

THE CRYSTAL STRUCTURE OF STENONITE AND THE CLASSIFICATION OF THE ALUMINOFLUORIDE MINERALS

F.C. HAWTHORNE

Department of Earth Sciences, University of Manitoba,
Winnipeg, Manitoba R3T 2N2

ABSTRACT

The crystal structure of stemonite, $\text{Sr}_2[\text{AlF}_5\text{CO}_3]$, a 5.450(2), b 8.704(2), c 13.150(3) Å, β 98.72(2)°, V 616.6(1) Å³, $Z = 4$, space group $P2_1/n$ has been solved by direct methods and refined to a residual $R = 6.0\%$ for 1219 observed (3σ) reflections. The AlO_6 octahedron (\emptyset : unspecified anion) and CO_3 triangle link by corner-sharing to form a finite $[\text{AlCO}_3\text{F}_5]^{4-}$ cluster. These clusters are linked into a three dimensional structure by [8]- and [9]-co-ordinated Sr cations. No structural relationship has been observed with any of the other aluminofluoride or carbonate-fluoride minerals.

A structural classification of the aluminofluoride minerals is set up on the premise that *crystal structures may be classified according to the polymerization of co-ordination polyhedra with higher bond-valences*. The minerals are divided first into two categories: (1) simple aluminofluorides and (2) compound aluminofluorides containing another strongly bonded complex anionic group. They are further subdivided according to the polymerization of the AlO_6 octahedra, in (1), or of these octahedra with other complex anionic groups, in (2). The aluminofluoride minerals are thus ordered into a coherent structural hierarchy. The degree of polymerization within the complex aluminofluorides is shown to be a function of the Lewis basicity of the constituent cation polyhedra.

Keywords: stemonite, crystal structure, classification, aluminofluoride minerals.

SOMMAIRE

On a déterminé la structure cristalline de la stemonite $\text{Sr}_2[\text{AlF}_5\text{CO}_3]$, a 5.450(2), b 8.704(2), c 13.150(3) Å, β 98.72(2)°, V 616.6(1) Å³, $Z = 4$, dans le groupe spatial $P2_1/n$ par méthodes directes et on l'a affinée sur 1219 réflexions observées (3σ) jusqu'au résidu $R = 6.0\%$. L'octaèdre AlO_6 (\emptyset anion non-spécifié) et le triangle CO_3 , unis par des sommets mis en commun, forment le groupe fini $[\text{AlCO}_3\text{F}_5]^{4-}$. Un assemblage tridimensionnel de tels groupes se forme lorsqu'ils se relient par des cations en coordination [8] et [9]. Aucune relation structurale n'a été observée avec un autre minéral, ni aluminofluorure, ni fluorocarbonate.

Une classification structurale des aluminofluorures a été établie; elle utilise la polymérisation des polyèdres de coordination à hautes valences de liaison comme principe de classement de leurs structures cristallines. Ces minéraux se divisent en deux catégories: (1) aluminofluorures simples et (2) aluminofluorures composés, contenant un groupement anionique complexe supplémentaire, fortement lié. Ils se subdivisent ensuite d'après la polymérisation des octaèdres

AlO_6 , en (1), ou de ces octaèdres avec anion complexe associé, en (2). Les minéraux de groupe des aluminofluorures s'ordonnent ainsi en une hiérarchie structurale cohérente. Le degré de polymérisation des aluminofluorures complexes se trouve être une fonction de la basicité de Lewis des polyèdres cationiques constitutifs.

(Traduit par la Rédaction)

Mots-clés: stemonite, structure cristalline, classification, aluminofluorures.

INTRODUCTION

Stemonite is a rare carbonate aluminofluoride mineral, $\text{Sr}_2\text{Al}(\text{CO}_3)\text{F}_5$, found at the Ivigtut cryolite locality, Greenland. It occurs mainly in the contact zone between siderite-cryolite and masses rich in fluorite. It is closely associated with the Sr aluminofluoride mineral *jarlite* and a wide variety of fluorides and sulfides (Pauly 1962). As part of a continuing study of the structures of the aluminofluoride minerals (Hawthorne 1982, 1983a, Hawthorne & Ferguson 1975, 1981, 1983), the structure of stemonite has been solved in order to determine its structural relationship to the other aluminofluoride minerals.

EXPERIMENTAL

Single-crystal X-ray precession photographs display monoclinic symmetry with systematic absences $h0l$, $h + l = 2n + 1$, $0k0$, $k = 2n + 1$; this uniquely determines the space group as $P2_1/n$ rather than $P2_1/m$ as given in previous work (Pauly 1962). Cell dimensions (Table 1) were determined by least-squares refinement of 15 reflections aligned automatically on a Syntex $P2_1$ 4-circle diffractometer.

A cleavage fragment $\sim 0.18 \times 0.10 \times 0.12$ mm 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 2242 reflections was measured over one asymmetric unit to a maximum 2θ of 60° ($\sin\theta/\lambda = 0.704$). The data were corrected for Lorentz, polarization, absorption (ψ scan method) and background effects, and were

TABLE 1. CRYSTALLOGRAPHIC DATA FOR STENONITE

a	5.450(2) Å	crystal size	~0.18x0.10x0.12mm
b	8.704(2) Å	Rad/mon	Mo/Gr
c	13.150(3) Å	total F _o	2242
β	98.72(2)°	No. F _o > 3σ	1219
Space Group	P2 ₁ /n	Final R(obs)	6.0%
D _{calc}	3.847 Mg m ⁻³	μ(cm ⁻¹)	183 cm ⁻¹
Unit-cell contents:	4[Sr ₂ AlF ₅ CO ₃]		
Temperature-factor form:	exp[-∑ _{i=1} ³ ∑ _{j=1} ³ h _i h _j β _{ij}]		
	R = ∑(F _o - F _c) / ∑ F _o		
	R _w = [∑w(F _o - F _c) ² / ∑wF _o ²] ^{1/2} , w = 1		

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 2242 unique reflections, 1219 were considered as observed.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from Cromer & Mann (1968), with coefficients of anomalous dispersion 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 compatible with the assigned formula for stenorite. The structure refined rapidly to *R* and *R_w* indices of 6.7 and 7.3% with individual isotropic temperature-factors. Temperature factors were con-

TABLE 2. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE-FACTORS FOR STENONITE

	x	y	z	B _{equiv.} (Å ²)
Sr(1)	0.2163(3)	0.3597(4)	0.9104(1)	1.57(4)
Sr(2)	0.2084(3)	-0.1108(5)	0.9014(1)	1.71(4)
Al	0.8666(9)	0.1271(9)	0.6689(3)	1.58(7)
C	0.3136(32)	0.8774(27)	0.1380(11)	1.9(2)
F(1)	0.1998(24)	0.2245(12)	0.0905(8)	2.2(2)
F(2)	0.1754(26)	0.5047(14)	0.0873(8)	2.5(2)
F(3)	0.5634(23)	0.2280(12)	0.2349(8)	2.0(2)
F(4)	0.5524(25)	0.5265(12)	0.2264(9)	2.2(2)
F(5)	0.5827(18)	0.3707(15)	0.0698(6)	1.7(1)
O(1)	0.4979(22)	0.8773(22)	0.0877(8)	2.0(2)
O(2)	0.0919(20)	0.8759(17)	0.0902(8)	1.8(2)
O(3)	0.3576(21)	0.8695(21)	0.2356(9)	2.4(2)

TABLE 3. ANISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS*

	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Sr(1)	156(5)	44(3)	23(1)	1(3)	9(1)	-2(1)
Sr(2)	158(5)	55(4)	24(1)	6(3)	10(1)	-1(1)
Al	169(15)	43(4)	22(2)	1(11)	8(5)	5(4)
C	226(55)	34(13)	29(7)	47(33)	6(16)	-6(13)
F(1)	245(46)	72(12)	22(5)	-53(20)	12(13)	-12(7)
F(2)	253(49)	113(16)	21(6)	55(24)	29(14)	3(7)
F(3)	210(42)	60(12)	24(6)	47(19)	12(13)	4(6)
F(4)	236(45)	63(12)	29(6)	-53(20)	13(13)	-4(7)
F(5)	213(33)	28(8)	29(5)	17(23)	31(10)	-7(7)
O(1)	173(38)	64(12)	32(6)	-36(32)	26(12)	3(10)
O(2)	145(34)	61(12)	27(5)	-23(24)	6(11)	7(9)
O(3)	134(37)	105(16)	38(7)	21(29)	24(13)	1(12)

*β_{ij} = β_{ij} × 10⁴

verted to the anisotropic form given in Table 1, and full-matrix least-squares refinement of all variables resulted in convergence at *R* indices of 6.0 (observed) and 10.9% (all data) and *R_w* indices of 6.6

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES IN STENONITE

Al-F(1)	1.810(12)		
Al-F(2)	1.793(13)		
Al-F(3)	1.792(12)	C-O(1)	1.284(19)
Al-F(4)	1.775(13)	C-O(2)	1.275(19)
Al-F(5)	1.885(10)	C-O(3)	1.271(17)
Al-O(3)	1.880(12)	<C-O>	1.277
<Al-β>	1.823		
Sr(1)-F(1)	2.658(11)	Sr(2)-F(1)	2.451(13)
Sr(1)-F(2)	2.685(11)	Sr(2)-F(3)	2.545(11)
Sr(1)-F(2)'	2.444(13)	Sr(2)-F(4)	2.443(12)
Sr(1)-F(3)	2.454(10)	Sr(2)-F(5)	2.535(12)
Sr(1)-F(4)	2.548(12)	Sr(2)-O(1)	2.578(16)
Sr(1)-F(5)	2.668(9)	Sr(2)-O(1)'	2.707(11)
Sr(1)-F(5)'	2.586(13)	Sr(2)-O(2)	2.632(14)
Sr(1)-O(1)	2.583(17)	Sr(2)-O(2)'	2.656(10)
Sr(1)-O(2)	2.651(13)	<Sr(2)-β>	2.568
<Sr(1)-β>	2.586		
AlO ₅ octahedron			
F(1)-F(2)	2.443(12)	F(1)-Al-F(2)	85.4(5)
F(1)-F(3)	2.529(17)	F(1)-Al-F(3)	89.2(6)
F(1)-F(5)	2.494(17)	F(1)-Al-F(5)	84.9(6)
F(2)-F(4)	2.542(18)	F(2)-Al-F(4)	90.9(7)
F(2)-F(5)	2.549(16)	F(2)-Al-F(5)	87.7(6)
F(3)-F(4)	2.601(11)	F(3)-Al-F(4)	93.6(5)
F(3)-F(5)	2.517(15)	F(3)-Al-F(5)	86.4(6)
F(4)-F(5)	2.491(15)	F(4)-Al-F(5)	85.8(6)
O(3)-F(1)	2.672(17)	O(3)-Al-F(1)	92.8(7)
O(3)-F(2)	2.640(17)	O(3)-Al-F(2)	91.9(7)
O(3)-F(3)	2.684(18)	O(3)-Al-F(3)	93.9(7)
O(3)-F(4)	2.729(18)	O(3)-Al-F(4)	96.6(7)
<β-β>	2.574	<β-Al-β>	89.9
CO ₃ triangle			
O(1)-O(2)	2.218(16)	O(1)-C-O(2)	120(1)
O(1)-O(3)	2.196(15)	O(1)-C-O(3)	119(1)
O(2)-O(3)	2.217(15)	O(2)-C-O(3)	121(2)
<O-O>	2.210	<O-C-O>	120

TABLE 5. VIBRATION ELLIPSOIDS FOR STENONITE

	R.M.S. displacement	Angle to X-axis	Angle to Y-axis	Angle to Z-axis
Sr(1)	0.128(4) (\AA^2)	94(6) ^o	18(12) ^o	72(12) ^o
	0.142(2)	89(11)	73(12)	161(12)
	0.151(2)	4(6)	87(7)	97(10)
Sr(1)	0.141(3)	112(11)	48(28)	46(33)
	0.145(3)	105(20)	53(26)	136(33)
	0.155(3)	24(12)	63(13)	95(9)
Al	0.121(9)	88(13)	35(16)	125(16)
	0.142(9)	91(25)	125(16)	144(16)
	0.158(7)	2(18)	92(20)	98(18)
C	0.09(3)	113(12)	25(11)	79(21)
	0.16(2)	103(28)	87(20)	158(28)
	0.20(3)	27(15)	66(11)	108(25)
F(1)	0.12(2)	74(15)	52(15)	46(22)
	0.15(2)	124(14)	122(19)	44(22)
	0.21(2)	39(12)	126(10)	86(11)
F(2)	0.12(2)	114(15)	83(12)	17(18)
	0.17(2)	133(14)	52(11)	107(18)
	0.23(2)	53(10)	39(11)	86(7)
F(3)	0.12(2)	57(13)	144(11)	83(35)
	0.14(2)	78(22)	96(31)	173(35)
	0.20(2)	36(11)	55(10)	91(15)
F(4)	0.13(2)	58(11)	34(9)	84(24)
	0.16(2)	79(17)	85(22)	174(24)
	0.21(2)	35(10)	124(9)	91(15)
F(5)	0.09(3)	108(11)	26(13)	69(11)
	0.15(2)	120(18)	116(13)	36(15)
	0.19(1)	36(15)	86(13)	63(16)
O(1)	0.12(3)	45(12)	51(13)	116(17)
	0.17(2)	87(40)	121(43)	149(35)
	0.18(2)	45(13)	126(35)	74(52)
O(2)	0.13(2)	48(32)	46(16)	112(39)
	0.15(2)	121(44)	81(33)	139(40)
	0.18(2)	57(22)	135(15)	122(26)
O(3)	0.13(2)	17(14)	101(15)	111(16)
	0.18(2)	101(20)	80(43)	158(18)
	0.20(2)	77(16)	15(30)	85(42)

(observed) and 12.9% (all data). Final parameters are given in Tables 2 and 3; 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 4 and 5.

DISCUSSION

Description of the structure

Carbon is surrounded by a triangle of oxygen atoms; the $\langle C-O \rangle$ distance of 1.28 Å is typical of inorganic carbonates, and the individual C-O bonds show no significant deviation from the mean value. The O-C-O bond angles do not deviate significantly from their ideal values of 120°, and there is no significant variation in the O-O edges of the CO₃ group. Al is co-ordinated by five fluorine atoms and one oxygen atom in a distorted octahedral arrangement. The Al-O (O: unspecified ligand) bond lengths

TABLE 6. EMPIRICAL BOND-VALENCE TABLE FOR STENONITE*

	Sr(1)	Sr(2)	Al	C	Σ
F(1)	0.179	0.257	0.489		0.925
F(2)	0.171	0.260	0.509		0.940
F(3)	0.256	0.217	0.510		0.983
F(4)	0.216	0.261	0.532		1.009
F(5)	0.176	0.221	0.411		1.012
O(1)	0.271	0.274		1.330	2.070
		0.195			
O(2)	0.226	0.237		1.372	2.058
		0.223			
O(3)			0.531	1.391	1.922
Σ	1.957	1.885	2.982	4.093	

* calculated from the parameters of Brown (1981); bond-valences in v.u. (valence units).

fall into two populations with mean values of 1.79 Å and 1.88 Å, respectively; the short bond-lengths involve ¹⁹F whereas the long bond-lengths involve ¹⁸F and O; as indicated by Table 6, this can be rationalized in terms of the anion bond-valence requirements. There are two Sr positions in stenorite, a [9]-co-ordinate site surrounded by seven fluorine and two oxygen atoms and an [8]-co-ordinate site surrounded by four fluorine and four oxygen atoms. A comparison of the observed mean bond-lengths in the large-cation co-ordination polyhedra with the sum of the relevant cation and anion radii [Sr(1) 2.59(2.63), Sr(2) 2.57(2.60) Å] for observed (calculated) distances shows that the observed distances are slightly less than expected. However, they are in line with mean bond-lengths in similar polyhedra in boggildite (Hawthorne 1982).

The empirical bond-valence table for stenorite, calculated using the curves of Brown (1981), is given in Table 6. The observed bond-length variations may be rationalized in terms of the anion bond-valence requirements. This is particularly noticeable with regard to the one long Al-F bond, which is to F(5), the only [4]-co-ordinate F atom in the structure.

Views of the stenorite structure are given in Figures 1 and 2. The Al octahedron and the CO₃ triangle are linked by corner-sharing to form a finite [AlCO₃F₅]⁴⁻ cluster; this motif is shaded in Figures 1 and 2, but in Figure 1 the CO₃ group is seen edge-on and the cluster resembles an angular tadpole. These clusters are linked into a three-dimensional structure by [8]- and [9]-co-ordinate Sr cations. The [AlCO₃F₅]⁴⁻ finite cluster is the principal motif of the stenorite structure, and as there are no other carbonate aluminofluorides, the structure is not related to that of any other aluminofluoride mineral.

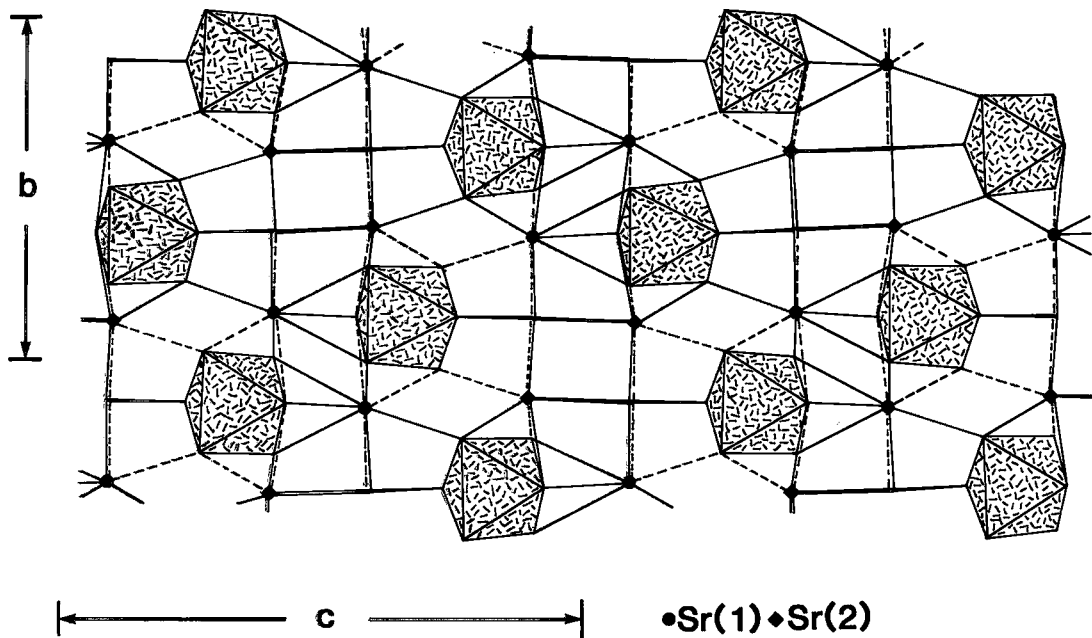


FIG. 1. The crystal structure of stemonite projected on (100). The AlO_6 octahedra are shaded with dashes. The CO_3 triangles are seen edge-on in this view and are perpendicular to the Y axis; they link to the octahedra on the opposite side to the $\text{Sr}(1)$ and $\text{Sr}(2)$ cations.

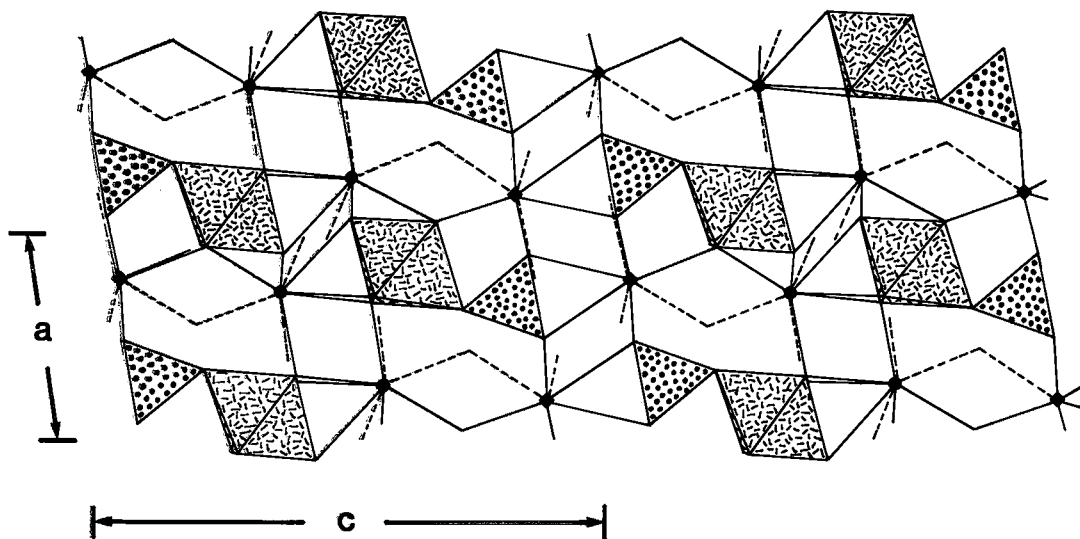


FIG. 2. The crystal structure of stemonite projected on (010). The AlO_6 octahedra and the CO_3 triangles are shaded with dashes and dots, respectively.

Hawthorne (1982) proposed that the AlO_6 and CO_3 groups in stemonite should be linked together. The rationale for this prediction is as follows: the oxygen atoms of the $(CO_3)^{2-}$ group have the largest bond-valence deficiency of the strongly bonded cation co-ordination polyhedra in the structure, the C-O contribution being 1.33 v.u. The resulting deficiency of 0.67 v.u. is most easily and simply satisfied by further bonding to an Al to contribute a further 0.50 v.u.; this gives a total of 1.83 v.u., and the remaining bond-valence requirements can be satisfied by further bonding to the alkaline earth cations. Although the two polyhedra are linked, a convincing argument cannot be developed along similar lines as to the type of octahedral-triangular linkage actually found. Within the limits of the stemonite stoichiometry, the AlO_6 and CO_3 groups can link into an $[Al(CO_3)F_3]^{4-}$ finite cluster, an $[Al(CO_3)F_4]^{3-}$ chain and an $[Al(CO_3)F_3]^{2-}$ sheet; these motifs require Sr_2 , Sr_2F and Sr_2F_2 , respectively, to produce the stoichiometry of stemonite. Detailed bond-valence considerations of the possible structures give no indication as to preferred configuration. It may be significant that the observed configuration has all the F atoms bonded to Al.

Classification of the aluminofluoride minerals

Hawthorne (1983b) has proposed that *crystal*

(*mineral*) structures may be ordered or classified according to the polymerization of those co-ordination polyhedra (not necessarily of the same type) with highest bond-valences. Although such an approach to mineral classification is not restricted by chemistry, it may be applied to minerals of a particular chemical type; here I consider the aluminofluoride minerals. The classification is based on the type of polymerization of the AlO_6 octahedra, together with any other strongly bonded complex anionic groups that occur. The minerals considered are listed in Table 7; they are divided into two categories, the first being the aluminofluorides proper, and the second being the 'mixed' aluminofluorides that contain another complex anionic group.

Pabst (1950) introduced a structural classification of the aluminofluoride minerals proper based on the

TABLE 8. STRUCTURAL CLASSIFICATION OF THE ALUMINOFLUORIDE MINERALS

Group	Structural motif	Mineral
SIMPLE ALUMINOFLUORIDES		
Separate octahedra	Isolated octahedra $[AlO_6]$	Carlhinzite(?) Colquirite Cryolite Cryolithionite Elpasolite Pachnolite Thomsenolite Usovite Weberite
	Edge-sharing dimer $[Al_2O_{10}]$	Gearksutite(?) Tikhonokovite
Finite clusters	Corner-sharing trimer $[Al_3O_{16}]$	Calcjarlite Jarlite
	Edge-sharing chains $[AlO_4]$	Prosopite
Chains	Corner-sharing sheets $[Al_3O_{14}]$	Chiolite
Sheets	Corner-sharing framework $[AlO_3]$	Ralstonite
COMPOUND ALUMINOFLUORIDES		
Separate polyhedra	Isolated octahedra and tetrahedra: $[AlO_6]_2[TO_4]$	Chukhrovite
	Isolated octahedral dimers and tetrahedra: $[Al_2O_{10}][TO_4]$	Creedite
Finite clusters	Corner-sharing $[AlO_5CO_3]$	Stenonite
	Corner-sharing $[Al_2PO_4F_9]$	Bøggildite
Chains	Edge-sharing octahedra cross-linked by tetrahedra	Topaz

TABLE 7. THE ALUMINOFLUORIDE MINERALS

MINERAL	FORMULA	REFERENCE
Calcjarlite ¹	see jarlite (?)	-
Carlhinzite ²	$Ca_2AlF_7 \cdot H_2O$	-
Chiolite	$Na_3Al_2F_{12}$	Brosset (1938)
Colquirite	$LiCaAlF_6$	Viebahn (1971)
Cryolite	Na_3AlF_6	Hawthorne & Ferguson (1975)
Cryolithionite	$Na_3Al_2Li_3F_{12}$	Geller (1971)
Elpasolite	K_2NaAlF_6	Morss (1974)
Gearksutite ³	$CaAl(OH)F_4 \cdot H_2O$	-
Jarlite	$Na_2(Sr, Na, Ca)_{14}Al_{12}(Mg, Ca)_2F_{64}(OH, H_2O)_4$	Hawthorne (1983a)
Pachnolite	$NaCaAlF_6 \cdot H_2O$	Hawthorne & Ferguson (1981, 1983)
Prosopite	$CaAl_2(OH, F)_8$	Giaccovazzo & Menchetti (1969)
Ralstonite	$Al_2(OH)_2F_8$	Pabst (1939)
Thomsenolite	$NaCaAlF_6 \cdot H_2O$	Cocco et al. (1967)
Tikhonokovite	$SrAl(OH)F_4 \cdot H_2O$	Pudovkina & Pyatenko (1967)
Usovite	$BaMgAl_2F_{12}$	Litvin et al. (1980)
Weberite	Na_2MgAlF_7	Giuseppetti & Tadini (1978)
Yaroslavite ⁴	$Ca_3Al_2F_{10}(OH)_2 \cdot H_2O$	-
Bøggildite	$Na_2Sr_2Al_2(PO_4)_9$	Hawthorne (1982)
Chukhrovite ⁵	$Ca_3(Y, Ce)Al_2(SO_4)F_{13} \cdot 10H_2O$	Bokiy & Gorogotskaya (1965)
Creedite	$Ca_3Al_2(SO_4)F_6(OH)_2 \cdot 2H_2O$	Bortsov et al. (1965)
Stenonite	$Sr_2Al(CO_3)F_5$	This study

¹presumably isostructural with jarlite. ²crystals unsuitable for structure work (Dunn et al. (1979)). ³Formula suggests isostructuralism with tikhonokovite, but no work has been done on this as yet. ⁴Pauly (1982) suggests that this is not a valid mineral species but may be a poorly analyzed sample of OH-bearing carlhinzite. ⁵The study of Mathew et al. (1981) suggests 12 H₂O rather than 10 H₂O.

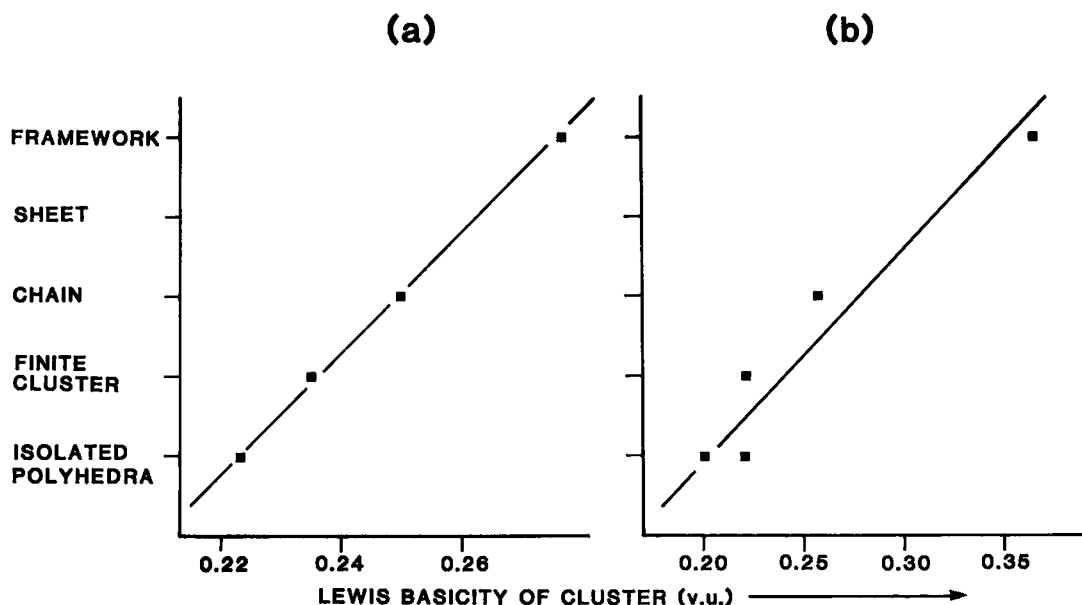


FIG. 3. Structure type in the compound aluminofluorides as a function of Lewis basicity of the cation polyhedra; (a) is plotted using basicity values for the individual polyhedra; (b) is plotted using basicity values for the heteropolyhedral clusters.

type of polymerization of the AlF_6 octahedra, listing the following types of structural motifs: (i) separate octahedra, (ii) chains, (iii) interrupted sheets, (iv) sheets, (v) interrupted frameworks, and (vi) frameworks. The term 'interrupted' is not useful with regard to the type of polymerization of the AlO_6 octahedra; hence we will dispense with categories (iii) and (v), and introduce an additional category, finite clusters. The resulting classification, together with the constituent minerals, is given in Table 8. Certain of the generalizations of Pabst (1950) require modification in light of the more recent structures of Table 7. Octahedra sharing an odd number of corners are found; they are a constituent of the $[Al_3O_{16}]$ trimer in jarlite. Edge-sharing octahedra are found, notably in the $[Al_2O_{10}]$ dimers in tikhonenkovite and creedite, and in the $[AlO_4]_{\infty}$ chain in prospite, although it may be significant that all of these minerals contain amounts of hydroxyl, unlike most of the remaining minerals.

For the compound aluminofluorides, in which there is an additional complex anion, the classification is based on the polymerization of the $[AlO_6]$ group and the complex anion. Although not normally thought of as an aluminofluoride mineral, topaz is included in Table 8 as a representative of the framework-type compound aluminofluoride

category; the paragenesis of topaz also suggests its inclusion in this group. Hawthorne (in prep.) has suggested that the degree of polymerization of the fundamental polyhedra in a structural hierarchy is a function of the Lewis basicity (Brown 1981; Hawthorne, in prep.) of these polyhedra. Figure 3 shows the structure type as a function of Lewis basicity of the polyhedra (calculated for a mean coordination number of [3] for the anion) in the compound aluminofluorides. As with the ${}^{vi}M^{iv}T_2O_n$ structures (Hawthorne 1983c), a well-developed relationship is exhibited, even with the small number of structure refinements available in this group.

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