

STRUCTURE OF INORGANIC COMPOUNDS

Dedicated to the memory of G. B. Bokiĭ on the occasion of his 100th birthday

Crystal Structures of Oxalate-Bearing Cancrinite with an Unusual Arrangement of CO₃ Groups and Sulfate-Rich Davyne

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Abstract—The crystal structures of two unusual varieties of cancrinite-group minerals—oxalate-bearing cancrinite from the Kovdor massif (Kola Peninsula) and the sulfate end member of the davyne series from the Sar-e Sang mine (Badakhshan, Afghanistan)—were studied by single-crystal X-ray diffraction. The unit-cell parameters of the hexagonal cells are $a = 12.688(4)$ Å, $c = 5.189(1)$ Å and $a = 12.773(1)$ Å, $c = 5.334(1)$ Å, sp. gr. $P6_3$; the R factors are 0.034 and 0.035, respectively. The presence of oxalate groups in cancrinite as admixtures is one of the factors responsible for the shift of CO₃ groups in wide channels.

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INTRODUCTION

Cancrinite-group minerals are zeolite-like aluminosilicates containing wide channels and cavities occupied by large cations (Na⁺, K⁺, and Ca²⁺), (CO₃)²⁻, (SO₄)²⁻, Cl⁻ anions, and H₂O molecules. In this study we investigated the crystal structures of oxalate-bearing cancrinite from the alkaline-ultrabasic Kovdor massif (Kola Peninsula) and sulfate-rich davyne from the Sar-e Sang lapis-lazuli mine (Badakhshan, Afghanistan).

The chemical compositions and the IR spectra of a representative collection of cancrinite-group minerals from various rocks and pegmatites of alkaline massifs located in Russia and nearby foreign countries have been previously studied.

Unusual cancrinite was found in hydrothermally altered apaitic pegmatites from the Kovdor alkaline-ultrabasic massif (Kola Peninsula). The IR spectrum of this mineral specimen shows bands at 1708, 1642, 1490, 1460, 1425, and 1375 cm⁻¹ in the C—O-stretching and the HOH-bending range. This mineral differs from typical cancrinite in that its IR spectrum shows rather weak stretching bands of oxalate groups at 1708 and 1375 cm⁻¹ and strongly shifted bands of carbonate groups (in the 1400–1520 cm⁻¹ region) (Fig. 1). The reliability of assigning the bands at 1708 and 1375 cm⁻¹ to the stretching vibrations of oxalate groups, which do not overlap with the bands of carbonate groups, is confirmed by the study of kyanoxalite, which has been recently approved as a new mineral by the Commission on New Minerals, Nomenclature, and Classifica-

tion of the International Mineralogical Association (IMA No. 2008-041). Studies by three independent methods (X-ray diffraction, IR spectroscopy, and ion chromatography) showed the presence of oxalate groups and the absence of carbonate groups in kyanoxalite [1]. The IR spectrum of the mineral specimen under consideration has bands of both oxalate and carbonate groups, making the quantitative determination of these groups difficult. However, the amount of oxalate groups evaluated from the IR spectrum is several times less than the amount of carbonate groups, and the number of C atoms belonging to CO₃ groups is most likely greater than the number of C atoms belonging to C₂O₄ groups.

The davyne specimen from the Sar-e Sang metasomatic lapis-lazuli mine (Afghanistan) has attracted our attention due to the abnormally high sulfur content. As opposed to typical vishnevite from the locality at Vishnevye Mountains, the S—O stretching band in the IR spectrum of the new specimen is unsplit, and the bands of CO₃ groups in the 1300–1600 cm⁻¹ range are completely absent (Fig. 1).

EXPERIMENTAL AND STRUCTURE REFINEMENT

The chemical composition of the cancrinite specimen under study is described by the empirical formula $\text{Na}_{7.14}\text{K}_{0.36}\text{Ca}_{0.07}\text{B}_{0.01}(\text{Si}_{6.5}\text{Al}_{5.5}\text{O}_{24}) \times (\text{CO}_3)_{1.0}\text{Cl}_{0.03}(\text{SO}_4)_{0.03}(\text{H}_2\text{O})_{-1}$, where all carbon atoms are arbitrarily included in the carbonate groups,

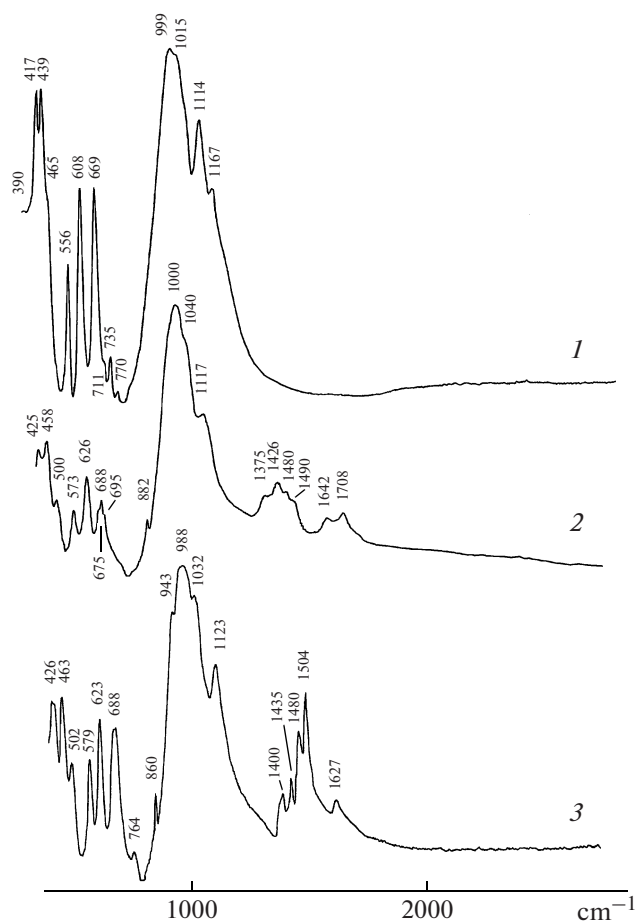


Fig. 1. IR spectra of (1) sulfate-rich davyne, (2) oxalate-bearing cancrinite, and (3) typical cancrinite.

because the $\text{CO}_3:\text{C}_2\text{O}_4$ ratio is unknown. Based on the IR spectroscopic data, it can only be stated that $\text{CO}_3 \gg \text{C}_2\text{O}_4$ (molar amounts). The X-ray data collection and refinement results are given in Table 1.

The atomic positions in the channels and cavities in the framework were located in a series of difference-electron-density maps. The occupancies and compositions of the sites were refined, including with the use of mixed atomic scattering curves.

The Si and Al atoms are distributed in an ordered fashion over two tetrahedral sites, as evidenced by the average cation–anion distances in the tetrahedra (Si–O, 1.610 Å; Al–O, 1.728 Å). The cavity on a threefold axis contains a mixed (Na,Ca) site and an H_2O molecule shifted along the threefold axis. Because the distance between the water molecules located around the axis is 1.1 Å, these molecules can statistically occupy only one of the three subsites in each unit cell. Consequently, the occupancy of each subsite is 1/3 of the total water content in this microregion. This results in the formation of $-(\text{Na}, \text{Ca})-\text{H}_2\text{O}-(\text{Na}, \text{Ca})-\text{H}_2\text{O}-$ zigzag chains along the threefold axis. The large channels running along the 6_3 axes have two Na sites and a

statistically occupied mixed (Na,K) site. The (CO_3) groups statistically occupy two sites on the 6_3 axis. Refining the C and O sites revealed the mobility of the carbonate groups along the channels. The fixed sites correspond to the most probable location of the C and O atoms. We failed to locate oxalate groups because of their low content in the specimen, high mobility, and the fact that they overlap with the statistically arranged CO_3^{2-} groups and water molecules. The location of the O atoms of oxalate groups in sp. gr. $P6_3$ is impossible because of the planar configuration of this group. Hence, only the positions of the carbon atoms of this groups can be determined. The distance between the C(2) atom at the height $z = 0.427$ and the C(1)' atom at the height $z = 0.787$ is 1.66 Å, which is rather close to the standard C–C bond length (1.55 Å). The supposed position of the oxalate group in this structure correlates with the position of this group in the kyan-oxalite structure [1], where the C(1A) and C(2A) atoms are located at the height $z = 0.703$ and 0.413, respectively.

In turn, it is difficult to locate CO_3 groups due to the presence of oxalate groups. To confirm the reliability of the results, we repeated the refinement for another specimen. The X-ray diffraction data for the latter specimen were collected on a Bruker SMART CCD diffractometer (Mo K_α) at the University of Toledo (United States). The results of refinement based on both X-ray data sets are similar. The atomic coordinates and the characteristics of the coordination polyhedra for the mineral under study are given in Tables 2 and 3, respectively.

The chemical composition of the sulfate-rich specimen is similar to that of davyne [4]. The new specimen differs from davyne in that it contains a larger amount of Na, a smaller amount of K, and a smaller amount of S. The empirical formula of the mineral is $\text{Na}_{5.39}\text{Ca}_{2.01}\text{K}_{0.81}(\text{Si}_{6.1}\text{Al}_{5.9}\text{O}_{24}) \times \text{Cl}_{1.96}(\text{SO}_4)_{1.13}(\text{OH}, \text{H}_2\text{O})_{0.1}$.

The X-ray diffraction data for this specimen were collected on a Bruker SMART CCD diffractometer at the University of Toledo (United States). The crystallographic data are given in Table 1. The unit-cell parameters ($a = 12.773(1)$ Å, $c = 5.334(1)$ Å, sp. gr. $P6_3$) are consistent with the unit-cell parameters of davyne, which is characterized by a larger c parameter than carbonate-bearing cancrinite. The crystal structure was refined anisotropically to $R = 0.035$ with the use of the AREN program. The atomic positions in the channels and cavities of the framework were located in a series of difference-electron-density maps. The compositions and occupancies of these positions were refined, including with the use of the mixed atomic scattering curve.

The atomic coordinates and the characteristics of the coordination polyhedra for the sulfate-rich mineral are given in Tables 4 and 5, respectively.

Table 1. Crystallographic characteristics, the X-ray data collection, and refinement results

Parameters	Oxalate-bearing cancrinite	Sulfate-rich davyne
Crystal system, sp. gr., Z	Hexagonal, $P6_3$, 1	Hexagonal, $P6_3$, 1
a , Å	12.688(4)	12.773(3)
c , Å	5.189(1)	5.334(1)
V , Å ³	723.4	753.7
D_{calc} , g/cm ³	2.183	2.46
Radiation; λ , Å	MoK α ; 0.71073	MoK α ; 0.71073
Crystal dimensions, mm	0.2 × 0.2 × 0.3	0.1 × 0.15 × 0.1
Diffractometer	ENRAF NONIUS	Bruker SMART CCD
θ_{max} , deg	45	30
h , k , l Ranges	−20 < h < 20; −20 < k < 20; 0 < l < 8	−11 < h < 16; −16 < k < 12; −5 < l < 6
umber of measured/independent reflections > $n\sigma$, R_{int}	5834/1042 $ F > 3\sigma(F)$, 0.046	2622/420 $ F > 2\sigma(F)$, 0.028
R	0.034	0.035
Refinement program	AREN [2]	AREN [2]
Program for absorption correction	DIFABS [3]	DIFABS [3]

RESULTS AND DISCUSSION

Several cancrinite varieties that clearly differ in the arrangement of carbonate groups can be distinguished based on the IR spectroscopic data.

Typical cancrinite [5] belongs to the first and main type, which includes most of the known CO₃^{2−}-dominant specimens from different formations of both agpaitic and hyperagpaitic rocks and pegmatites. Typical representatives of cancrinites were found in nepheline rocks and albitites from the Azov region (Ukraine), in nepheline-feldspar pegmatites from the Il'mensky-Vishnevogorsky miaskite complex (Urals, Russia), in pseudomorphs after nepheline from rocks and pegmatites of the Khibiny-Lovozero complex, in peralkaline paragenesis from the Dara-i Pioz massif (Tadzhikistan), in rock-forming cancrinite syenites of the Kovdor massif, etc. In the IR spectrum of typical cancrinite, the stretching band of CO₃^{2−} groups is split into a series of narrow lines with maxima at 1504, 1480, 1435, and 1400 cm^{−1}. This fact indicates that the cancrinite structure contains CO₃^{2−} groups in different local states. In addition, the IR spectrum of cancrinite shows bending bands of carbonate groups at 860 cm^{−1} and near 764 cm^{−1}.

The IR spectra of type 2 specimens show a strong C—O stretching band in the 1458–1463-cm^{−1} range and two very weak absorption maxima at 1390 and 1500 cm^{−1}. The bending vibrations of CO₃^{2−} groups appear as the only band in the 860–865-cm^{−1} region. This mineral was approved as a new species under the name cancrisilite [6]. This species is much rarer than cancrinite and was discovered only in a few pegmatites of the Lovozero and Khibiny massifs.

The chemical compositions and IR spectra of types 1 and 2 cancrinites are related by gradual transitions, but these intermediate varieties are rather rare and their formation is associated with hyperagpaitic rocks [7].

The resonance absorption of IR radiation by carbonate groups of types 3 and 4 specimens is observed at 1489, 1444, 1396, 860, 760, and 735 cm^{−1} and at 1525, 1510, 1503, 1474, 1442, 1425, 1388, 860, and 764 cm^{−1}, respectively. The crystal structures of these cancrinite varieties have been studied earlier [8].

Finally, the CO₃^{2−}-dominant oxalate-bearing cancrinite-like mineral (which is investigated in this study and has been preliminarily characterized in [9]) belongs to type 5. So far, we have discovered this variety only in the hydrothermally altered pegmatite from one of the alkaline massifs in the Kola Peninsula. Compared to the known carbonate-bearing cancrinites [5], including cancrisilite [6] and hydroxycancrinite [10], the C and O sites in the specimen under study are shifted along the 6₃ axis, resulting in another arrangement of CO₃ groups (Table 6). Because the C site is split into two approximately equally occupied subsites, both components are shifted in the same direction so that their average coordinate approaches 0.5 and, correspondingly, (as a result of the 6₃ symmetry) to 0 along the z axis.

The new mineral radically differs from the cancrisilite and cancrinites studied earlier in the arrangement of CO₃ groups. In the already-known minerals, the average coordinate is approximately equal to $z = 0.25$ and 0.75 (Table 6). If it is remembered that Na atoms in all specimens are located within $z = 0.22$ – 0.29 (on the average, are ~ 0.25), the formation of

Table 2. Fractional atomic coordinates, site multiplicities (Q), site occupancies (q), and equivalent thermal displacement parameters B_{eq} ($\text{\AA}^2$) for the structure of oxalate-bearing cancrinite

Atom	x/a	y/b	z/c	Q	q	B_{eq}
Si	0.3302(1)	0.4133(1)	0.7506(1)	6	1	1.35(5)
	0.3301(1)	0.4131(1)	0.7506(1)	6	1	1.1(1)
Al	0.0762(1)	0.4141(1)	0.7513(2)	6	1	1.34(5)
	0.0762(1)	0.4142(1)	0.7512(3)	6	1	1.1(1)
O1	0.2031(1)	0.4042(2)	0.6740(4)	6	1	2.3(2)
	0.2034(2)	0.4045(2)	0.6747(6)	6	1	2.0(3)
O2	0.1191(2)	0.5657(1)	0.7278(7)	6	1	2.9(2)
	0.1191(2)	0.5653(2)	0.7293(9)	6	1	2.8(4)
O3	0.0253(2)	0.3536(2)	0.0552(3)	6	1	2.4(2)
	0.0260(2)	0.3538(2)	0.0541(5)	6	1	2.1(3)
O4	0.3220(2)	0.3608(2)	0.0385(3)	6	1	2.4(2)
	0.3226(2)	0.3608(2)	0.0375(5)	6	1	2.1(3)
Na1*	0.6667	0.3333	0.1273(8)	2	0.74(1)	2.9(1)
	0.6667	0.3333	0.1254(9)	2	0.77(1)	2.5(1)
Na2	0.1311(2)	0.2635(2)	0.2824(6)	6	0.46(1)	3.0(1)
	0.1326(2)	0.2674(2)	0.2883(8)	6	0.52(1)	2.4(1)
Na3*	0.1092(5)	0.2215(5)	0.298(1)	6	0.28(1)	4.3(1)
	0.1102(5)	0.2202(5)	0.287(2)	6	0.26(1)	4.7(1)
Na4	0.1473(4)	0.3011(5)	0.284(1)	6	0.26(1)	3.1(1)
	0.1539(6)	0.3134(6)	0.281(2)	6	0.22(1)	2.6(1)
C1	0	0	0.287(7)	2	0.20(1)	2.8(3)
	0	0	0.297(8)	2	0.20(1)	3.2(2)
O5	0.115(1)	0.057(1)	0.285(5)	6	0.20(1)	3.3(2)
	0.116(2)	0.060(2)	0.303(7)	6	0.20(1)	5.5(3)
C2	0	0	0.427(8)	2	0.30(1)	2.4(2)
	0	0	0.512(9)	2	0.30(1)	2.4(5)
O6	0.090(2)	0.095(2)	0.491(9)	6	0.30(2)	4.0(1)
	0.102(2)	0.090(2)	0.524(7)	6	0.30(1)	5.2(2)
H ₂ O	0.300(1)	0.608(1)	0.188(3)	6	0.25(1)	3.8(2)
	0.306(2)	0.620(1)	0.190(3)	6	0.25(2)	4.0(5)

Note: The upper row corresponds to the experimental data obtained on an Enraf Nonius diffractometer; the lower row corresponds to the data obtained on a Bruker SMART CCD diffractometer.

* Na(1) = (Na_{1.41}Ca_{0.07}); Na(3) = Na_{1.33}K_{0.35}.

these two different varieties can be attributed to steric hindrance in the coordination of Na atoms by O atoms of the carbonate groups located at the same height. In the structure of the new mineral, the channels are filled by a relatively small amount of carbonate groups (and by an even lower amount of C₂O₄ groups) which should coordinate two Na atoms; consequently, the CO₃ group should be located between two Na atoms (at $z = 0.25$ and 0.75 , respectively). In other specimens, which contain smaller amounts of carbonate groups or whose deficiency is compensated by SO₄ tetrahedra and/or H₂O molecules (Cl atoms), the car-

bonate groups are arranged at the same height as Na atoms, whereas additional anions are shifted to the levels intermediate between the levels of Na.

Another difference in the specimen under study is that it contains CO₃ groups in four orientations with respect to the 6₃ axis, whereas only two orientations of CO₃ groups are observed in cancrisilite (which is apparently associated with different degrees of disorder of Na atoms (Fig. 2)). The crystal-chemical formula of oxalate-bearing cancrinite can be written as ($Z = 1$) [Na_{1.41}Ca_{0.07}H₂O_{1.48}][Na_{5.65}K_{0.35}(CO₃)_{1-x}(C₂O₄)_x][Si_{6.5}Al_{5.5}O₂₄] ($x \ll 1$; the compositions in the

Table 3. Interatomic distances (Å) in the structure of oxalate-bearing cancrinite (based on the experimental data obtained on an Enraf Nonius diffractometer)

Si tetrahedron		Al tetrahedron		C triangles	
Si—O2	1.6031(8)	Al—O(2)	1.721(2)	C(1)—O(5)	1.26(1) × 3
O1	1.608(2)	O(1)	1.723(3)	C(2)—O(6)	1.23(3) × 3
O3	1.613(2)	O(3)	1.730(2)		
O4	1.617(2)	O(4)	1.734(1)		
	⟨1.610⟩		⟨1.727⟩		
Na seven-vertex polyhedra				Na eight-vertex polyhedra	
Na2—O4	2.450(3)	Na(4)—O(3)	2.298(8)	Na(1)—O(7)	2.36(1)
O3	2.455(5)	O(1)	2.318(6)	O(2)	2.410(2) × 3
O6	2.51(3)	O(4)	2.331(6)	O(1)	2.892(2) × 3
O5	2.52(2)	O(6)	2.56(3)	O(7)	2.98(1)
O1	2.553(4)	O(4)	2.830(7)		⟨2.66⟩
O3	2.886(4)	O(3)	2.836(7)		
O4	2.925(4)	O(5)	2.869(8)		
	⟨2.61⟩		⟨2.58⟩		
Na3—O3	2.704(8)				
O4	2.731(6)				
O1	2.798(7)				
O5	2.91(5)				
O3	3.004(6)				
O4	3.015(8)				
O6	3.10(2)				
	⟨2.89⟩				

Table 4. Fractional atomic coordinates, site multiplicities, site occupancies, and equivalent thermal displacement parameters U_{eq} (Å²) for the structure of sulfate-rich davynite

Atom	x/a	y/b	z/c	Q	q	U_{eq}
Al	0.3385(1)	0.4102(1)	0.7440(1)	6	1	0.0091(2)
Si	0.0811(1)	0.4114(1)	0.7446(4)	6	1	0.0098(2)
O1	0.2128(3)	0.4253(3)	0.704(1)	6	1	0.019(6)
O2	0.1079(3)	0.5490(3)	0.735(1)	6	1	0.019(6)
O3	0.0234(4)	0.3449(4)	0.0073(9)	6	1	0.019(6)
O4	0.3275(3)	0.3358(4)	0.023(1)	6	1	0.016(6)
Ca	0.6669(1)	0.3333(1)	0.2042(3)	2	1	0.011(1)
Cl	0.3331(1)	0.6666(1)	0.2079(8)	2	1	0.085(2)
S	0	0	0.265(4)	2	0.50(1)	0.011(1)
O5	0.069(3)	0.110(4)	0.14(1)	6	0.25(1)	0.057(4)*
O6	0.031(4)	0.109(2)	0.38(1)	6	0.25(2)	0.045(4)*
O7	0	0	0.51(1)	2	0.50(1)	0.069(4)*
Na	0.1579(3)	0.3108(4)	0.268(1)	6	0.50(1)	0.025(1)
Na**	0.1163(4)	0.2292(5)	0.267(2)	6	0.50(1)	0.049(2)

* Isotropic thermal parameters.

** Na = (Na_{2.19}K_{0.81}).

Table 5. Interatomic distances (Å) in the structure of sulfate-rich davyne

Al tetrahedron		Si tetrahedron		S tetrahedron	
Al–O2	1.715(1)	Si–O(3)	1.613(5)	S–O(7)	1.29(7)
O1	1.723(5)	O(1)	1.615(5)	O(5)	1.41(5) × 3
O3	1.725(4)	O(2)	1.615(5)		⟨1.38⟩
O4	1.731(5)	O(4)	1.622(4)	S–O(7)	1.37(7)
	⟨1.724⟩		⟨1.616⟩	O(6)	1.37(3) × 3
					⟨1.37⟩
Ca eight-vertex polyhedra		Na seven-vertex polyhedra		Na** polyhedron	
Ca–O2	2.500(4) × 3	Na–O(6)	2.330(2)	Na**–O(4)	2.67(1)
Cl	2.647(4)	O(5)	2.330(4)	O(3)	2.69(1)
O1	2.670(4) × 3	O(4)	2.411(7)	O(6)	2.81(4)
Cl	2.686(4)	O(3)	2.411(8)	O(4)	2.82(1)
	⟨2.605⟩	O(4)	2.617(7)	O(5)	2.82(5)
		O(1)	2.648(7)	O(7)	2.83(3)
		O(3)	2.651(7)	O(3)	2.85(1)
			⟨2.485⟩	O(7)	2.89(3)
				O(5)	3.08(5)
				O(6)	3.16(4)
					⟨2.86⟩

brackets correspond to the cavity, the large channel, and the framework, respectively). The new mineral is similar to silicon-rich cancrisilite [6] in composition, but it has lower symmetry and differs in the arrangement of CO₃ groups and water molecules. In the new mineral, water molecules are present only in the cavities, whereas water molecules in cancrisilite are located both in the cavities and channels.

Table 6. Comparative characteristics of the positions and site occupancies (*q*) of CO₃ groups in the channels of selected structurally characterized cancrinite-group minerals

Mineral	Atom	<i>z/c</i>	<i>z_{aver}</i>	<i>q</i>
1. Cancrisilite [6]	C1	0.192(4)	0.292	0.31
	C2	0.391(6)		0.30
2. Cancrinite [5]	C1	0.1729	0.293	0.38
	C2	0.4134		0.38
3. Hydroxycancrinite [10]	C1	0.11(1)	0.11	0.30
4. Davyne [4]	C1	0.167(4)	0.274	0.29
	C2	0.380(6)		0.10
5. Oxalate-bearing cancrinite* [9, the present study]	C1	0.287(7)	0.357	0.30
	C2	0.427(8)		0.20
	C1	0.297(7)	0.404	0.30
	C2	0.512(9)		0.20

* Based on the results of two experiments.

Therefore, the results of both refinements confirmed that the C and O sites actually differ from those known from the literature [5, 6] (Fig. 2). Our structural data correspond to one of the above-described five main types of IR spectra and, accordingly, to one of the modes of arrangement of CO₃ groups in cancrinites.

In the structure of sulfate-rich davyne, Si and Al atoms are distributed in an ordered fashion over two tetrahedral sites in the framework, as is evidenced by the average cation–anion distances in the tetrahedra (Si–O, 1.616 Å; Al–O, 1.724 Å). In the cavities on a threefold axis, the sites occupied by Ca atoms alternate with the Cl sites to form –Ca–Cl–Ca–Cl– chains along the threefold axis. These chains are typical of davyne. The large channels are occupied by SO₄ groups. The S atoms half-occupy one site on the 6₃ axis, which corresponds to the maximum possible occupancy of the channels by SO₄ groups (the S–S distance is 2.67 Å) (Fig. 3). The SO₄ tetrahedra have two orientations along the 6₃ axis with the statistical participation of O atoms (average S–O distances are 1.37 and 1.38 Å, respectively). Two split sites statistically occupied by Na and Na + K atoms are located around the axis.

The crystal-chemical formula of the sulfate-rich end member of davynes can be written as (*Z* = 1) [Ca₂Cl₂][Na_{5.2}K_{0.8}(SO₄)_{1.0}][Si₆Al₆O₂₄] (the compositions in the brackets correspond to the cavity, the large channel, and the framework, respectively). SO₄, CO₃,

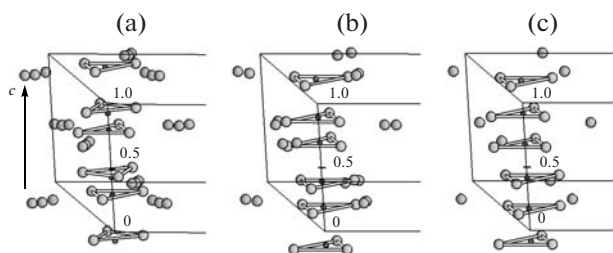


Fig. 2. Arrangement of CO_3 groups (filled and open circles) and large cations (dashed circles) within the channels in (a) oxalate-bearing cancrinite, (b) cancrisilite, and (c) typical cancrinite.

and Cl anions were found in different combinations in the davynes studied earlier. Even in carbonate-free specimens, the number of SO_4 groups is no larger than 0.7 per structural formula. The new mineral does not contain CO_3 groups, but it has the maximum possible amount of sulfate groups (one group per formula unit). Hence, this mineral is the sulfate-rich end member of the cancrinite–davine series. The difference in 0.13 sulfur atoms (compared to the empirical formula) can be associated with the fact that a small amount of sulfur exists in the reduced S or S_2 forms. Additional sulfide anions are typical of sodalite- and cancrinite-group minerals from lazurite-bearing metasomatites (in particular, the presence of sulfide anions was established in lazurite and bystrite). If the site of sulfide sulfur is split, its location presents a difficulty if there is a low content of these atoms.

CONCLUSIONS

The data on the crystal structure of oxalate-bearing cancrinite provide evidence that cancrinite is characterized by a crystal-chemical diversity manifested primarily in the arrangement of carbonate groups. Structural varieties of cancrinite are clearly distinguished by IR spectra. A smaller amount of carbonate groups and the presence of oxalate groups as admixtures are apparently responsible for the shifts of CO_3^{2-} groups in wide channels.

It was found that there is a complete isomorphous davine series that combines minerals with AB -type frameworks, chains $(\text{Ca}-\text{Cl}-\text{Ca})_\infty$ in narrow channels, and the variable content of SO_4^{2-} groups, including the end member of this series containing one SO_4 group per formula unit.

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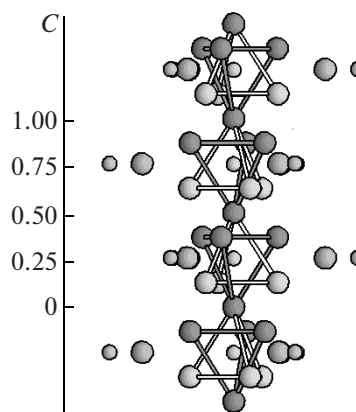


Fig. 3. Arrangement of SO_4 groups and cations within the channels in the sulfate-rich mineral of the cancrinite group.

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