

## The crystal structure of kogarkoite, $\text{Na}_3\text{SO}_4\text{F}$

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**SUMMARY.** The crystal structure of synthetic kogarkoite has been determined from X-ray data collected on an automatic diffractometer. The refinement was performed by a least-squares method employing anisotropic thermal parameters. The 3157 reflections with  $I > 3\sigma(I)$  converged to a conventional  $R$  value of 0.033. The cell content is 12  $\text{Na}_3\text{SO}_4\text{F}$ , the space-group  $P2_1/m$ ,  $a = 18.074$ ,  $b = 6.958$ ,  $c = 11.443$  Å,  $\beta = 107.71^\circ$ .

Kogarkoite presents a marked trigonal subcell with  $c'$  corresponding to  $[102]$  of the monoclinic cell. The three-dimensional framework can be considered built up by nine differently stacked layers of Na atoms approximately perpendicular to the  $c'$  axis (five sheets are present in galeite, six in sulphohalite, and seven in schairerite). The very close structural relationships between these minerals are discussed.

KOGARKOITE,  $\text{Na}_3\text{SO}_4\text{F}$ , represents a natural phase in the system  $\text{Na}_2\text{SO}_4$ -NaF-NaCl. This mineral was first found by Kogarko (1961) in the Lovozero syenites (Kola peninsula) and subsequently in hot-springs deposits at Mt. Princeton, Colorado (Sharp, 1970). A compound corresponding to the mineral can be easily synthesized by evaporation of aqueous  $\text{Na}_2\text{SO}_4$  and NaF solutions. Indeed artificial sodium fluoride sulphate was described by De Marignac (1859) and later by Wolters (1910) and Foote and Schairer (1930). Pabst *et al.* (1963) and Pabst and Sharp (1973) reported the results of crystallographic studies, assigning kogarkoite to the monoclinic system, with a marked rhombohedral pseudo-cell.

The present work on the crystal structure of kogarkoite is a further contribution to the crystallochemical study of the group of multiple salts having composition ranging from  $\text{Na}_3\text{SO}_4\text{F}$  to  $\text{Na}_6(\text{SO}_4)_2\text{FCl}$  (sulphohalite, Sakamoto, 1968). Previously

reported results concern the minerals schairerite,  $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$  (Fanfani *et al.*, 1975*a*) and galeite,  $\text{Na}_{15}(\text{SO}_4)_4\text{F}_4\text{Cl}$  (Fanfani *et al.*, 1975*b*).

*Experimental.* Crystals suitable for structural study were prepared by evaporation at  $25^\circ\text{C}$  of an aqueous solution of sodium sulphate, sodium fluoride, and sodium chloride. Identical crystals were obtained by evaporation at room temperature of an aqueous solution of sodium sulphate and sodium fluoride. All synthetic crystals, being tabular, have a habit similar to that of fig. 6B in the Pabst and Sharp (1973) study.

Intensity data were collected from a small crystal of synthetic kogarkoite (average dimension 0.030 cm) using a Philips PW 1100 automated four-circle diffractometer with graphite monochromatized Mo-K $\alpha$  radiation. The 4314 independent reflections based on  $2/m$  Laue symmetry were measured by the  $\omega$ -scan technique for  $2^\circ < \theta < 30^\circ$ . Three check reflections were measured at 3-hour intervals and showed no substantial changes. The intensities were corrected for Lorentz-polarization and absorption effects ( $\mu = 9.4 \text{ cm}^{-1}$ ) and were processed according to Davies and Gatehouse (1973) to yield values of  $F_0$  and  $\sigma(F_0)$ . The 3157 reflections with  $I > 3\sigma(I)$  were regarded as observed.

The unit-cell parameters were obtained with one of the standard programmes of the Philips 1100 single-crystal diffractometer. With this program (LAT) the rows ( $h00$ ), ( $0k0$ ), ( $00l$ ), ( $h0h$ ), ( $\bar{h}0h$ ) have been investigated in the range  $3 \leq \theta \leq 50^\circ$  (Mo-K $\alpha$ ). By using the circle with the highest precision,  $\omega$  (with coupled  $2\theta$ ), the profiles of the four most intense reflections (as weighted by  $\tan \theta$ ) in each row were scanned in the positive and in the

negative  $\theta$ -region. The centres of gravity of these eight profiles were used in a least-squares refinement of  $\lambda d^*$ . The  $d$ -spacings of the five investigated rows were then used to obtain  $a$ ,  $b$ ,  $c$ , and  $\beta$  cell parameters. The unique systematic absence ( $oko$ ) =  $2n + 1$  indicated two possible space groups:  $P2_1$  or  $P2_1/m$ . The latter was selected on the basis of the  $E$ -statistic (Karle *et al.*, 1965), Table 1, and was confirmed by the structure solution.

The crystallographic data are reported below:

Space group	$P2_1/m$	
$a$	18.079(2) Å	$Z = 12$
$b$	6.958(1) Å	$V = 1371.24 \text{ Å}^3$
$c$	11.443(2) Å	
$\beta$	107.71°	
specific gravity calc.	2.676 g. cm <sup>-3</sup>	
specific gravity meas.	2.667 g. cm <sup>-3</sup>	

*Structure analysis.* Kogarkoite exhibits a marked trigonal subcell with  $a' = 12.2$  and  $c' = 24.4$  Å,  $c'$  corresponding to  $[102]$  in the monoclinic cell. The relations between the two lattices are defined by the following matrices: monoclinic to trigonal subcell:  $\frac{1}{4} - \frac{3}{2} - \frac{1}{4}; \frac{1}{4} \frac{3}{2}, -\frac{1}{4}; 102$ ; trigonal to monoclinic:  $\frac{4}{3} \frac{1}{3}; -\frac{1}{3} \frac{1}{3} 0; -\frac{2}{3} - \frac{2}{3} \frac{1}{3}$ . The value for  $a'$ , closely similar to that observed in schairerite and galeite, indicates an atomic arrangement not greatly different for all these structures, with planes of Na coordination polyhedra parallel to the basal plane of the subcell, corresponding to the monoclinic plane (101), and with sulphur tetrahedra and halogen atoms lying on the pseudo-ternary axes. When the different size of fluorine atoms with respect to the chlorine atoms and the consequent shortening of the distance between the two Na layers sandwiching Cl atoms replaced by F are taken into account,

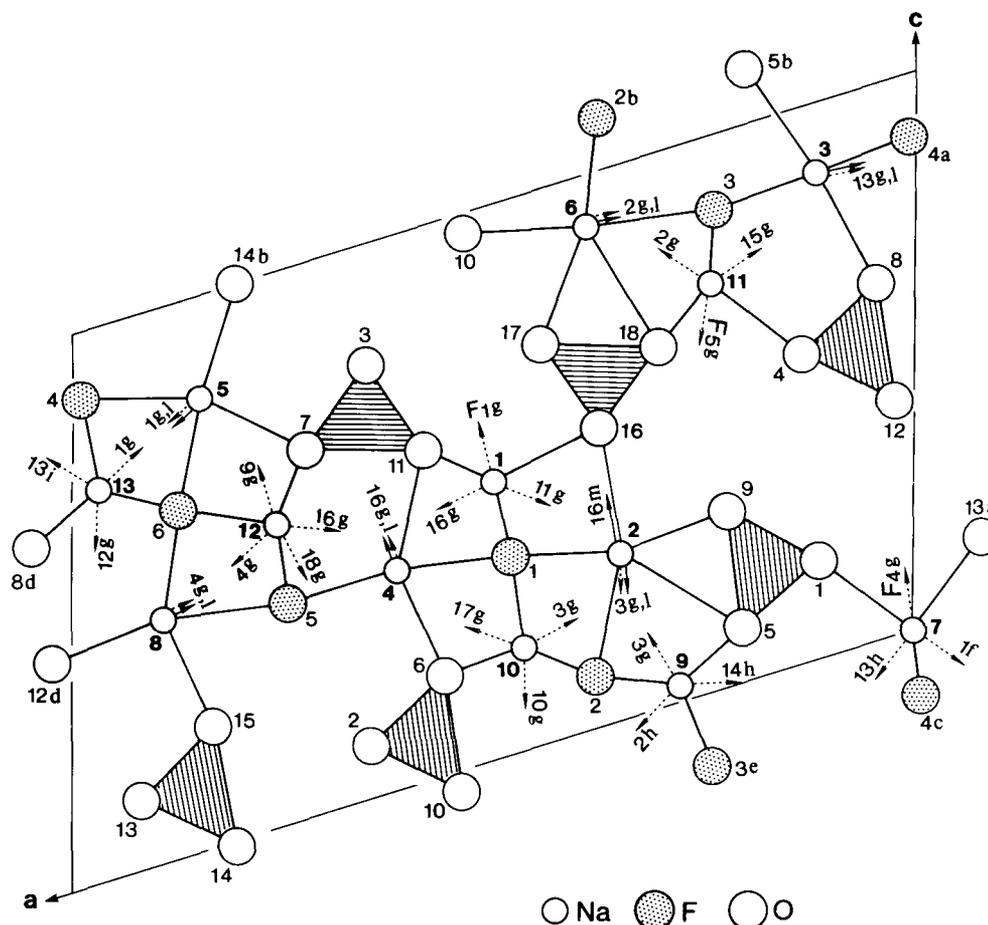


FIG. 1. The crystal structure of kogarkoite projected along the  $b$  axis included in a slab between  $b = 0$  and  $b = 1/4$ .

the  $c'$  value suggests that the periodicity along the pseudoternary axes occurs across nine sheets of  $\text{Na}^+$  coordination polyhedra, instead of five as in galeite and seven as in shairerite. A smaller subcell corresponding to the sulphohalite cubic unit-cell referred to trigonal axes can be recognized in kogarkoite as in shairerite and galeite. Therefore it was possible to suggest some atomic arrangements for kogarkoite derived from those of shairerite, galeite, and sulphohalite. By selecting reflections with monoclinic indices having  $h + 2k + l = 4n$ , corresponding to the sulphohalite-type subcell, a Patterson function was computed and interpreted on the basis of these hypotheses. In this way an approximate crystal structure for the trigonal subcell of kogarkoite was determined and refined by several cycles of least-squares calculations to an  $R$  value of 0.21.

At this stage a Patterson synthesis was computed employing as coefficients the squared structure factors of reflections not attributable to the pseudo-cell, in an attempt to derive the 'distortion structure' (Takeuchi, 1972) originating from the substructure. The true structure was then refined by the usual Fourier and least-squares methods.

Scattering factors for neutral atoms were those listed by Cromer and Waber (1974). After three cycles of full matrix least-squares refinement with the computer program ORFLS (Busing *et al.*, 1962), allowing also for variation in the isotropic temperature factors as well as in the scale factor, the conventional  $R$  lowered to 0.058. At this stage anisotropic temperature factors were included in the refinement and after three cycles  $R$  was 0.033. The final parameter shifts were considerably smaller than the standard deviations.

The final atomic coordinates and the anisotropic thermal parameters with their standard deviations are listed in Table II. S-O bond lengths and angles are included in Tables III and IV, Na-F and Na-O distances are listed in Table V. The tables containing bond angles of Na-polyhedra and observed and calculated structure factors are deposited in the library of the Department of Mineralogy, British Museum (Natural History).

The crystal structure of kogarkoite projected along the  $b$  axis is shown in fig. 1. The average S-O bond length is 1.472 Å, with values in the range 1.457-1.477 Å; O-S-O angles range from 108.9 to 110.5°.

**Discussion.** The sulphate tetrahedra are aligned together with fluorine atoms along [102], corresponding to the direction of the pseudo-ternary axes. Along these axes the succession consists of alternate triplets of sulphur tetrahedra and triplets of halogen atoms. These alignments on adjacent pseudoaxes are reciprocally shifted, with shifts ap-

proximately consistent with the translational symmetry found in sulphohalite. The apices of sulphate tetrahedra along different pseudo-ternary axes are or up-up-up, or down-down-down, or up-up-down, or down-down-up, due to the existence of inversion centres. On each pseudo-ternary axis one tetrahedron of a triplet is rotated by 60° with respect to the orientation of the two others. The arrangement of sulphate tetrahedra and halogen atoms along [102] direction is sketched in fig. 2. A schematic projection of the sulphate motif along [102] is drawn in fig. 3. Na ions are located on planes parallel to (101). In each plane they are arranged on a framework formed by triangles and

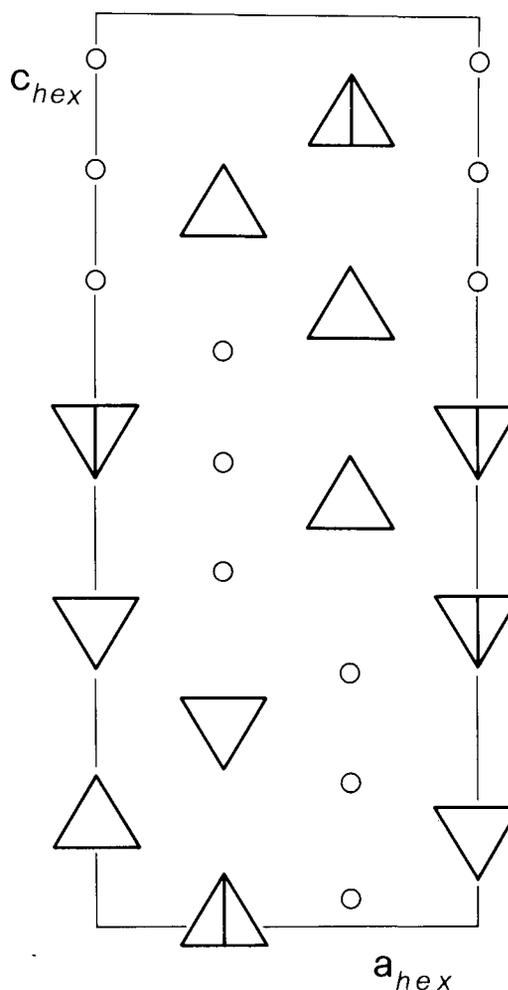


FIG. 2. The four different alignments of  $\text{SO}_4$  tetrahedra and fluorine atoms in kogarkoite as viewed along the  $[2\bar{3}2]$  direction (corresponding to  $[100]$  axis in shairerite-type pseudo-cell).

Table 11. Fractional atomic coordinates, equivalent isotropic temperature factors ( $\text{\AA}^2$ ) after Hamilton (1959) and final anisotropic thermal parameters ( $\times 10^3$ ), with e.s.d.'s in parentheses.

Atom	x/a	y/b	z/c	B <sub>eq.</sub>	b <sub>11</sub>	b <sub>22</sub>	b <sub>33</sub>	b <sub>12</sub>	b <sub>13</sub>	b <sub>23</sub>
S(1)	0.1619(1)	1/4	0.1931(1)	0.59	5(0)	28(2)	15(1)	0	4(0)	0
S(2)	0.3970(1)	1/4	0.0821(1)	0.67	5(0)	37(2)	15(1)	0	3(0)	0
S(3)	0.6577(1)	1/4	0.7028(1)	0.58	5(0)	30(2)	12(1)	0	2(0)	0
S(4)	0.8829(1)	1/4	0.5298(1)	0.65	6(0)	30(2)	16(1)	0	4(0)	0
S(5)	0.3749(1)	1/4	0.6120(1)	0.66	6(0)	32(2)	15(1)	0	4(0)	0
S(6)	0.8697(1)	1/4	0.1194(1)	0.58	5(0)	30(2)	13(1)	0	3(0)	0
Nn(1)	1/2	0	1/2	1.30	10(1)	62(4)	31(2)	-4(1)	5(1)	6(2)
Nn(2)	0.3494(1)	1/4	0.3096(2)	1.66	10(1)	72(5)	52(2)	0	9(1)	0
Nn(3)	0.1166(1)	1/4	0.8734(2)	1.37	8(1)	57(4)	42(2)	0	6(1)	0
Nn(4)	0.6149(1)	1/4	0.3974(1)	1.25	9(1)	64(4)	30(2)	0	6(1)	0
Nn(5)	0.8519(1)	1/4	0.8160(2)	1.16	11(1)	60(4)	23(1)	0	6(1)	0
Nn(6)	0.3934(1)	1/4	0.9026(2)	1.51	17(1)	62(4)	31(2)	0	10(1)	0
Nn(7)	0	0	0	1.24	12(1)	63(4)	24(1)	2(1)	6(1)	10(2)
Nn(8)	0.8932(1)	1/4	0.4280(2)	1.25	14(1)	51(4)	26(1)	0	8(1)	0
Nn(9)	0.2790(1)	0.0274(2)	0.0296(2)	1.10	9(0)	58(3)	22(1)	0(1)	5(1)	2(1)
Nn(10)	0.4651(1)	0.0180(2)	0.1908(1)	1.38	10(0)	66(3)	39(1)	1(1)	8(1)	2(1)
Nn(11)	0.7377(1)	0.0230(2)	0.2301(1)	1.25	7(0)	53(3)	24(1)	-4(1)	6(1)	-6(2)
Nn(12)	0.7777(1)	0.0223(2)	0.5531(1)	1.52	11(0)	67(3)	35(1)	5(1)	7(1)	8(2)
Nn(13)	0.9780(1)	0.0333(2)	0.7084(1)	1.22	11(0)	57(3)	29(1)	1(1)	7(1)	2(2)
F(1)	0.4788(1)	1/4	0.3766(2)	1.10	8(1)	73(6)	19(2)	0	4(1)	0
F(2)	0.3776(1)	1/4	0.0935(2)	1.05	9(1)	48(6)	22(2)	0	2(1)	0
F(3)	0.2376(1)	1/4	0.8631(2)	1.11	10(1)	61(6)	22(2)	0	6(1)	0
F(4)	0.9901(1)	1/4	0.8760(2)	0.98	8(1)	48(6)	22(2)	0	4(1)	0
F(5)	0.2427(1)	1/4	0.3925(2)	1.13	11(1)	56(6)	23(2)	0	6(1)	0
F(6)	0.9759(1)	1/4	0.6471(2)	0.98	9(1)	59(6)	16(2)	0	4(1)	0
O(1)	0.1129(1)	0.0733(2)	0.1787(1)	1.36	12(1)	45(4)	40(1)	-10(1)	9(1)	-3(2)
O(2)	0.6528(1)	0.0768(2)	0.0945(1)	1.38	13(1)	45(4)	41(1)	8(1)	9(1)	-4(2)
O(3)	0.6523(1)	0.0764(2)	0.7756(1)	1.30	13(1)	51(4)	28(1)	-3(1)	6(1)	14(2)
O(4)	0.1334(1)	0.0768(2)	0.5235(1)	1.27	11(1)	39(3)	39(1)	6(1)	9(1)	-1(2)
O(5)	0.2021(1)	1/4	0.0991(2)	1.38	14(1)	73(6)	31(2)	0	15(1)	0
O(6)	0.5988(1)	1/4	0.1796(2)	1.35	11(1)	95(6)	24(2)	0	10(1)	0
O(7)	0.7242(1)	1/4	0.6634(2)	1.45	10(1)	80(6)	43(2)	0	15(1)	0
O(8)	0.0275(1)	1/4	0.6666(2)	1.49	16(1)	71(6)	35(2)	0	18(1)	0
O(9)	0.5950(1)	1/4	0.0820(2)	1.37	10(1)	81(6)	38(2)	0	-1(1)	0
O(10)	0.4596(1)	1/4	0.9816(2)	1.72	11(1)	35(6)	14(2)	0	-5(1)	0
O(11)	0.3388(1)	1/4	0.5949(2)	1.72	11(1)	72(6)	21(2)	0	-3(1)	0
O(12)	0.0244(1)	1/4	0.4223(2)	1.60	12(1)	96(6)	23(2)	0	-3(1)	0
O(13)	0.9181(1)	0.0771(2)	0.1284(1)	1.49	13(1)	55(4)	38(1)	12(1)	6(1)	2(2)
O(14)	0.8079(1)	1/4	0.0003(2)	1.25	9(1)	90(6)	16(2)	0	-1(1)	0
O(15)	0.8344(1)	1/4	0.2195(2)	1.46	13(1)	102(6)	25(2)	0	10(1)	0
O(16)	0.3747(1)	0.0782(2)	0.5374(1)	1.82	22(1)	52(4)	43(1)	-1(1)	13(1)	-19(2)
O(17)	0.4639(1)	1/4	0.7203(2)	2.84	21(1)	150(8)	44(2)	0	-12(1)	0
O(18)	0.3644(1)	1/4	0.6503(2)	2.90	22(1)	89(7)	122(3)	0	25(2)	0

(\*) in the form:  $\exp[-h^2 b_1^2 + \dots + 2hb_1 b_2 + \dots]$

Table 11. Sulfur-oxygen distances. Standard deviations are  $\leq 0.002 \text{ \AA}$ .

S(1) - O(1)	1.473 \AA	x 2	1.474 \AA
S(2) - O(2) <td>1.470</td> <td>x 2</td> <td>1.473</td>	1.470	x 2	1.473
S(3) - O(3) <td>1.477</td> <td>x 2</td> <td>1.477</td>	1.477	x 2	1.477
S(4) - O(4) <td>1.475</td> <td>x 2</td> <td>1.469</td>	1.475	x 2	1.469
S(5) - O(5) <td>1.468</td> <td>x 2</td> <td>1.469</td>	1.468	x 2	1.469
S(6) - O(6) <td>1.473</td> <td>x 2</td> <td>1.473</td>	1.473	x 2	1.473
S(7) - O(7) <td>1.472</td> <td>x 2</td> <td>1.476</td>	1.472	x 2	1.476
S(8) - O(8) <td>1.473</td> <td>x 2</td> <td>1.471</td>	1.473	x 2	1.471
S(9) - O(9) <td>1.469</td> <td>x 2</td> <td>1.471</td>	1.469	x 2	1.471

Table 11. Sulfur-oxygen distances. Standard deviations are  $\leq 0.1^\circ$ .

O(2) - S(2)	109.4°	x 2	109.7°
O(3) - S(3) <td>109.5</td> <td>x 2</td> <td>109.7</td>	109.5	x 2	109.7
O(4) - S(4) <td>109.4</td> <td>x 2</td> <td>109.3</td>	109.4	x 2	109.3
O(5) - S(5) <td>109.7</td> <td>x 2</td> <td>109.2</td>	109.7	x 2	109.2
O(6) - S(6) <td>109.6</td> <td>x 2</td> <td>108.9</td>	109.6	x 2	108.9
O(7) - S(7) <td>109.1</td> <td>x 2</td> <td>110.3</td>	109.1	x 2	110.3
O(8) - S(8) <td>109.8</td> <td>x 2</td> <td>108.9</td>	109.8	x 2	108.9
O(9) - S(9) <td>109.5</td> <td>x 2</td> <td>109.4</td>	109.5	x 2	109.4
O(10) - S(10) <td>110.2</td> <td>x 2</td> <td>109.5</td>	110.2	x 2	109.5
O(11) - S(11) <td>109.1</td> <td>x 2</td> <td>109.3</td>	109.1	x 2	109.3
O(12) - S(12) <td>108.9</td> <td>x 2</td> <td>109.6</td>	108.9	x 2	109.6
O(13) - S(13) <td>110.5</td> <td>x 2</td> <td>109.5</td>	110.5	x 2	109.5

Symmetry code:

- none x y z
- a x y z
- b x y z
- c x y z
- d 1-x y z
- e x y z-1
- f 1-x y z
- g 1-x y z-1
- h 1-x y z
- i 1-x y z
- j 1-x y z
- k 1-x y z
- l 1-x y z
- m 1-x y z
- n 1-x y z
- o 1-x y z
- p 1-x y z
- q 1-x y z
- r 1-x y z
- s 1-x y z
- t 1-x y z
- u 1-x y z
- v 1-x y z
- w 1-x y z
- x 1-x y z
- y 1-x y z
- z 1-x y z

Table V. Bond distances of Na-polyhedra. Standard deviations are  $\leq 0.003$  Å.

Na(1) - F(1)	x 2	2.340	Å	Na(8) - F(5)	2.613	Å
- O(11)	x 2	2.345		- F(6)	2.281	
- O(16)	x 2	2.489		- O(4,1)	2.332	x 2
Na(2) - F(1)		2.230		- O(12,d)	2.434	
- F(2)		2.576		- O(15)	2.401	
- O(3,1)	x 2	2.429		Na(9) - F(2)	2.307	
- O(5)		2.947		- F(3,e)	2.392	
- O(9)		2.406		- O(2,h)	2.359	
- O(16)	x 2	2.864		- O(3,g)	2.309	
				- O(5)	2.374	
Na(3) - F(3)		2.225		- O(14,h)	2.446	
- F(4,a)		2.298		Na(10) - F(1)	2.452	
- O(5,b)		2.577		- F(2)	2.294	
- O(8)		2.573		- O(3,g)	2.382	
- O(13,l)	x 2	2.360		- O(6)	2.382	
Na(4) - F(1)		2.361		- O(10,g)	2.541	
- F(5)		2.320		- O(17,g)	2.500	
- O(6)		2.386		Na(11) - F(3)	2.314	
- O(11)		2.490		- F(5,g)	2.330	
- O(16,l)	x 2	2.392		- O(2,g)	2.393	
Na(5) - F(4)		2.381		- O(4)	2.456	
- F(6)		2.327		- O(15,g)	2.421	
- O(1,l)	x 2	2.360		- O(18)	2.385	
- O(7)		2.435		Na(12) - F(5)	2.329	
- O(14,b)		2.470		- F(6)	2.385	
Na(6) - F(2,b)		2.251		- O(4,g)	2.438	
- F(3)		2.709		- O(7)	2.379	
- O(2,l)	x 2	2.382		- O(9,g)	2.406	
- O(10)		2.476		- O(16,g)	2.657	
- O(17)		2.543		- O(18,g)	2.984	
- O(18)		2.877		Na(13) - F(4)	2.424	
Na(7) - F(4,c)	x 2	2.217		- F(6)	2.303	
- O(1)	x 2	2.469		- O(1,g)	2.362	
- O(13,a)	x 2	2.440		- O(8,d)	2.390	
				- O(12,g)	2.440	
				- O(13,l)	2.403	

Table VI. Charge balance in kogarkoite.

	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	Na(1)	Na(2)	Na(3)	Na(4)	Na(5)	Na(6)	Na(7)	Na(8)	Na(9)	Na(10)	Na(11)	Na(12)	Na(13)	
F(1)	-	-	-	-	-	-	0.34*	0.16	-	0.17	-	-	-	-	-	0.32*	-	-	-	0.99
F(2)	-	-	-	-	-	-	-	0.12	-	-	-	0.18	-	-	-	0.34*	0.36*	-	-	1.00
F(3)	-	-	-	-	-	-	-	-	0.19	-	-	0.12	-	-	-	0.32*	-	0.36	-	0.99
F(4)	-	-	-	-	-	-	-	-	0.18	-	0.17	-	0.38*	-	-	-	-	-	0.32*	1.05
F(5)	-	-	-	-	-	-	-	-	-	0.18	-	-	-	0.14	-	-	0.34*	0.32*	-	0.98
F(6)	-	-	-	-	-	-	-	-	-	-	0.17	-	-	0.18	-	-	-	0.30*	0.36*	1.01
O(1)	1.50	-	-	-	-	-	-	-	-	-	0.17	-	0.15	-	-	-	-	-	0.17	1.99
O(2)	-	1.50	-	-	-	-	-	-	-	-	-	0.16	-	-	0.17	-	0.17	-	-	2.00
O(3)	-	-	1.50	-	-	-	0.14	-	-	-	-	-	-	-	0.18	0.17	-	-	-	1.99
O(4)	-	-	-	1.50	-	-	-	-	-	-	-	-	-	0.18	-	-	0.16	0.15	-	1.99
O(5)	1.51	-	-	-	-	-	0.09	0.14	-	-	-	-	-	-	-	0.32*	-	-	-	2.06
O(6)	-	1.51	-	-	-	-	-	-	0.17	-	-	-	-	-	-	0.34*	-	-	-	2.02
O(7)	-	-	1.50	-	-	-	-	-	-	0.16	-	-	-	-	-	-	-	0.32*	-	1.98
O(8)	-	-	-	1.50	-	-	-	0.14	-	-	-	-	-	-	-	-	-	-	0.34*	1.98
O(9)	1.49	-	-	-	-	-	0.14	-	-	-	-	-	-	-	-	-	-	0.30*	-	1.93
O(10)	-	1.50	-	-	-	-	-	-	-	-	0.15	-	-	-	-	0.30*	-	-	-	1.95
O(11)	-	-	1.50	-	-	-	0.34*	-	-	0.15	-	-	-	-	-	-	-	-	-	1.99
O(12)	-	-	-	1.49	-	-	-	-	-	-	-	-	-	0.16	-	-	-	-	0.32*	1.97
O(13)	-	-	-	-	1.50	-	-	0.17	-	-	-	0.16	-	-	-	-	-	-	0.16	1.99
O(14)	-	-	-	-	-	1.49	-	-	-	0.16	-	-	-	-	0.32*	-	-	-	-	1.97
O(15)	-	-	-	-	-	-	1.51	-	-	-	-	-	-	0.17	-	-	0.32*	-	-	2.00
O(16)	-	-	-	-	1.49	-	0.15	0.10	-	0.17	-	-	-	-	-	-	-	0.12	-	2.03
O(17)	-	-	-	-	-	1.52	-	-	-	-	-	0.14	-	-	-	0.32*	-	-	-	1.98
O(18)	-	-	-	-	1.49	-	-	-	-	-	-	0.11	-	-	-	-	0.32*	0.20*	-	2.12

(\*) - Sum of two Na-F or Na-O bonds.

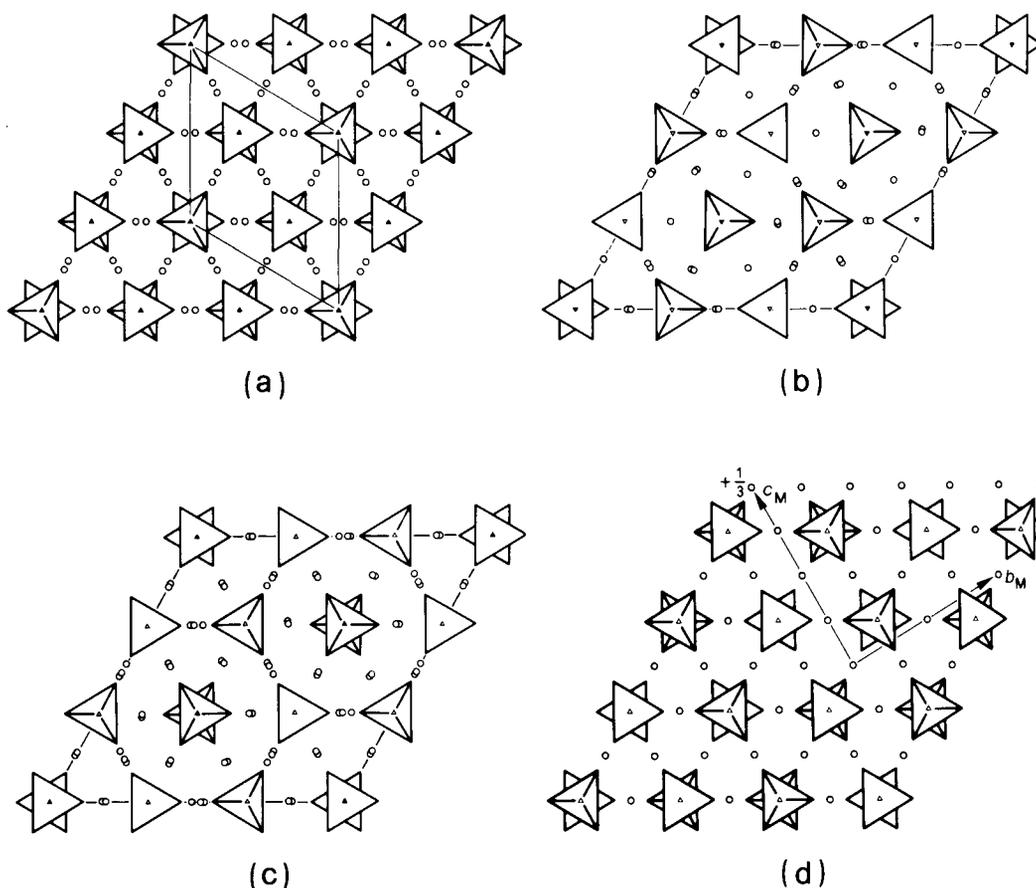


FIG. 3. Schematic view of the atomic arrangement in the four minerals of the system  $\text{Na}_2\text{SO}_4\text{-NaF-NaCl}$ , projected along the direction of ternary axes ( $\blacktriangle$ ) and/or pseudo-ternary axes ( $\triangle$ ). The figure shows  $\text{SO}_4$  tetrahedra,  $\text{Na}^+$  positions and the actual translation vectors of the lattice for: (a) sulphohalite; (b) galeite; (c) schairerite; (d) kogarkoite.

hexagons with the same shape found in schairerite and galeite. These planar networks are reciprocally shifted as in the trigonal-related minerals and the stacking sequence along the pseudo-ternary axes,  $[102]$  in the monoclinic cell, can be described as BCACABABC, when the same notation used in fig. 3 of the schairerite paper is adopted. The separation between adjacent Na planes is roughly constant and its mean value 2.72 Å. Ten of the thirteen independent  $\text{Na}^+$  ions exhibit distorted octahedral coordination, forming  $\text{Na}(\text{OSO}_3)_4\text{F}_2$  complexes. Na(2) is eight-fold coordinated, having 3 O and 2 F atoms at distances less than 2.575 Å and three additional oxygen bonds at distances 2.864, 2.864, and 2.946 Å. Na(6) and Na(12) have seven-fold coordination: Na(6) links four O and one F atoms at distances less than 2.544 Å, one

additional F at 2.710 Å and one O at 2.877 Å; Na(12) links four O and two F atoms with bond lengths less than 2.657 Å and one additional O at 2.983 Å. Neglecting the additional ligands considered above Na-O distances range from 2.308 to 2.557 Å (mean value 2.414 Å); Na-F bond lengths are in the range 2.217 to 2.618 Å (mean value 2.340 Å). The halogen ligands are bound in *trans*-configuration by Na(3), Na(7), and Na(11). In all the other cases the resulting configuration of ligands is the *cis*-one.

A balance of the electrostatic charges for F and O atoms is given in Table VI. The calculation is made after Ferguson (1974) and the bond strengths are assumed as inversely proportional to the squared cation-anion distances. The results are satisfactory.

*Structural relationships in the system*  $\text{Na}_2\text{SO}_4$ - $\text{NaF}$ - $\text{NaCl}$ . In the system  $\text{Na}_2\text{SO}_4$ - $\text{NaX}$ , where  $X = \text{F}$  or  $\text{Cl}$ , kogarkoite represents the term with  $X = \text{F}$ . Its structure, despite the different lattice symmetry, is related to those which are partially chlorinated, termed sulphohalite, galeite, and schairerite, having F/Cl ratios 1:1, 4:1, and 6:1 respectively. All these structures can be derived from that of cubic sulphohalite (space group  $Fm\bar{3}m$ ) which was first determined by Pabst (1934) and independently by Watanabe (1934). The distortion arising from the different ratio F/Cl leads to different atomic arrangements consistent with space groups  $P\bar{3}1m$  (schairerite and galeite) and  $P2_1/m$  (kogarkoite). It may be interesting to note that only sulphohalite and kogarkoite crystallize in centrosymmetrical space groups. The structures consist of a very compact three-dimensional arrangement of Na coordination polyhedra sharing corners, edges, and faces. These polyhedra are distorted octahedra in all structures with the exception of kogarkoite, where some  $\text{Na}^+$  ions have higher coordination. These frameworks can be described in terms of Na layers with trigonal or approximately trigonal symmetry differently stacked according to the A, B, and C sequence of layers described in the schairerite paper. The number of these layers is 5 in galeite, 6 in sulphohalite, 7 in schairerite, and 9 in kogarkoite. The stacking sequences found in the four minerals are: BABAC (galeite), BACBAC (sulphohalite), BABACAC (schairerite), and BCACABABC (kogarkoite). The arrangement of  $\text{Na}^+$  ions is centrosymmetrical for all structures but that of galeite. The non-centrosymmetrical morphological habit of this mineral can be probably ascribed to this feature.

A total number of sulphur,  $(\text{SO}_4)$ -oxygen, and halogen atoms corresponding to the number of Na layers in the structure are aligned along the three-fold (or pseudo-three-fold) axes. In galeite the five atoms are 3 F, 1 S, and 1 O, or one halogen (Cl or F), 2 S, and 2 oxygen atoms. In sulphohalite the arrangement on each ternary axis is obviously equal, with 1 Cl, 1 F, 2 S, and 2 oxygen atoms. In schairerite there are two different series: 1 Cl, 3 S, and 3 O, or 3 F, 2 S, and 2 O. Finally in kogarkoite 3 F, 3 S, and 3 O lie on the pseudo-ternary axes.

In conclusion, taking into account the four structures, the replacement of 1 S + 1 O by 2 F, or the substitution of fluorine by chlorine, seems possible without great changes in the general features of the atomic arrangement, but is responsible for the different reciprocal stacking of Na formal layers. In particular the substitution of F by Cl causes an increase of the mean separation of the layers sandwiching chlorine. A schematic representation of the atomic arrangements in these minerals is shown in fig. 3, allowing an immediate comparison of the structural motif. However the atomic arrangement of kogarkoite deviates significantly from the representation of the figure.

## REFERENCES

- Busing (W. R.), Martin (K. O.), and Levy (H. A.), 1962. *Oak Ridge National Laboratory Report ORNL-TM-305*, Oak Ridge, Tennessee.
- Cromer (D. T.) and Waber (J. T.), 1974. *International Tables for X-ray Crystallography*, **IV**, 71.
- Davies (J. E.) and Gatehouse (B. M.), 1973. *Acta Cryst.* **B29**, 1934.
- De Marignac (Ch.), 1859. *Ann. des Mines*, **15**, 221.
- Fanfani (L.), Nunzi (A.), Zanazzi (P. F.), Zanzari (A. R.), and Sabelli (C.), 1975a. *Mineral. Mag.* **40**, 131.
- , 1975b. *Ibid.*, **40**, 357.
- Ferguson (R. B.), 1974. *Acta Cryst.* **B30**, 2527.
- Foote (H. W.) and Schairer (J. F.), 1930. *J. Am. Chem. Soc.* **52**, 4202.
- Karle (I. L.), Dragonette (K. S.), and Brenner (S. A.), 1965. *Acta Cryst.* **19**, 713.
- Kogarko (L. N.), 1961. *Dokl. Akad. Nauk SSSR*, **139**, 435.
- Pabst (A.), 1934. *Z. Krist.* **89**, 514.
- , Sawyer (D. L.), and Switzer (G.), 1963. *Am. Mineral.* **48**, 485.
- and Sharp (W. N.), 1973. *Am. Mineral.* **58**, 116.
- Sakamoto (Y.), 1968. *J. Sci. Hiroshima Univ. Ser. A-II* **32**, 101.
- Sharp (W. N.), 1970. *U.S. Geol. Surv. Prof. Pap.* **700-B**, B-14.
- Takeuchi (Y.), 1972. *Z. Krist.* **135**, 120.
- Watanabe (T.), 1934. *Proc. Imperial Acad. (Japan)*, **10**, 575.
- Wolters (A.), 1910. *Neues Jahrb. Mineral. Beil.* **Bd. 30**, 55.

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