms of water molecules are red spheres

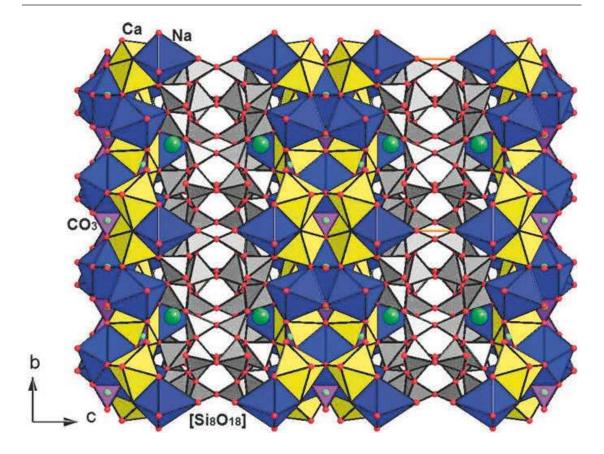


**Fig. 5** Crystal structure of fedorite. Si-tetrahedra are shown in gray, Ca,Na mixed octahedra are yellow, sodium atoms are blue spheres, potassium atoms are green spheres, oxygen atoms of water molecules are red spheres

Information on the position of diagnostic bands in the infrared spectra of the silicates under study is given in Table 1.

Tinaksite and tokkoite (Fig. 7) contain a strong and narrow band at 681 and 683 cm<sup>-1</sup>, respectively, apparently associated with Ti–O stretching vibration. On the spectra of fedorite and fluorcarletonite (Fig. 9), the presence of Si–O stretching vibrational bands in the region of 900–1000 cm<sup>-1</sup> was not observed. In the region of 660–880 and 1300–1600 cm<sup>-1</sup> fluorcarletonite has strong bands due to bending and stretching vibrations of CO<sub>3</sub> molecule (Fig. 9).

In the region of O–H stretching vibration (3000–4000 cm<sup>-1</sup>) the silicates of different groups clearly differ. Fluorcarletonite may have three bands in this area (Fig. 9). Tinaksite and tokkoite (Fig. 7), frankamenite (Fig. 8) have two distinct peaks in this region, while the agrellite (Fig. 8) has a weakly manifested band of O–H vibration and a band of H–O–H. Fedorite (Fig. 9) has a large number of lines.



**Fig. 6** Crystal structure of fluorcarletonite. Si-tetrahedra are shown in gray, Ca-octahedra are yellow, Na-octahedra are blue, potassium atoms are green spheres, and CO<sub>3</sub> groups are purple triangles

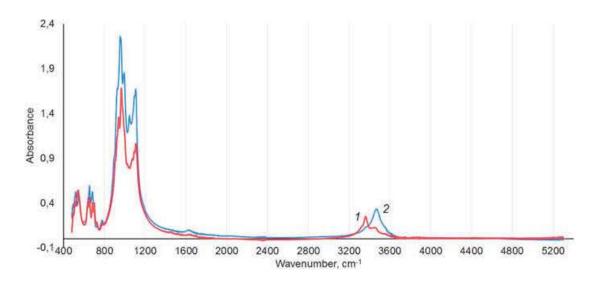


Fig. 7 IR spectra of tinaksite (1, red line) and tokkoite (2, blue line)

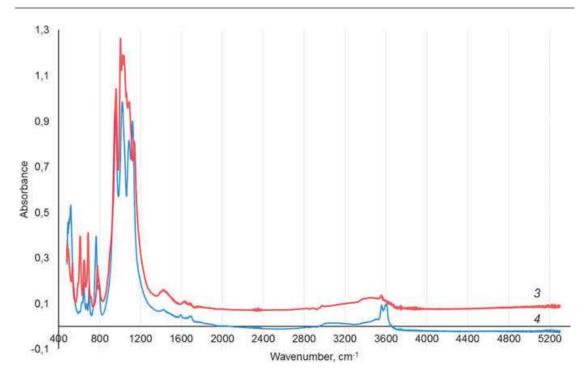


Fig. 8 Infrared spectra of agrellite (3, red line) and frankamenite (4, blue line)

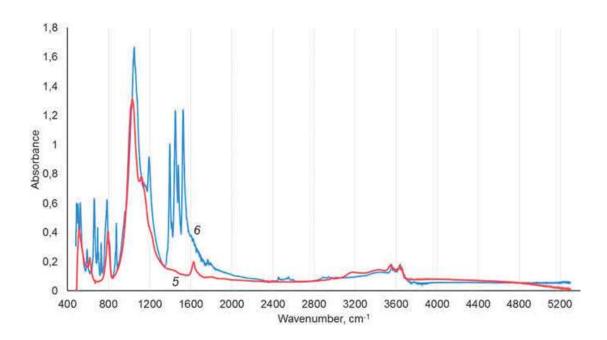


Fig. 9 IR spectra of fedorite (5, red line) and fluorcarletonite (6, blue line)

In the region of 1500–1800 cm<sup>-1</sup>, all minerals have a band of H–O–H deformation oscillations.

The close intergrowth and germination of minerals crystallizing in the charoitites of the Malyy Murun massif indicate their constitutional relationship. The crystal structures of the alkaline silicates discussed here contain rare-type silicon-oxygen

radicals. They are curved ribbons, tubes, layers of silicon-oxygen rings having wide cavities or channels along one or two crystallographic axes. K or Na cations fasten silicon-oxygen chains condensed into tubes or layers. Silicate channels are located between the chains or walls of the polyhedra. From a chemical point of view, it is noted that the minerals of the Murun massif, in comparison with similar minerals from other deposits, contain more F in the positions usually occupied by the OH group and F.

In general, the diversity of structures, chemical compositions and conditions of origin of alkaline minerals of the Murun massif provides for the manifestation of various mechanisms of isomorphic substitutions. Knowledge of the features of the atomic structure, as well as the distinctive properties of the mechanisms of transformation of minerals, is important for understanding the essence of geological processes leading to the formation of such unique deposits.

**Acknowledgements** The research was done with the financial support of the Integration Project of the Research Center of the Russian Academy of Sciences, Block 1.4. and the study was performed by the governmental assignment in terms of Project IX. 129.1.4.

# References

- 1. Rogov, Y.G., Rogova, V.P., Voronkov, A.A., Moleva, V.A.: Tinaksite, NaK<sub>2</sub>Ca<sub>2</sub>Ti-Si<sub>7</sub>O<sub>19</sub>(OH)—new mineral. DAN USSR **162**(3), 658–661 (1965). [in Russian]
- 2. Bissert, G.: Verfeinerung der Struktur von Tinaksit, Ca<sub>2</sub>K<sub>2</sub>NaTiO[Si<sub>7</sub>O<sub>18</sub>(OH)]. Acta Crystal **B36**, 259–263 (1980). https://doi.org/10.1107/S0567740880003068
- 3. Rozhdestvenskaya, I.V., Nikishova, L.V., Lazebnik, K.A.: Crystal structure features of tinaksite group minerals. Mineralogichesky Zhurnal **13**(4), 3–12 (1991). [in Russian]
- 4. Kostyleva-Lobuntsova, E.E., Borutsky, B.E., Sokolova, M.N., Shlyukova, Z.V., Dorfman, M. D., Dudkin, O.B., Kozyreva, L.V.: Mineralogy of the Khibiny Massif (Minerals), vol. 2. Science Publishing House, Moscow (1978). [in Russian]
- 5. Lazebnik, K.A., Nikishova, L.V., Lazebnik, Yu.D.: Tokkoite—a new mineral of charoitites. Mineralogichesky Zhurnal **8**(3), 85–89 (1986). [in Russian]
- Rozhdestvenskaya, I.V., Nikishova, L.V., Lazebnik, Yu.D., Lazebnik, K.A.: The crystal structure of tokkoite and its relation to the structure of tinaksite. Z Kristallogr 189, 195–204 (1989). https://doi.org/10.1524/zkri.1989.189.3-4.195
- 7. Lacalamita, M., Mesto, E., Kaneva, E., Scordari, F., Pedrazzi, G., Vladykin, N., Schingaro, E.: Structure refinement and crystal chemistry of tokkoite and tinaksite from the Murun massif (Russia). Min. Mag. **81**(2), 251–272 (2017). https://doi.org/10.1180/minmag.2016.080.094
- 8. Rozhdestvenskaya, I.V., Nikishova, L.V.: Crystal-chemical features of alkaline calcium silicates from charoitites. Kristallografiya **47**(4), 602–611 (2002). [in Russian]
- 9. Gittins, J., Bown, M.G., Sturman, D.: Agrellite, a new rock-forming mineral in regionally metamorphosed against alkalic rocks. Can. Min. 14, 120–126 (1976)
- 10. Konev AA, Vorobiev EI, Sapozhnikov AN, Paradina LF, Lapides IL, Ushchapovskaya ZF (1987)Sr-containing agrellite from Murun alkaline massif. Mineralogichesky Zhurnal **9** (3):73–79. [in Russian]
- 11. Pakhomovsky, Ya.A., Ivanyuk, G.Yu., Yakovenchuk, V.N.: Loparite-(Ce) in rocks of Lovozero stratified complex of Karnasurt and Kedikvyrpakhk mountains. Zapiski Ross Mineral Obshc 143(1), 68–87 (2014). [in Russian]
- 12. Falster, A.: Minerals of the pegmatite bodies in the Wausau Pluton. Rocks and Minerals **62** (3), 188–193 (1987). https://doi.org/10.1080/00357529.1987.11762652

13. Semenov, E.I., Dusmatov, V.D.: Agrellite—the first discovery in the USSR. Miner. of Tajikistan (Dushanbe) **8**, 3–5 (1989). [in Russian]

- 14. Faiziev, A.R.: Comparative mineralogical characteristics of the Dunkeldyk and Darai-Piez alkaline massifs (Tajikistan). Zapiski Ross Mineral Obshc 145, 20–29 (2016). [in Russian]
- 15. Ghose, S., Wan, C.N.: Agrellite, Na(Ca, RE)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>F: a layer structure with silicate tubes. Amer. Min. **64**(5-6), 563–572 (1979)
- 16. Rozhdestvenskaya, I.V., Nikishova, L.V., Lazebnik, K.A.: Diagnostics of agrellitepolytypes by X-ray powder diffraction data. Apiski Ross Mineral Obshc **127**(1), 89–94 (1998)
- 17. Rozhdestvenskaya, I.V., Nikishova, L.V.: Crystal structure of strontium agreliite Na(Ca, Sr<sub>2</sub>S<sub>i</sub>4<sub>O1</sub>0F from charoitites of Yakutia. Polytypy of Agrellite. Kristallographiya **43**(4), 637–645 (1998)
- 18. Kaneva, E., Shendrik, R., Mesto, E., Bogdanov, A., Vladykin, N.: Spectroscopy and crystal chemical properties of NaCa<sub>2</sub>[Si<sub>4</sub>O<sub>10</sub>]F natural agrellite with tubular structure. Chem. Phys. Lett. **738**, 136868 (2020). https://doi.org/10.1016/j.cplett.2019.136868
- 19. Kaneva, E.V., Vladykin, N.V., Mesto, E., Lacalamita, M., Scordari, F., Schingaro, E.: Refinement of the crystal structure of vlasovite from Burpala massif (Russia). Crystallogr. Rep. **63**, 1092–1098 (2018). https://doi.org/10.1134/S1063774518070106
- 20. Kaneva, E., Bogdanov, A., Shendrik, R.: Structural and vibrational properties of agrellite. Sci. Rep. **10**, 15569 (2020). https://doi.org/10.1038/s41598-020-72631-1
- 21. Evdokimov, M.D., Regir, E.P.: Canasite in charoitites of Murun alkaline complex ("Lilac stone" deposit). Zapiski Ross Mineral Obshc 1, 104–118 (1994). [in Russian]
- 22. Nikishova, L.V., Lazebnik, K.A., Rozhdestvenskaya, I.V., Emelianova, N.N., Lazebnik, Y. D.: Triclinic canasite from charoitites of Yakutia. Mineralogichesky Zhurnal **14**(1), 71–77 (1992). [in Russian]
- 23. Nikishova, L.V., Lazebnik, K.A., Rozhdestvenskaya, I.V., Emelianova, N.N., Lazebnik, Y. D.: Frankamenite K<sub>3</sub>Na<sub>3</sub>Ca<sub>5</sub>(Si<sub>12</sub>O<sub>30</sub>)F<sub>3</sub>(OH)·nH<sub>2</sub>O—a new mineral. Triclinic analogue of canasite from charoitites. Zapiski Ross Mineral Obshc **125**(2), 106–108 (1996). [in Russian]
- 24. Rozhdestvenskaya, I.V., Nikishova, L.V., Lazebnik, K.A.: The crystal structure of frankamenite. Min. Mag. 60, 897–905 (1996). https://doi.org/10.1180/minmag.1996.060.403.05
- 25. Kuharenko, A.A., Orlova, M.P., Bulakh, A.G., Bagdasarov, E.A., Rimskaya-Korsakova, O. M., Nefedov, E.I., Ilyinsky, G.A., Sergeev, A.S., Abakumova, N.B.: Caledonian complex of ultrabasic, alkaline rocks and carbonatites of the Kola Peninsula and North Karelia. Subsoil, Leningrad (1965). [in Russian]
- 26. Konev, A.A., Vorobiev, E.I., Lazebnik, K.A.: Mineralogy of Murun massif. Siberian Branch of Russian Academy of Sciences, Novosibirsk (1996). [in Russian]
- 27. Ferraris, G.: Polysomathism as a tool for correlating properties and structure. In: Merlino, S. (ed.) Modular Aspects of Minerals. European Mineralogical Union, Notes in Mineralogy, vol. 1, pp. 275–295. Springer, Berlin (1997). https://doi.org/10.1180/EMU-notes.1
- 28. Sokolova, G.V., Kashaev, A.A., Dritz, V.A., Ilyukhin, V.V.: Crystal structure of fedorite. Kristallographiya **28**, 170–172 (1983). [in Russian]
- 29. Joswig, W., Drits, V.A., Sokolova, G.V.: Refinement of the structure of fedorite. Sov. Phys. Crystallogr. **33**, 763–765 (1988)
- 30. Mitchell, R.H., Burns, P.C.: The structure of fedorite: a re-appraisal. Can. Min. **39**, 769–777 (2001). https://doi.org/10.2113/gscanmin.39.3.769
- 31. Kaneva, E.V., Shendrik, R.Yu., Radomskaya, T.A., Suvorova, L.F.: Fedorite from Murun alkaline complex (Russia): spectroscopy and crystal chemical features. Minerals **10**(8), 702 (2020). https://doi.org/10.3390/min10080702
- 32. Chao, G.: Carletonite, KNa<sub>4</sub>Ca<sub>4</sub>Si<sub>8</sub>O<sub>18</sub>(CO<sub>3</sub>)<sub>4</sub>(F,OH)·H<sub>2</sub>O, a new mineral from Mount St. Hilaire, Quebec. Amer. Min. **56**, 855–1865 (1971)
- 33. Kaneva, E., Radomskaya, T., Suvorova, L., Sterkhova, I., Mitichkin, M.: Crystal chemistry of fluorcarletonite, a new mineral from the Murun alkaline complex (Russia). Eur. J. Mineral 32, 137–146 (2020). https://doi.org/10.5194/ejm-32-137-2020

Crystal-Chemical Features of Rare and Complex Silicates ...

- 34. Chao, G.Y.: The crystal structure of carletonite, KNa<sub>4</sub>Ca<sub>4</sub>Si<sub>8</sub>O<sub>18</sub>(CO<sub>3</sub>)<sub>4</sub>(F, OH)·<sub>H</sub>2O, a double-sheet silicate. Amer. Min. **57**, 765–778 (1972)
- 35. Pohwat, P.W., Cook, R.B.: Carletonite, Mont Saint-Hilaire, La Vallèe-du-Richelieu RCM, Montèrègie, Quèbec, Canada. Rocks and Minerals **91**, 48–51 (2016). https://doi.org/10.1080/00357529.2016.1099133
- 36. Bruker, A.X.S.: Topas V4: general profile and structure analysis software for powder diffraction data. Bruker AXS Inc., Karlsruhe, Germany (2008)