

The crystal structure of galeite, $\text{Na}_{15}(\text{SO}_4)_5\text{F}_4\text{Cl}$

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SUMMARY. The crystal structure of galeite from Searles Lake (California) has been determined by means of X-ray diffraction data on a single crystal. A possible structure was derived from that of schairerite on the basis of chemical and lattice analogies and was confirmed by comparison of the observed diffractometric structure factors with the calculated ones. The refinement was performed by least-squares methods employing isotropic thermal parameters and assuming that atoms related by translational pseudosymmetry exhibit equal thermal parameters. The final R value is 0.09. The cell content is $3[\text{Na}_{15}(\text{SO}_4)_5\text{F}_4\text{Cl}]$; the space group is $P31m$. The lattice dimensions are a 12.197(4) Å, c 13.955(10) Å. The marked subcell has $P3m1$ symmetry and a 7.042 Å, c 13.955 Å. The crystal structure of galeite consists of a three-dimensional framework, formed by coordination octahedra around Na^+ ions, including tetrahedral holes with sulphur atoms at the centres. The three-dimensional framework can be considered built up by five octahedral sheets (seven sheets can be recognized in schairerite and six in sulphohalite). The very close analogies occurring in the structures of galeite and schairerite are discussed.

THE present study follows the structural investigation of schairerite (Fanfani *et al.*, 1975) and represents a further contribution to the crystallochemical knowledge of the multiple salts with composition ranging from $\text{Na}_3\text{SO}_4\text{F}$ to $\text{Na}_6(\text{SO}_4)_2\text{FCl}$.

The first occurrence of galeite, at Searles Lake (California), was recorded by Pabst *et al.* (1955) who gave also some X-ray diffraction and chemical data. In 1956, Fleischer, in reporting the preliminary description by Pabst *et al.*, suggested that galeite is dimorphous with schairerite.

Pabst *et al.* (1963) confirmed that both minerals show the same diffraction symmetry $\bar{3}1mP$ and the same general chemical formula, $\text{Na}_2\text{SO}_4 \cdot \text{Na}(\text{F}, \text{Cl})$, but they cannot be considered dimorphous because of their different F/Cl ratio (probably 4 in galeite and 6 in schairerite). Syntactic intergrowths of galeite and schairerite are considered to be polycrystals. According to these authors a prominent subcell is present in both minerals, which can be related to the unit-cell of sulfohalite, $\text{Na}_6(\text{SO}_4)_2\text{FCl}$, when described in a trigonal setting.

A microprobe study by Brown and Pabst (1971) confirmed the chemical formulae previously reported for galeite, $\text{Na}_{15}(\text{SO}_4)_5\text{F}_4\text{Cl}$, and schairerite, $\text{Na}_{21}(\text{SO}_4)_7\text{F}_6\text{Cl}$; these formulae are in agreement with the cell dimensions of the two minerals (galeite: a 12.17 Å, c 13.94 Å, Z 3; schairerite: a 12.17 Å, c 19.29 Å, Z 3). In 1973 Pabst and Sharp made a crystallographic study of kogarkoite, another natural member of the dry system Na_2SO_4 -NaF-NaCl recently discovered in USSR and Colorado, showing close relationships in the atomic arrangement of this mineral with those of the other members. The structural study of this mineral is in progress in our laboratory at this moment.

Experimental. A small nearly spherical crystal from the type locality, Searles Lake (California), was mounted on a Philips PW 1100 automated diffractometer with Mo radiation and graphite monochromator. The cell dimensions were determined from a least-squares refinement of 2θ values for twenty-five reflections. The crystallographic data are: a 12.197(4) Å, c 13.955(10) Å, Z 3, $\rho_{(\text{calc})}$ 2.596 g.cm⁻³, $\rho_{(\text{obs})}$ 2.605 g.cm⁻³. The lack of systematic extinctions is compatible with space groups $P\bar{3}1m$, $P31m$, and $P312$.

Intensity data were collected by the $\omega/2\theta$ scan technique out to $\theta = 35^\circ$. 3098 independent reflections were recorded. The resulting data were processed by a data correction routine that corrected for background and Lorentz-polarization effects. Only 2078 reflections, with $I > 3\sigma$, were used for the structure analysis.[†]

Structure analysis. Chemical and lattice similarities seem to indicate that the atomic arrangements in schairerite and galeite do not differ greatly. Diffraction intensities data and the equal a value indicate that the projections along the c axis of the two structures are analogous; the different c value suggests that in galeite the periodicity along this axis occurs across five sheets of Na⁺ ions while in schairerite this happens across seven sheets of Na⁺ ions. These arguments led us to think it was possible to derive the approximate structural building in galeite from that in schairerite. When in schairerite a chlorine atom is placed at the origin of the unit cell, seven layers of Na⁺ ions perpendicular to the c axis follow one another; the shift of these layers (according the notation of fig. 3 in Fanfani *et al.*, 1975) are of the kind BABACAC, indicating that chlorine atoms are located only in between C and B Na⁺ planes. In galeite if we place a chlorine ion at the origin of the unit-cell, a possible succession of the Na⁺ sheets is BABAC. This arrangement of sodium and chlorine atoms was tested by comparison of calculated and observed structure factors belonging to the substructure. The resulting R value was considered satisfactory and a first improvement was obtained by introduction into the calculations of fluorine and sulphur atoms at the expected positions. Finally, the complete atomic arrangement and the largest distortions from the substructure were derived by analogy with schairerite.

At this stage the R index was 0.15, assuming a general isotropic B value of 1.5 Å². An attempt to apply an isotropic refinement by full-matrix least-squares method to all observed reflections showed high correlations between many of the thermal parameters of atoms related by the translational pseudosymmetry present in the structure. Indeed one set of thermal parameters exhibits high values and the other corresponding set exhibits low values whereas, because of the closely similar environment around corresponding atoms, they are supposed to have similar and approximately intermediate thermal parameters. Consequently the refinement was continued, inserting in the computer program the constraint that atoms related by translational pseudosymmetry must have the same isotropic temperature factor. During the successive computing, no indication of strong correlation between parameters was ob-

[†] $\sigma(I) = [P + 0.25(B_1 + B_2)(T_P/T_B)^2 + (0.03 I)^2]^{1/2}$ where P is the total peak count in a scan of time T_P , B_1 and B_2 are the background counts each in a time T_B , I is the intensity equal to $[P - 0.5(T_P/T_B)(B_1 + B_2)]$ (Doedens and Ibers, 1967).

served; at the end of the refinement, including 79 positional parameters and 28 isotropic thermal factors, the R value was 0.09.

Atomic scattering factors for S, Cl⁻, F⁻, Na⁺, and O⁻ were taken from the *International Tables for X-ray Crystallography* (1962). Seven structure factors were excluded from the last refinement because they were suspected to be affected by extinction. Atomic coordinates and isotropic temperature factors are listed in Table I. A table containing observed and calculated structure factors is deposited in the library of the Department of Mineralogy, British Museum (Natural History), from whom copies may be purchased.

TABLE I. Fractional atomic coordinates and isotropic thermal parameters with standard deviations in parentheses

Atom	x/a	y/b	z/c	$B(\text{\AA}^2)$	Atom	x/a	y/b	z/c	$B(\text{\AA}^2)$
Cl	0	0	0	1.11(4)	F(1)	0.6795(7)	0	0.6394(8)	0.84(12)
Cl'	2/3	1/3	0.0447(5)	[1.11]	F(2)	0.6754(7)	0	0.2389(8)	0.70(11)
S(1)	0	0	0.3243(7)	0.63(5)	F(3)	0.6592(8)	0	0.4316(9)	1.59(13)
S(1')	2/3	1/3	0.3440(7)	[0.63]	F(4)	0.3494(9)	0	0.7962(10)	2.37(21)
S(2)	0	0	0.6957(7)	0.55(4)	O(1A)	0	0	0.2243(17)	1.70(20)
S(2')	2/3	1/3	0.7200(6)	[0.55]	O(1B)	0.8848(9)	0	0.3651(10)	1.42(9)
S(3)	0.6700(3)	0	0.9216(6)	0.46(4)	O(1A')	2/3	1/3	0.4441(13)	[1.70]
S(4)	0.3365(3)	0	0.5092(6)	0.51(4)	O(1B')	0.6704(7)	0.2209(8)	0.3098(8)	[1.42]
S(5)	0.3339(3)	0	0.1311(6)	0.64(4)	O(2A)	0	0	0.5887(13)	0.70(13)
Na(1)	0.5118(5)	0	0.7167(7)	1.22(5)	O(2B)	0.1142(10)	0	0.7345(10)	1.47(9)
Na(1')	0.1588(5)	0.3342(6)	0.7141(7)	[1.22]	O(2A')	2/3	1/3	0.8270(10)	[0.70]
Na(2)	0.8161(5)	0	0.5253(7)	1.29(6)	O(2B')	0.6677(7)	0.2202(8)	0.6872(8)	[1.47]
Na(2')	0.4852(4)	0.3326(4)	0.5310(6)	[1.29]	O(3A)	0.6693(9)	0	0.0231(8)	0.33(11)
Na(3)	0.1914(6)	0	0.8954(7)	1.19(6)	O(3B)	0.5536(9)	0	0.8853(9)	0.62(16)
Na(3')	0.8465(5)	0.3357(5)	0.9072(6)	[1.19]	O(3C)	0.7814(8)	0.1146(8)	0.8786(8)	1.07(12)
Na(4)	0.8251(5)	0	0.1324(7)	1.15(6)	O(4A)	0.3476(10)	0	0.3967(11)	1.67(21)
Na(4')	0.4782(5)	0.3300(5)	0.1414(6)	[1.15]	O(4B)	0.4506(9)	0	0.5484(9)	1.31(16)
Na(5)	0.5210(5)	0	0.3274(7)	1.18(6)	O(4C)	0.8843(8)	0.2179(9)	0.5412(8)	1.78(13)
Na(5')	0.1799(4)	0.3322(5)	0.3312(6)	[1.18]	O(5A)	0.3393(15)	0	0.0225(13)	3.04(28)
					O(5B)	0.4487(10)	0	0.1561(10)	1.23(20)
					O(5C)	0.3341(10)	0.1141(9)	0.1599(8)	1.64(14)

Discussion of the structure and relationships with schairerite. A schematic view of the structure of galeite, projected along the c axis, is shown in fig. 1. In the figure an overlap of one chlorine, two sulphur, and two oxygen atoms occurs on the threefold axes (marked by \blacktriangle symbols), while one sulphur, one oxygen, and three fluorine atoms or two sulphur, two oxygen, and one fluorine atoms are superimposed along threefold pseudoaxes (marked by \triangle symbols). Sulphur tetrahedra and Na⁺ positions are shown together with the outline of the subcell.

As in schairerite, all tetrahedra of SO₄²⁻ anions are oriented with one of their threefold axes parallel to the c direction and in such a way that along each threefold axis or pseudoaxis the S–O bonds lying along it are oriented in the same sense. The average S–O bond is 1.48 Å. The range is from 1.40 to 1.57 Å.

All Na⁺ ions in the asymmetric unit form distorted coordination octahedra with composition (Na(OSO₃)₄X₂ with X₂ = F₂ or FCl. The trans-configuration of halogen ligands is always present in the Na(OSO₃)₄FCl octahedra while the Na(OSO₃)₄F₂ octahedra exhibit cis- or trans-configuration. The interatomic distances range from

2.65 to 2.90 Å for Na–Cl bonds, from 2.22 to 2.46 Å for Na–F bonds and from 2.33 to 2.55 Å for Na–O bonds. The average values are respectively 2.78, 2.32 and 2.42 Å.

Coordination around halogen atoms is sixfold (each halogen being surrounded by six Na⁺ ions); oxygen atoms are fourfold-coordinated, with a sulphur atom and three Na⁺ cations bonded to each oxygen atom.

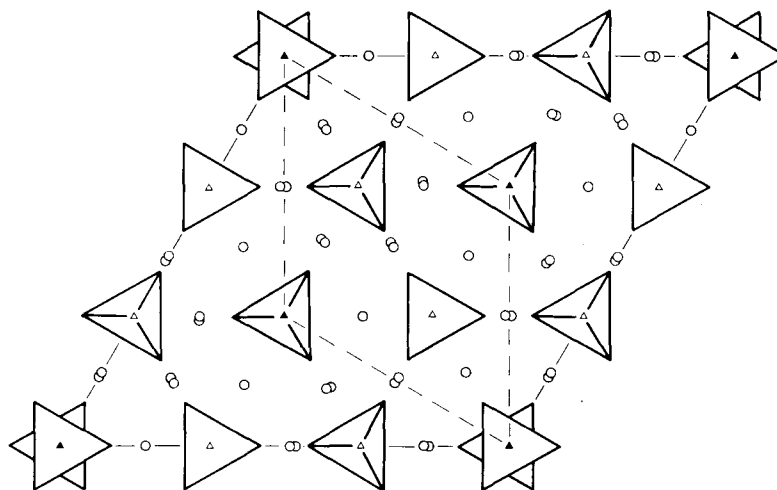


FIG. 1. SO_4^{2-} tetrahedra and Na^+ positions in galeite viewed along c direction. The outline of the subcell is drawn by broken lines.

Na^+ ions are located on five sheets perpendicular to the c axis. In each sheet they are arranged on a lattice formed by hexagons and triangles with the same shape as in schairerite. The succession of the sheets is BABAC. The arrangement of sodium ions is no longer centrosymmetric as in schairerite; assuming that the morphology of crystals of schairerite and galeite is related to the arrangement of Na^+ ions, it seems to justify the remark of Pabst *et al.* (1963), who find the morphology of schairerite to be centrosymmetric in contrast to the non-centrosymmetric habit of galeite. As in schairerite, sulphur atoms lie on the sheets at the centre of each hexagon, whilst halogen atoms lie between the sheets midway between the centres of two triangles. Because of the different size of the halogens, the separation of the Na^+ sheets sandwiching chlorine atoms is 3.29 Å while the mean separation of the other sheets is 2.67 Å. When one considers the connections among the Na^+ coordination octahedra in each of the five sheets, the same five motifs as in schairerite can be distinguished: the two sheets ($z \approx 0.90$, $z \approx 0.14$) sandwiching chlorine atoms have the same shape as in schairerite (compare fig. 4c and 4d of Fanfani *et al.*, 1975). The other three sheets (Na^+ ions at $z \approx 0.33$, 0.53, and 0.71) correspond to those in schairerite at $z \approx 0.24$, 0.38, and 0.52 (respectively fig. 4a, 4b and 4e of schairerite). It follows that the structural building of galeite can be easily obtained from that of schairerite by cutting off the octahedral double layer corresponding to the Na^+ ions at $z \approx 0.65$ and 0.79.

More generally, the crystal structure of galeite can be described as a three-dimensional framework of distorted octahedra including several tetrahedral holes with sulphur atoms at the centres. This three-dimensional framework originates from the sharing of corners, edges, and faces (represented by Cl, O, and F atoms) between octahedra belonging to adjacent sheets.

REFERENCES

- BROWN (F. H.) and PABST (A.), 1971. *Amer. Min.* **56**, 174-8.
DOEDENS (R. J.) and IBERS (J. A.), 1967. *Inorg. Chem.* **6**, 204-10.
FANFANI (L.), NUNZI (A.), ZANAZZI (P. F.), ZANZARI (A. R.), and SABELLI (C.), 1975. *Min. Mag.*, **40**, 131-9.
FLEISCHER (M.), 1956. *Amer. Min.* **41**, 672.
International Tables for X-ray Crystallography, 1962. **3**, 202.
PABST (A.), SAWYER (D. L.), and SWITZER (G.), 1955. *Bull. Geol. Soc. Amer.* **66**, 1658-9.
——— 1963. *Amer. Min.* **48**, 485-510.
——— and SHARP (W. N.), 1973. *Ibid.* **58**, 116-27.

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