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GEOCHEMISTRY

Crystal Structure of Alloriite

R. K. Rastsvetaeva[a], A. G. Ivanova[a], N. V. Chukanov[b], and I. A. Verin[a]

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The cancrinite–sodalite group includes about 30 minerals, which are being studied in depth owing to their adsorption and ion-exchange properties. The minerals consist of a framework of Si and Al tetrahedra combined into six-membered rings. The rings of the same level along z are linked not to each other but to rings of neighbor levels shifted by 1/3 along x and y. The succession of alternation of rings is designated by letters A, B, and C, where A designates the rings around the axis [2/3 1/3 z]; B, around [1/3 2/3 z]; and C, around [0 0 z]. Minerals with 2 to 28 layers, which correspond to parameters with $c \sim 5–74$ Å, are known in this group. The channels and cages within the framework are occupied by large cations and anions (mono- and/or multiatom), while some minerals also include the water molecules. As is accepted for zeolites, the cages and chan-

Table 1. Characteristics of crystals and experimental conditions

a, Å	12.892(3)
c, Å	21.340(5)
V, Å^3	3071.61
Space group; Z	$P31c$; 1
Radiation; λ, Å	MoK_α; 0.71073
Density ρ(meas.), g/cm^3	2.35
Crystal size, mm	$0.15 \times 0.25 \times 0.30$
Diffractometer	ENRAF-NONIUS
Region of record	$-20 < h < 18$
	$0 < k < 20$
	$0 < l < 34$
$\sin\theta/\lambda$	<0.81
Total number of reflections	10237 $F > 6\sigma(F)$
Number of independent reflections	3040 $F > 6\sigma(F)$
R-factor of averaging of the equivalent reflections	0.033
R-factor of anisotropic refinement	$R = 5.2$
Refinement program	AREN [4]
Program for absorption correction	DIFABS [5]

Table 2. Coordinate of framework atoms, equivalent (B_{equiv}) parameters of atomic shifts, and occupancy (q) of sites

Atom	x/a	y/b	z/c	B_{equiv}, Å^2
Si(1)	0.2506(1)	−0.0002(1)	0.4950(1)	1.69(3)
Si(2)	0.9198(1)	0.5832(1)	0.3693(1)	1.62(3)
Si(3)	0.0026(1)	0.2539(1)	0.2461(1)	1.75(2)
Si(4)	0.9200(1)	0.5835(1)	0.1222(1)	1.63(2)
Al(1)	0.7451(1)	0.9998(1)	0.9951(1)	1.76(3)
Al(2)	0.0832(1)	0.4067(1)	0.8693(1)	1.78(3)
Al(3)	0.0038(1)	0.7464(1)	0.7461(1)	1.61(3)
Al(4)	0.0832(1)	0.4067(1)	0.6222(1)	1.83(2)
O(1)	0.6587(4)	0.0028(4)	0.1846(1)	2.9(1)
O(2)	0.0012(4)	0.3295(4)	0.1858(2)	3.2(2)
O(3)	0.9972(4)	0.6576(4)	0.3106(2)	3.1(2)
O(4)	0.0012(4)	0.3266(4)	0.3091(2)	3.4(2)
O(5)	0.2247(3)	0.1059(4)	0.2468(3)	2.8(2)
O(6)	0.6690(4)	0.0162(4)	0.4313(2)	3.3(2)
O(7)	0.3344(5)	0.0127(4)	0.4364(2)	3.4(2)
O(8)	0.6673(4)	0.0178(4)	0.0571(2)	2.9(2)
O(9)	0.3384(5)	0.0145(4)	0.0525(1)	3.1(2)
O(10)	0.1147(4)	0.2354(5)	0.0076(2)	3.8(2)
O(11)	0.1146(4)	0.2371(5)	0.4873(3)	4.7(2)
O(12)	0.1227(4)	0.2482(4)	0.2476(5)	4.0(2)
O(13)	0.5426(4)	0.4614(4)	0.1227(3)	4.2(3)
O(14)	0.4593(4)	0.5422(4)	0.8717(2)	3.7(2)
O(15)	0.4502(4)	0.2318(3)	0.1293(2)	2.7(2)
O(16)	0.4470(4)	0.2310(3)	0.3652(2)	3.4(2)

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[a] *Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Moscow, 117333 Russia; e-mail: rast@ns.crys.ras.ru*

[b] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

Table 3. Coordinates of atoms, equivalent parameters (B_{equiv}) of atomic shifts, and occupancy (q) of sites of intraframework atoms

Atom	x/a	y/b	z/c	q	B_{eq}, Å^2
Ca(1a)	0.6667	0.3334	0.1400(1)	0.80(2)	3.31(4)
Ca(1b)	0.6667	0.3334	0.1048(3)	0.20(2)	2.2(1)
Ca(2a)	0.6667	0.3334	0.3581(2)	0.75(2)	4.21(4)
Ca(2b)	0.6667	0.3334	0.3276(6)	0.25(3)	4.0(1)
Ca(3)	0	0	0.2059(6)	0.23(4)	4.69(9)
K	0.2174(1)	0.4341(2)	0.3732(1)	0.72(2)	2.89(3)
Na(1)	0.2234(4)	0.4452(5)	0.3550(2)	0.28(3)	1.0(2)
Na(2)	0.2190(1)	0.4376(2)	0.1246(1)	1	2.5(1)
Na(3a)	0.4958(2)	0.5132(2)	0.2463(1)	0.81(2)	2.21(4)
Na(3b)	0.478(1)	0.529(1)	0.2574(5)	0.19(1)	2.8(2)
Na(4a)	–0.0008(2)	0.4966(2)	0.4962(1)	0.80(1)	2.44(3)
Na(4b)	0.550(5)	0.487(6)	–0.008(3)	0.20(1)	6.7(1)
Na(5)	0	0	0.2530(6)	0.77(3)	4.7(1)
Na(6a)	0	0	0.4993(6)	0.75(3)	4.4(1)
Na(6b)	0	0	0.443(1)	0.25(1)	4.2(3)
S(1a)	0.3334	0.6667	0.4675(1)	0.80(2)	3.80(5)
S(1b)	0.3334	0.6667	0.4847(5)	0.20(3)	1.6(2)
O(1a.1)	0.214(1)	0.609(1)	0.4428(7)	0.68(2)	3.7(1)*
O(1b.1)	0.207(2)	0.603(2)	0.474(1)	0.32(1)	3.7(2)*
O(1.2)	0.6667	0.3334	0.046(1)	0.80(3)	3.9(1)*
S(2)	0.3334	0.6667	0.2473(3)	0.70(1)	2.95(7)
O(2)	0.2132(8)	0.600(1)	0.2234(6)	0.70(3)	3.5(1)*
S(3a)	0.3334	0.6667	0.0207(1)	0.75(2)	2.97(6)
O(3a.1)	0.2070(6)	0.6032(6)	0.0405(3)	1	4.75(7)
O(3a.2)	0.6667	0.3334	0.4493(9)	0.61(3)	5.1(3)
S(3b)	0.3334	0.6667	0.066(3)	0.25(1)	2.5(1)*
O(3b)	0.3334	0.6667	0.136(2)	0.25(1)	4.2(4)
C	0.3334	0.6667	0.304(2)	0.31(4)	3.9(4)
O_c	0.236(2)	0.616(2)	0.297(1)	0.30(1)	5.3(2)
H_2O(1a)	0	0	0.3610(7)	0.75(5)	3.5(2)*
H_2O(1b)	0	0	0.401(4)	0.25(2)	4.3(4)*
H_2O(2a)	0	0	0.1217(7)	0.78(3)	4.6(3)*
H_2O(2b)	0.067(3)	0.046(4)	0.114(1)	0.22(1)	3.6(2)*
H_2O(3)	0.611(4)	0.209(5)	0.240(1)	0.23(1)	3.5(2)*
Cl	0.6667	0.3334	0.240(1)	0.17(1)	4.96(8)

Note: (*) B_{iso}.

nels can be represented as polyhedra formed by centers of Si and Al tetrahedra. Two-layer (*AB*) minerals of the cancrinite group (cancrinite and its analogs with diverse additional anions) have a wide channel and compact cancrinite cages consisting of five and six four-membered rings. In the multilayer minerals, the wide channel is missing, but cancrinite cages are supplemented with larger cages and their combination. In particular, the liottite cage found in the liottite structure, which is composed of 17 six-membered and 6 four-membered rings, can be combined with a cancrinite cage.

In this work, we studied alloriite,[1] a new representative of the cancrinite–sodalite group, found in the Sabatino volcanic complex (Latium, Italy)[1]. It is characterized by an 8-layer *ACACBCBC* package previously

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[1] Considered and approved by the International Mineralogical Association Commission on New Minerals and Mineral Names on August 31, 2006.

found in the structure of afghanite from the Baikal region [2] and from Pitigliano, Tuscany [3]. The parameters of the trigonal unit cell and experimental conditions are shown in Table 1; the coordinate and heat parameters of atoms, in Tables 2 and 3; and some interatomic distances and characteristics of polyhedra, in Table 4.

The empirical formula based on microprobe analysis at $Z = 1$ is as follows:

$Na_{18.4}K_6Ca_{4.8}[(Si_{6.6}Al_{5.4})_4O_{96}][SO_4]_{4.8}Cl_{0.8}(CO_3)x(H_2O)y$.

X-ray analysis of alloriite revealed the ordering of Si and Al in the framework at the average distances $\langle Si–O \rangle = 1.59–1.62$ and $\langle Al–O \rangle = 1.70–1.73$ Å. The chemically determined predominance of Si over Al is indirectly confirmed by X-ray structure analysis (based on the average Al–O distances in tetrahedra): a significantly lower value (1.702 Å) recorded only in one Al tetrahedron can be related to partial substitution of Al for Si.

In the majority of cases, the sites of intraframework atoms are partially occupied with splitting and random occupation. Sites of Ca are allocated at the three-order axes and split into two subsites with occupancy of 0.8 and 0.2, respectively and an interatomic distance equal to 0.65–0.75 Å. All Na positions, except for Na(2), are also split into two subsites spaced at 0.4–1.2 Å and occupancy within 0.7–0.8 for the main sites and 0.3–0.2 for additional subsites. Atoms of sulfur are allocated in a large liottite cage at axis 3 and $z \sim 0$, 0.25, and 0.5. Their sites, like those of the surrounding oxygen atoms, are also randomly occupied, while tetrahedron $S(3)O_4$ has two orientations along axis 3.

Alloriite belongs to the afghanite structural type: columns consisting of cancrinite cages are extended along the coordinate axis [0 0 *z*], while liottite cages are alternated with cancrinite ones along the axis [1/3 2/3 *z*] (Fig. 1). The cancrinite columns of afghanite from Pitigliano [3] demonstrate alternation of –Ca–Cl–Ca–Cl…, while the studied sample from the Baikal region [2] is characterized by a slightly different composition (–Ca–Cl–Ca–H_2O…). The Ca deficiency in alloriite is filled with Na to form –Na–H_2O–Na–H_2O… columns (Fig. 2). Cancrinite cages alternating with the liottite cage also differ in composition: they contain $Ca_4(H_2O)_2$ in the Baikal afghanite, Ca_4Cl_2 in the Pitigliano afghanite [3], and $Ca_4[(OH)_{1.6}Cl_{0.4}]$ in alloriite. The liottite cage is occupied by Na, K, and subordinate Ca linked by anionic groups. The anionic composition of the liottite cage is also different in these samples. In addition to sulfate groups [3], carbonate groups are present in the Baikal afghanite. Alloriite includes three types of anion groupings: SO_4, CO_3, and possibly SO_3 (Fig. 3). The pyramidal CO_3 and SO_3 groups are allocated in the central part of the liottite cage, and their cations randomly occupy two subsites spaced at 1.2 Å from each other with occupancy by 0.7S and 0.3C. Geometrically, the SO_3 group can be fitted out to tetrahedron by supplementing the C site randomly with oxygen atoms. However, when refining the mixed site (C + O) at complete occupancy, the value of the heat parameter turned out to be anomalously high. The SO_3 group is also allocated in the center of the liottite cage at random substitution for the SO_4 group in the previously reported tounkite structure [6].

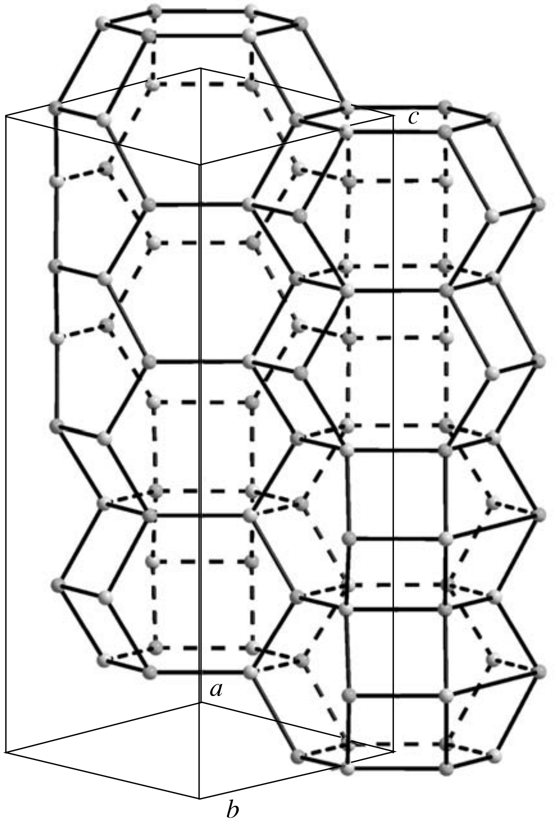

Fig. 1. Framework of the alloriite structure: column of cancrinite cages around [0 0 *z*] and column of alternating liottite and cancrinite cages around [1/3 2/3 *z*].

The Cl position is allocated in the cancrinite cage jammed between two liottite cages at axis 3 with occupancy 0.2. We identify the supplementary position around axis 3 with the oxygen atom of the hydroxyl group. The column of cancrinite cages also demonstrates splitting of the O site into two subsites located at and around the axis. We identified oxygen atoms as H_2O molecules and, to a lesser extent, as OH groups based on charge balance. It was taken into account that the substitution of a part of the framework oxygen atoms for OH groups is highly improbable owing to the predominance of Si over Al. This is also confirmed by the IR spectra indicating the absence of OH groups related to the framework cations. Based on X-ray structural analysis, we obtained the following crystallochemical formula ($Z = 1$): $\{Si_{26}Al_{22}O_{96}\}\{(Na_{3.54}Ca_{0.46})[(H_2O)_{3.54}(OH)_{0.46}]\}\{(Na_{16.85}K_6Ca_{1.15})[(SO_4)_4(SO_3,CO_3)_2]\}\{Ca_4[(OH)_{1.6}Cl_{0.4}]\}$, where braces enclose the

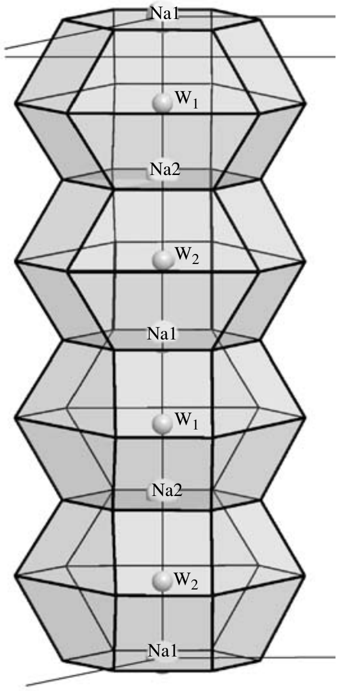

Fig. 2. Filling of columns of cancrinite cages by Na atoms (large balls) and H_2O molecules (small circles).

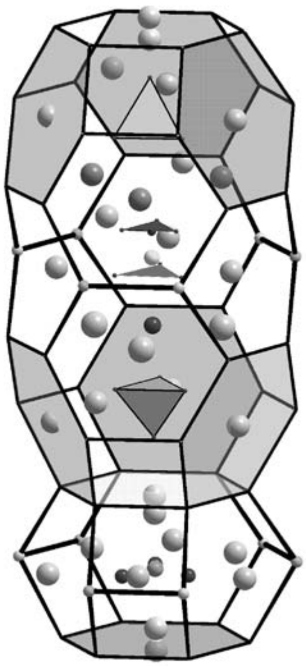

Fig. 3. Filling of liottite cage by Na, K, and Ca atoms (circles), SO_4 tetrahedra, triangular groups of SO_3 (gray triangle), and CO_3 (black triangle).

compositions of the framework, the column from cancrinite cages, the liottite cage, and the adjacent cancrinite cage, respectively.

Thus, we have established that, as compared to the previously studied afghanite samples, the structure of the Na-rich hydrous mineral alloriite contains a new type of alternation of cations and anions in the columns of cancrinite cages. Presumably, the mineral also includes SO_3 groups among anionic groupings in the liottite cage.

Table 4. Composition of some sites and characteristics of their coordination polyhedra*

Site	Composition ($Z = 1$)	CN	Cation–anion distance, Å		
			Min	Max	A
Ca(1a)	1.6Ca	6	2.427(4)	2.836(1)	2.63
Ca(2a)	1.5Ca	6	2.454(4)	2.807(6)	2.63
K	4.3K	6	2.67(1)	2.903(5)	2.79
Na(2)	4.32Na + 1.68K	6	2.759(5)	3.027(5)	2.87
Na(3a)	5.0Na + 0.5Ca	7	2.24(1)	2.899(7)	2.59
Na(4a)	4.2Na + 0.6Ca	8	2.458(7)	2.849(7)	2.60
Na(5)	1.54Na	8	2.30(2)	2.80(2)	2.62
Na(6a)	1.5Na	8	2.61(2)	2.95(2)	2.68
S(1a)	1.6S	4	1.42(1)	1.67(2)	1.48
S(2)	1.4S	3	1.43(1)	1.43(1)	1.43
S(3a)	1.5S	4	1.47(1)	1.52(2)	1.48
S(3b)	0.5S	4	1.50(7)	1.51(2)	1.51
C	0.6C	3	1.1(1)	1.1(1)	1.1

Note: (*) Weakly occupied sites of ligands were omitted.

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