

THE CRYSTAL STRUCTURE OF JARLITE

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ABSTRACT

The crystal structure of jarlite from Ivigtut, Greenland, a 15.942(4), b 10.821(5), c 7.241(2) Å, β 101.86(2)°, space group $C2/m$, has been solved by direct methods and refined by a full-matrix least-squares procedure to a residual $R = 5.3\%$ for 1027 observed (3σ) reflections. All previous formulae of jarlite are incorrect; both the structure and qualitative electron-microprobe data show Mg as an essential constituent, and infrared-absorption spectroscopy shows OH to be present. The general formula of jarlite is $\text{Na}_2(\text{Sr}, \text{Na}, \square)_{14}\text{Al}_{12}(\text{Mg}, \square)_2\text{F}_{64}(\text{OH}, \text{H}_2\text{O})_4$, with some additional replacement of Sr by Ca, Ba and K. The jarlite structure consists of corrugated (100) sheets of corner-linked Al, Mg and Na octahedra, intersecting (001) sheets of [9]- and [10]-co-ordinated (Sr, Na) polyhedra. This densely packed structure is not closely related to that of any of the previously described aluminofluorides.

Keywords: jarlite, crystal structure, mineral, aluminofluoride, fluoride, Ivigtut, Greenland.

SOMMAIRE

La structure cristalline de la jarlite de Ivigtut (Groënland), a 15.942(4), b 10.821(5), c 7.241(2) Å, β 101.86(2)°, groupe spatial $C2/m$, est obtenue par méthodes directes, et affinée par moindres carrés (matrice entière) jusqu'au résidu $R = 5.3\%$, sur 1027 réflexions observées (3σ). Les formules proposées pour la jarlite sont incorrectes. À la lumière de la structure et des données qualitatives de la microsonde électronique, le Mg s'avère constituant essentiel; les spectres d'absorption infra-rouge indiquent la présence d'hydroxyle. La formule généralisée s'écrit $\text{Na}_2(\text{Sr}, \text{Na}, \square)_{14}\text{Al}_{12}(\text{Mg}, \square)_2\text{F}_{64}(\text{OH}, \text{H}_2\text{O})_4$, dans laquelle un peu de Ca, Ba et K remplacent aussi le Sr. La structure cristalline comporte un empilement suivant (100) de feuillets ondulés d'octaèdres Al, Mg et Na à sommets communs, que recoupe parallèlement à (001) des feuillets de polyèdres (Sr, Na) à coordinence 9 et 10. Cette structure dense ne se relie à aucune des structures connues d'aluminofluorures.

(Traduit par la Rédaction)

Mots-clés: jarlite, structure cristalline, minéral, aluminofluorure, fluorure, Ivigtut (Groënland).

INTRODUCTION

Jarlite is a colorless to dirty white strontium-bearing aluminofluoride mineral, first described by

Bøgvad (1933) from the Ivigtut cryolite locality, Greenland. It generally occurs as flat, fan-shaped aggregates of crystals ~1 mm across, growing with thomsenolite and minor gearksutite in vugs in the cryolite. Bøgvad (1933) also reported grey, fan-shaped masses of a mineral similar to jarlite, intergrown with chiolite and associated with minor cryolite, fluorite, topaz and pyrite; this was found to be fairly similar to jarlite and was called *meta-jarlite*. On the basis of their X-ray powder patterns, Brosset (1942) concluded that jarlite and metajarlite are isostructural. Ferguson (1947) concluded that jarlite and metajarlite are the same species, with the latter as, at most, a compositional variety of jarlite. Both Brosset (1942) and Ferguson (1947, 1949) concluded that the formula assigned to jarlite, $\text{NaSr}_3\text{Al}_3\text{F}_{16}$, was wrong, on the basis of the lack of agreement between the observed specific gravity (3.87) and the calculated value (3.61).

As part of a continuing study of the structure of the aluminofluoride minerals (Hawthorne 1982, Hawthorne & Ferguson 1975, 1981, in prep.), the structure of jarlite was investigated to resolve the problem of its chemical formula and to determine its structural relationship to the other aluminofluoride minerals.

EXPERIMENTAL

Single-crystal X-ray precession photographs display monoclinic symmetry, with systematic absences hkl , $h+k = 2n+1$, consistent with the space groups $C2/m$, $C2$ and Cm ; $C2/m$ was assumed, and the structure refinement was satisfactory with this space group. Cell dimensions (Table 1) were determined by least-squares refinement of 15 reflections aligned automatically on a Syntex $P2_1$ 4-circle diffractometer.

An equidimensional fragment ~0.20 mm in diameter was used to collect the intensity data according to the experimental method of Hawthorne & Grundy (1976). Two standard reflections were monitored every 50 reflections to check for intensity fluctuations; no significant change in their intensities was observed during data collection. A total of 1495 reflections was measured over one asymmetric unit to a maximum 2θ of 60° ($\sin\theta/\lambda = 0.704$). The data were corrected for

TABLE 1. MISCELLANEOUS INFORMATION: JARLITE

a	15.942(4) \AA	Crystal size	$\sim 0.20\text{mm}$
b	10.821(5)	Rad/mono	Mo/Gr
c	7.241(2)	Total $ F_o $	1495
β	101.86(2) $^\circ$	No. $ F_o > 3\sigma$	1027
V	1222.5 \AA^3	Final R(obs)	5.3%
Space Group	C2/m	Final R_w (obs)	6.6%

Unit cell contents: $[\text{Na}_2(\text{Sr}, \text{Na}, \square)_{14}\text{Al}_{12}(\text{Mg}, \square)_2\text{F}_{64}(\text{OH}, \text{H}_2\text{O})_4]$

Temperature factor form: $\exp \left[-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j R_{ij}^2 \right]$

$$R = \frac{\sum (|F_o| - |F_c|) / \sum |F_o|}{\sum |F_o|}$$

$$R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}}{\sum w} \quad w = 1$$

Lorentz, polarization, absorption (spherical approximation) and background effects, and were reduced to structure factors. A reflection was considered as observed if its magnitude exceeded that of three standard deviations based on counting statistics; of the 1495 unique reflections, 1027 were considered as observed.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from Cromer & Mann (1968), with anomalous dispersion coefficients from Cromer & Liberman (1970). R indices are of the form given in Table 1 and are expressed as percentages.

The structure was determined using the weighted tangent formula method (Main *et al.* 1978). The phase set with the maximum combined figure of merit resulted in an E map with an atomic arrangement incompatible with the nominal jarlite formula. Nevertheless, this solution gave an R index of 43%, and refinement of positional parameters and isotropic temperature-factors converged at an R index of $\sim 20\%$. At this stage, the model contained 14 Sr and 12 Al in the unit cell, and the "formula" was not balanced. A three-dimensional difference Fourier map calculated at this stage showed two more positions; the observed density of electrons and the local stereochemistry suggested that one of these atoms was Na and the other was Mg. Insertion of these into the model led to convergence at an R index of 11%. This solution was still not considered satisfactory, as the "formula" was still not balanced.

Chemical compositions of jarlite and metajarlite are reported by Bøgvad (1933); these are given in Table 2. Brosset (1942) and Ferguson (1947, 1949) concluded that the nominal formula of jarlite was

TABLE 2. CHEMICAL COMPOSITIONS OF JARLITE AND METAJARLITE*

	Jarlite	68(F)	68(F+OH)	metajarlite	68(F+OH)			
Na	3.23	4.20	} 4.54	3.92	} 4.24	3.54	4.17	} 4.33
Li	0.08	0.34		0.32		0.04	0.16	
Sr	35.60	12.14	} 12.77	11.34	} 11.92	28.70	8.86	} 11.46
Ba	0.99	0.22		0.20		2.25	0.44	
Ca	0.55	0.41	} 0.38	0.38	} 0.38	3.20	2.16	} 2.16
Mg	0.90	1.11		1.03		1.38	1.53	
Al	12.16	13.47	} 13.56	12.57	} 12.65	12.49	12.52	} 12.67
Fe	0.17	0.09		0.08		0.31	0.15	
F	43.23	68.00	} 68.00	63.50	} 68.00	45.50	64.78	} 68.00
H ₂ O ⁺	2.91	4.83		4.50		2.14	3.22	
H ₂ O ⁻	0.08	-	-	-	-	0.08	-	-
Sum	99.90	-	-	-	-	99.63	-	-

* Compositions from Bøgvad (1933); formula unit normalized on 68 F and 68 (F+OH).

wrong. Presumably on the basis of the Na and H₂O in the analysis, both authors suggested that the material used for analysis was contaminated with thomsenolite and, possibly, cryolite. At this stage in the structure refinement and solution, Fourier maps showed 68 atoms interpretable as anions in the unit cell. However, normalizing the chemical composition on 68 fluorine atoms gave 17.3 (Sr + large cations) and 13.6 (Al + Fe) per unit cell, whereas the structural model at this stage had 14 Sr and 12 Al per unit cell. Including the H₂O in the normalization procedure gave much more satisfactory results (see Table 2). Infrared-absorption spectra of both jarlite and metajarlite (Fig. 1) show a strong OH absorption at 3610 cm⁻¹, with a possible very weak H₂O absorption at lower wavenumbers. The renormalized composition of jarlite suggests 4 Na, 12 Sr and 12 Al (and other components) in the unit cell. The solution at this stage had 14 Sr per unit cell, but the isotropic temperature-factors of the atoms at the three positions were significantly different [$X(1)$ 0.61, $X(2)$ 1.17, $X(3)$ 0.91 \AA^2]. As the co-ordinations of the atoms at the three positions are similar, this difference suggests significant variation in scattering power among the three positions. At this stage, the occupancy of the three X sites were set at 12 Sr + 2 Na, and the occupancies of the three sites were refined, with the total bulk-chemistry constrained to the above composition. The isotropic temperature-factor of the Mg position (0.50 \AA^2) suggested that it was fully occupied, although this is not in accord with the chemical analysis nor with the observed mean bond-length.

Both jarlite and metajarlite were examined qualitatively with the electron microprobe operating in the energy-dispersion mode. Both samples showed prominent Sr, Al and Na peaks, with smaller peaks of Mg, K, Ca and Ba; compositions are variable from point to point, and suggest replacement of Sr by K, Ca and Ba, with increasing Mg. Such variability could easily lead to high Mg in the crystal used for the collection of the intensity data.

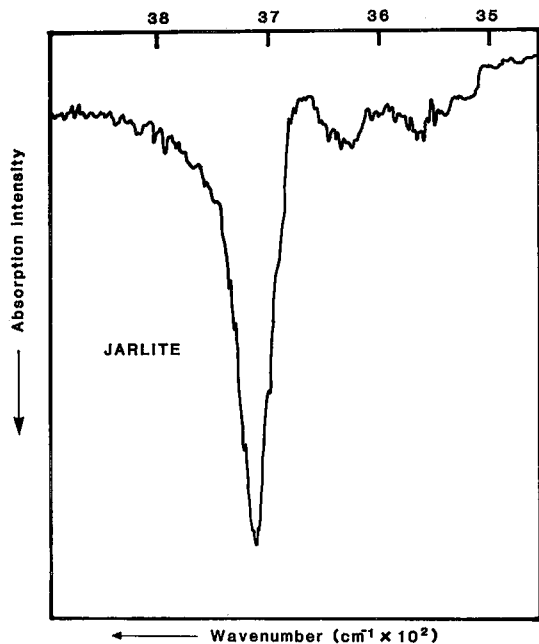


FIG. 1. The infrared spectrum of jarlite in the principal (OH) stretching region.

The fact that the content of hydroxyl calculated from the analytical data is ~ 4.0 suggests that OH occupies a special position of rank 4. The fact that Mg is variable in jarlite suggests that the O(1) position is occupied by OH or H₂O, depending on whether or not the Mg position is occupied; this would lead to a charge-balancing mechanism that also contributes to local bond-valence requirements. Full-matrix least-squares refinement of all variables for an anisotropic thermal model led to convergence at an *R* index of 5.3%. The vibration ellipsoids of the atoms occupying the Na, Mg and O(1) positions were nonpositive definite. The equivalent isotropic temperature-factors suggest that these sites are fully occupied; attempts to refine the occupancies were unsuccessful. One might suspect positional disorder, with the possible occurrence of vacancies at the Mg position, but this was not apparent on Fourier maps. The inadequacy of the model in this regard may result from systematic error in the intensity data due to the high absorption. Final parameters are given in Tables 3 and 4; observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Interatomic distances and angles, and the magnitudes and orientations of the principal axes of the thermal ellipsoids, calculated with the program ERRORS (L.W. Finger, pers. comm.), are given in Tables 5 and 6.

TABLE 3. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE-FACTORS FOR JARLITE

		x	y	z	Bequiv. (<i>R</i> ²)
X(1)	2a	0	0	0	0.71(7)
X(2)	4i	0.2601(1)	0	0.1232(2)	0.85(5)
X(3)	8j	0.35030(7)	0.1964(1)	0.6966(1)	0.80(3)
Al(1)	4i	0.1640(3)	0	0.5412(7)	0.78(7)
Al(2)	8j	0.1073(2)	0.2458(3)	0.7982(4)	0.71(5)
Na	2b	0	1/2	0	1.4(2)
Mg	2d	0	1/2	1/2	0.8(1)
O(1)	4i	0.4290(8)	0	0.7078(14)	0.8(2)
F(2)	4i	0.2435(7)	0	0.7562(14)	1.5(2)
F(3)	4i	0.0944(9)	0	0.3174(16)	2.7(2)
F(4)	8j	0.1161(5)	0.3705(7)	0.9688(9)	1.2(1)
F(5)	8j	0.2276(5)	0.1168(7)	0.4539(10)	1.5(1)
F(6)	8j	0.2181(4)	0.2594(7)	0.8061(9)	1.3(1)
F(7)	8j	0.0034(4)	0.2280(7)	0.2100(10)	1.5(1)
F(8)	8j	0.0881(6)	0.3627(9)	0.6121(11)	2.3(2)
F(9)	8j	0.0984(5)	0.1216(9)	0.6195(11)	2.3(2)
F(10)	8j	0.1274(4)	0.1350(7)	0.9918(9)	1.2(1)

TABLE 4. ANISOTROPIC TEMPERATURE-FACTORS ($\times 10^4$)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
X(1)	4(1)	23(2)	25(5)	0	-8(1)	0
X(2)	8(1)	21(2)	38(4)	0	2(1)	0
X(3)	6(1)	26(1)	26(2)	1(1)	-3(1)	0(1)
Al(1)	10(2)	22(4)	14(7)	0	-3(3)	0
Al(2)	7(1)	20(2)	20(6)	1(1)	-3(2)	1(3)
Na	6(3)	77(11)	0(15)	0	-5(6)	0
Mg	8(3)	28(7)	12(12)	0	-7(5)	0
O(1)	17(5)	11(8)	-5(17)	0	-12(7)	0
F(2)	12(4)	48(9)	30(17)	0	-18(7)	0
F(3)	38(7)	55(11)	51(21)	0	-29(9)	0
F(4)	19(3)	21(6)	36(12)	0(3)	1(5)	-1(7)
F(5)	15(3)	33(6)	65(14)	-4(3)	2(5)	20(7)
F(6)	8(2)	48(7)	45(12)	-10(3)	6(5)	-14(7)
F(7)	6(2)	51(7)	73(14)	-1(3)	1(4)	-1(8)
F(8)	26(4)	64(9)	59(14)	4(5)	0(6)	30(9)
F(9)	22(3)	64(8)	71(15)	3(4)	-4(6)	-37(9)
F(10)	11(3)	43(7)	35(12)	1(3)	1(4)	16(7)

DISCUSSION

Description of the structure

In the jarlite structure, there are two crystallographically unique Al positions, with point symmetries *m* and 1, respectively. They are each coordinated by six fluorine atoms arranged in a slightly distorted octahedral array. There is one Mg position with point symmetry 2/*m*; it is surrounded by a slightly distorted octahedral array of four fluorine and two oxygen atoms, the latter being in a *trans* configuration. There is one position completely occupied by Na, point symmetry 2/*m*, that is surrounded by four fluorine and two oxygen atoms with the latter in a *trans* configuration. There are three

TABLE 5. INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN JARLITE

Al(1)-F(2)	1.795(10)	Na-O(1) x2	2.185(10)
Al(1)-F(3)	1.765(12)	Na-F(4) x4	2.368(7)
Al(1)-F(5) x2	1.813(8)	<Na-O,F>	2.307
Al(1)-F(9) x2	1.842(9)		
<Al(1)-F>	1.812	X(2)-F(2)	2.616(10)
		X(2)-F(4) x2	2.616(8)
Al(2)-F(4)	1.816(8)	X(2)-F(5) x2	2.848(8)
Al(2)-F(6)	1.762(7)	X(2)-F(6) x2	2.662(8)
Al(2)-F(7)	1.763(8)	X(2)-F(10) x2	2.596(7)
Al(2)-F(8)	1.828(9)	<X(2)-O>	2.671
Al(2)-F(9)	1.850(9)		
Al(2)-F(10)	1.822(8)	X(3)-O(1)	2.461(6)
<Al(2)-F>	1.807	X(3)-F(2)	2.811(7)
		X(3)-F(4)	2.480(7)
Mg-O(1) x2	2.060(12)	X(3)-F(5)	2.499(7)
Mg-F(8) x4	2.090(9)	X(3)-F(5) ^f	2.502(7)
<Mg-O,F>	2.080	X(3)-F(6)	2.495(7)
		X(3)-F(7)	2.433(7)
X(1)-F(3) x2	2.475(11)	X(3)-F(8)	2.697(9)
X(1)-F(7) x4	2.892(8)	X(3)-F(10)	2.866(7)
X(1)-F(10) x4	2.513(7)	<X(3)-O,F>	2.583
<X(1)-F>	2.657		
Al(1) octahedron			
F(2)-Al(1)-F(5) x2	87.5(5)	F(2)-F(5) x2	2.495(11)
F(2)-Al(1)-F(9) x2	94.4(4)	F(2)-F(9) x2	2.669(12)
F(3)-Al(1)-F(5) x2	88.3(5)	F(3)-F(5) x2	2.493(13)
F(3)-Al(1)-F(9) x2	89.7(5)	F(3)-F(9) x2	2.543(13)
F(5)-Al(1)-F(5)	88.4(6)	F(5)-F(5)	2.527(15)
F(5)-Al(1)-F(9) x2	90.2(4)	F(5)-F(9) x2	2.588(12)
F(9)-Al(1)-F(9)	91.3(6)	F(9)-F(9)	2.633(19)
<F-Al(1)-F>	90.0	<F-F>	2.561
Al(2) octahedron			
F(4)-Al(2)-F(6)	88.8(4)	F(4)-F(6)	2.503(10)
F(4)-Al(2)-F(7)	92.3(4)	F(4)-F(7)	2.582(10)
F(4)-Al(2)-F(8)	88.0(4)	F(4)-F(8)	2.531(10)
F(4)-Al(2)-F(10)	89.4(3)	F(4)-F(10)	2.558(10)
F(6)-Al(2)-F(8)	88.9(4)	F(6)-F(8)	2.514(11)
F(6)-Al(2)-F(9)	90.9(4)	F(6)-F(9)	2.575(11)
F(6)-Al(2)-F(10)	90.8(4)	F(6)-F(10)	2.551(10)
F(7)-Al(2)-F(8)	92.1(4)	F(7)-F(8)	2.585(11)
F(7)-Al(2)-F(9)	88.0(4)	F(7)-F(9)	2.510(11)
F(7)-Al(2)-F(10)	88.3(4)	F(7)-F(10)	2.498(10)
F(8)-Al(2)-F(9)	90.6(4)	F(8)-F(9)	2.614(13)
F(8)-Al(2)-F(10)	92.1(4)	F(8)-F(10)	2.643(11)
<F-Al(2)-F>	90.0	<F-F>	2.555
Mg octahedron			
O(1)-Mg-F(8) x4	81.8(3)	O(1)-F(8) x4	2.718(12)
O(1)-Mg-F(8) ^f x4	98.2(3)	O(1)-F(8) ^f x4	3.137(14)
F(8)-Mg-F(8) ^f x2	89.4(5)	F(8)-F(8) ^f x2	2.941(17)
F(8)-Mg-F(8) ^f x2	90.6(5)	F(8)-F(8) ^f x2	2.971(19)
<F-Mg-O,F>	90.0	<F-F>	2.937
Na octahedron			
O(1)-Na-F(4) x4	99.6(3)	O(1)-F(4) x4	3.480(12)
O(1)-Na-F(4) ^f x4	80.4(3)	O(1)-F(4) ^f x4	2.942(12)
F(4)-Na-F(4) ^f x2	72.5(4)	F(4)-F(4) ^f x2	2.802(14)
F(4)-Na-F(4) ^f x2	107.5(4)	F(4)-F(4) ^f x2	3.819(14)
<F-Na-O,F>	90.0	<F-O,F>	3.244

TABLE 6. VIBRATION ELLIPSOIDS

	R.M.S. displacement	Angle to X-axis	Angle to Y-axis	Angle to Z-axis
X(1)	0.025(22) ^R	46(3) ⁰	90 ⁰	56(3) ⁰
	0.111(5)	44(3)	90	146(3)
	0.118(5)	90	0	90
X(2)	0.094(5)	48(20)	90	54(20)
	0.103(5)	42(20)	90	144(20)
	0.113(4)	90	0	90
X(3)	0.063(4)	53(3)	92(2)	49(3)
	0.105(3)	38(3)	94(6)	139(3)
	0.125(3)	86(5)	4(5)	92(5)
Al(1)	0.054(17)	76(8)	90	26(8)
	0.113(9)	90	0	90
	0.118(9)	14(8)	90	116(8)
Al(2)	0.060(11)	64(8)	95(8)	38(8)
	0.104(7)	40(28)	119(37)	125(14)
	0.112(7)	62(33)	30(37)	104(23)
Na	non-positive definite			
	0.04(4)	68(12)	90	34(12)
Mg	0.12(2)	158(12)	90	56(12)
	0.13(2)	90	0	90
O(1)	non-positive definite			
F(2)	0.02(9)	58(8)	90	44(8)
	0.16(2)	32(8)	90	134(8)
	0.17(2)	90	0	90
F(3)	0.08(3)	69(5)	90	33(5)
	0.18(2)	90	0	90
	0.25(2)	21(5)	90	123(5)
F(4)	0.09(2)	85(9)	82(46)	19(19)
	0.11(2)	89(13)	172(45)	83(44)
	0.16(1)	6(9)	89(12)	107(9)
F(5)	0.10(2)	99(21)	132(12)	42(12)
	0.13(1)	150(15)	106(19)	104(20)
	0.17(1)	119(14)	46(9)	52(9)
F(6)	0.08(2)	25(26)	69(8)	88(37)
	0.10(1)	73(35)	99(15)	170(9)
	0.18(1)	108(6)	23(6)	100(7)
F(7)	0.09(2)	17(12)	88(7)	85(12)
	0.14(1)	73(12)	90(16)	175(12)
	0.17(1)	92(8)	2(7)	90(16)
F(8)	0.10(2)	83(7)	112(6)	29(6)
	0.18(1)	172(13)	96(24)	73(13)
	0.21(1)	93(26)	23(9)	67(10)
F(9)	0.10(2)	81(9)	65(6)	33(6)
	0.17(1)	155(10)	66(10)	81(10)
	0.22(1)	68(10)	37(8)	122(5)
F(10)	0.08(2)	83(20)	108(8)	27(15)
	0.12(1)	172(18)	96(13)	73(20)
	0.16(1)	94(13)	19(8)	71(8)

X (large cation) positions occupied predominantly by Sr + Na, with point symmetries $2/m$, m and 1 and site occupancies $X(1) = 0.91(2)\text{Sr} + 0.09\text{Na}$, $X(2) = 0.81(1)\text{Sr} + 0.19\text{Na}$, $X(3) = 0.87(2)\text{Sr} + 0.13\text{Na}$. The X(1) position is surrounded by ten fluorine atoms, the X(2) position is surrounded by nine fluorine atoms and the X(3) position is surrounded by eight fluorine and one oxygen atoms; details of the co-ordination polyhedra are given in Figure 2.

Compared with most of the other aluminofluoride minerals, the structure of jarlite is quite complicated. The Al(1) and Al(2) octahedra link to form a corner-sharing trimer of composition $[\text{Al}_3\text{F}_{16}]^{7-}$. These trimers are linked by the Mg and Na octahedra to

form corrugated sheets // (100) as shown in Figure 3. The linking Mg and Na octahedra form a vertex-sharing $[\text{MgNaF}_3\text{O}_2 \equiv (\text{M}\text{O}_5)_2]$ chain than runs parallel to Z within the corrugated sheet. The cross-linking role of the Mg octahedron is further shown in Figure 4, where it can be seen that adjacent sheets are staggered such that the corrugations intermesh to provide a denser packing of the sheets.

The packing of the X polyhedra is illustrated in Figure 5. The [10]-co-ordinated X(1) polyhedron is situated at the corners of the unit cell and at the C-face-centred position. The [9]-co-ordinated X(2) polyhedra lie on either side of X(1) in the mirror plane, forming an edge-sharing trimer. Adjacent trimers link in the Y direction through corner-sharing of adjacent X(2) polyhedra to form an open network or sheet of X(1) and X(2) polyhedra at $z=0$. One may also envisage this sheet as made of corner-linked

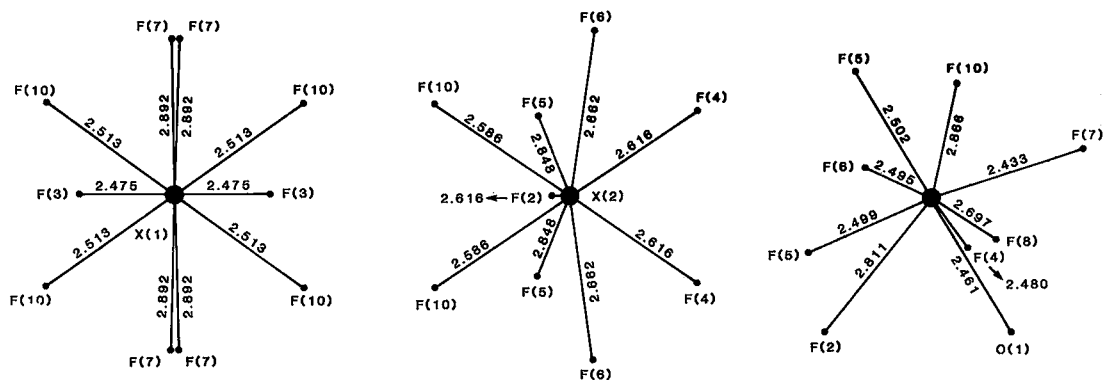


FIG. 2. The co-ordination details of the X(1), X(2) and X(3) sites in jarlite.

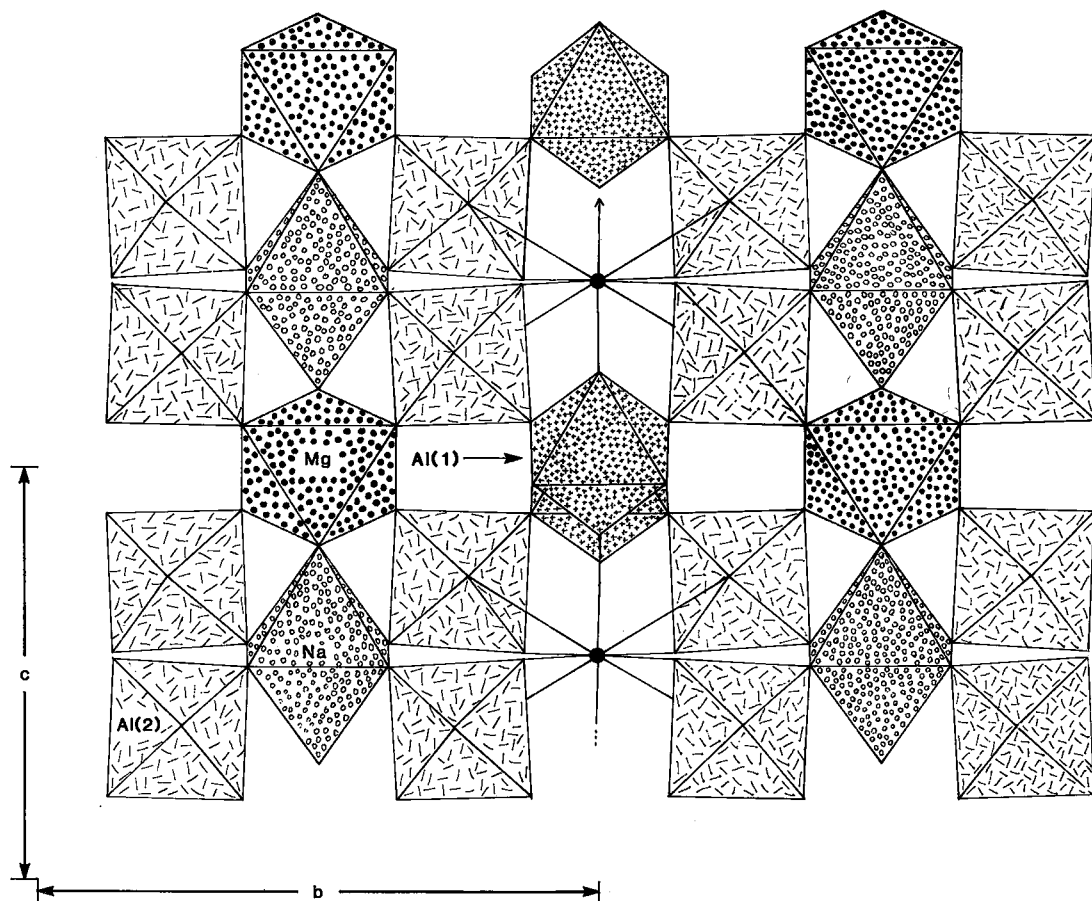


FIG. 3. The sheet of octahedrally co-ordinated cations in jarlite, viewed $\perp(100)$; the vertex-sharing $[MgNaF_8O_2]$ chain runs parallel to Z and is prominent in this view.

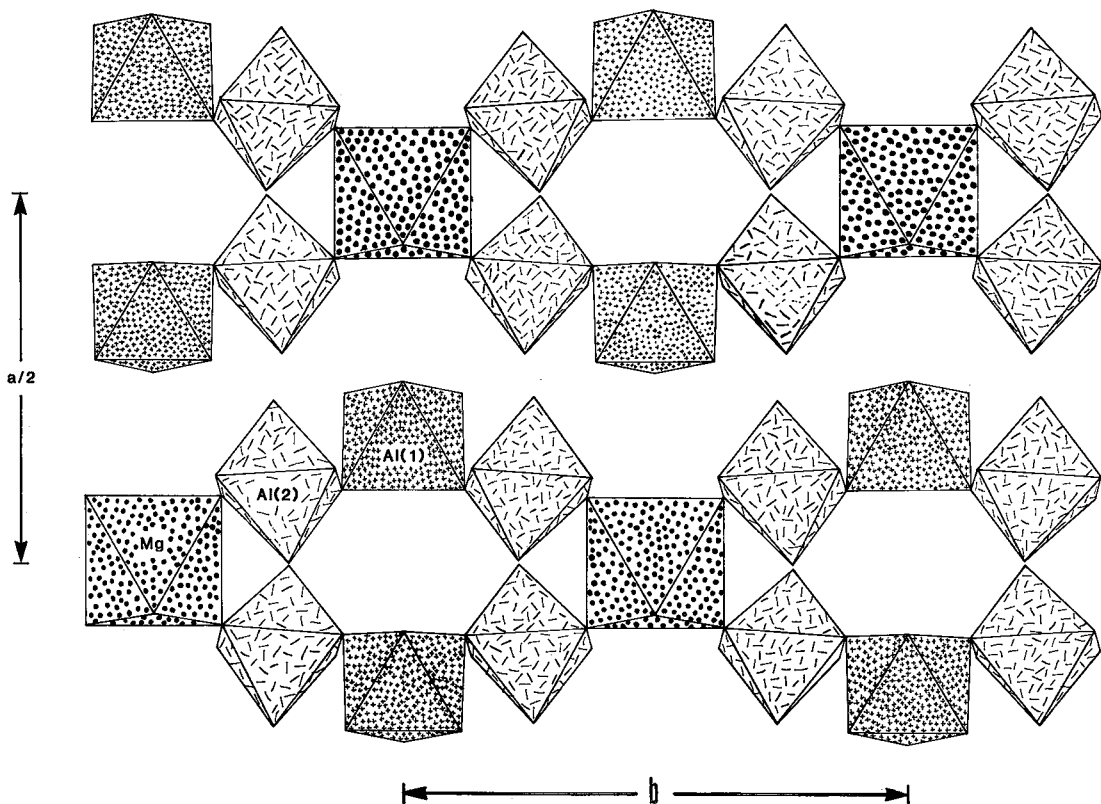


FIG. 4. The octahedral sheets in jarlite viewed edgewise \perp (001); note how the $[Al_3F_{16}]$ trimers in adjacent sheets are staggered, providing a closer packing of adjacent sheets.

chains of $X(2)$ polyhedra extending parallel to Y and cross-linked by edge-sharing to $X(1)$ polyhedra. The sheet is linked by corner-, face- and edge-sharing to $X(3)$ edge-sharing dimers above and below the level ($z=0$) of the $X(1)$ - $X(2)$ sheet.

Although the jarlite structure is a dense and fairly isodesmic structure, it can be considered as a layered structure in the compositional sense. At $z \sim 0$, the structure consists of Sr and Na polyhedra (Fig. 5) whereas at $z \sim 0.5$, the structure consists predominantly of Al and Mg octahedra (Fig. 3). It is interesting that the continuous sheets of octahedra identified in Figure 4 are actually orthogonal to this compositional layering. Jarlite does not seem to be closely related to any other of the aluminofluoride structures.

Chemical composition

The nominal formula of jarlite from the refined structure is $Na_2(Sr_{12}Na_2)Mg_2Al_{12}F_{64}(OH)_4$. This gives a calculated density of 3.80 g/cm^3 , much closer to the observed value of 3.89 than that given

by the previous formula. However, this agreement cannot be considered satisfactory, and suggests either that the formula is still deficient or that the density determinations are wrong. Certain aspects of the structure also suggest that this formulation is not completely satisfactory. Table 7 shows the empirical bond-valence table for jarlite, calculated using the curves of Brown (1981). The bond-valence sums around the $X(2)$ and Mg atoms (1.446 and 1.770 v.u.) are significantly less than their ideal values of 1.81 and 2.0 v.u. , respectively. This suggests the presence of additional components (other cations or vacancies) at these sites; since the scattering power at $X(2)$ seems reasonably satisfactory, this position may be partially vacant, with the total amount of Na at the $X(1,2,3)$ sites being less than 2.0 . The low bond-valence sum around Mg suggests that the site is not fully occupied, and this is in line with the bulk chemical composition of Table 1. Thus we may write a general formula for jarlite as: $Na_2(Sr_{13-x}Na_y \square_{1+x-y})Al_{12}Mg_zF_{64}(OH)_{y+2z-2x}(H_2O)_{4+2x-y-2z}$. Local bond-valence requirements suggest further restrictions on this formula; if the

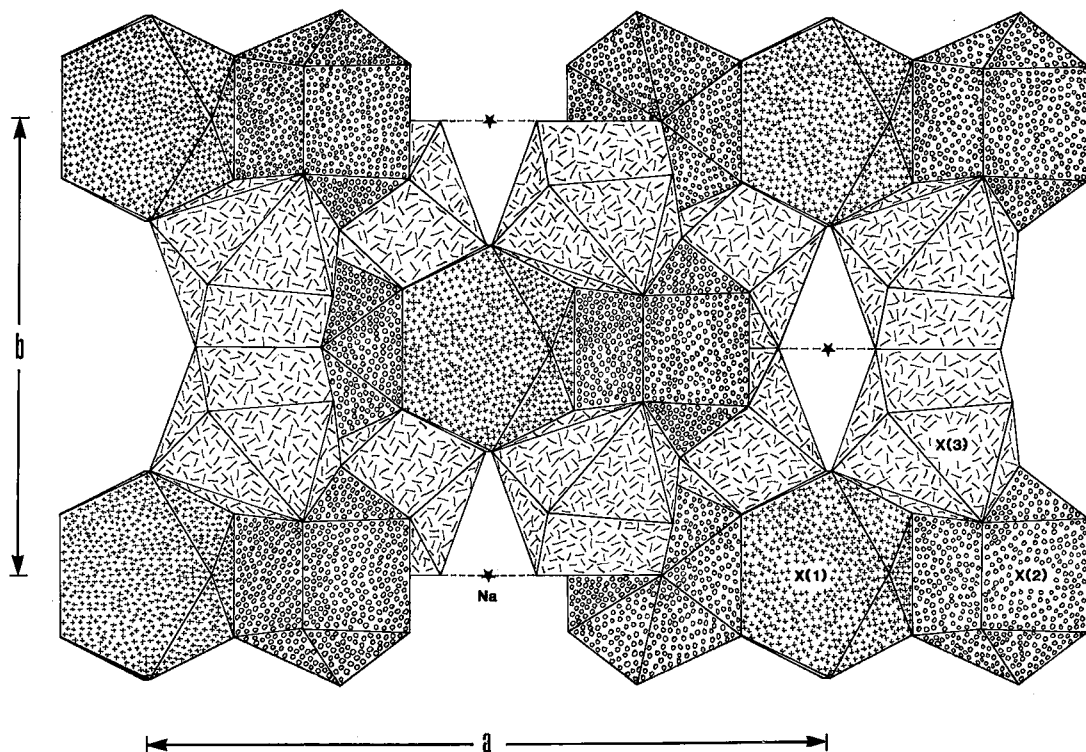


FIG. 5. The packing of the *X* polyhedra in jarlite, viewed $\perp(001)$; the density of the packing is very prominent in this view.

TABLE 7. EMPIRICAL BOND-VALENCE TABLE FOR JARLITE

	X(1)	X(2)	X(3)	Al(1)	Al(2)	Na	Mg	Σ
O(1)			$0.339x_2^2$			$0.279x_2^2$	$0.359x_2^2$	1.316*
F(2)		0.174	$0.130x_2^2$	0.507				0.941
F(3)	$0.238x_2^2$			0.549				0.787
F(4)		$0.173x_2^2$	0.228		0.482	$0.154x_2^4$		1.037
F(5)		$0.119x_2^2$	0.220 0.219	$0.486x_2^2$				1.044
F(6)		$0.161x_2^2$	0.222		0.549			0.932
F(7)	$0.119x_2^4$		0.247		0.549			0.915
F(8)		0.157			0.469		$0.263x_2^4$	0.889
F(9)				$0.455x_2^2$	0.446			0.901
F(10)	$0.223x_2^4$	$0.183x_2^2$	0.119		0.476			1.001
Σ	1.844	1.446	1.881	2.938	2.971	1.174	1.770	

*hydrogen bonds to F(8)

Mg site is occupied, the O(1) anion is OH, whereas if the Mg site is not occupied, the O(1) anion is H₂O, which hydrogen-bonds to adjacent F(8) anions to compensate for the absent Mg-F(8) bonds. Thus we may identify an ideal end-member formula Na₂(Sr₁₃□)Al₁₂□₂F₆₄(H₂O)₄ (with $x=y=z=0$ in

the above formula) in which there are two principal substitutions: 1) Sr, □ \rightleftharpoons Ca, Ba, 2Na, 2K and 2) □ + 2H₂O \rightleftharpoons Mg + 2(OH). These substitutions can proceed without any radical change in the structural arrangement, and are in line with the findings of Ferguson (1947, 1949) that jarlite and metajarlite are compositional variants of the same structure. Thus the compositions given in Table 2 correspond to the following x, y, z values in the above formula: jarlite $x \sim z \sim 1.1$, $y \sim 2.0$; metajarlite $x \sim z \sim 1.5$, $y \sim 2.0$.

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