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Painite, $CaZrB[Al_9O_{18}]$: Its crystal structure and relation to jeremejevite, $B_5[\square_3Al_6(OH)_3O_{15}]$, and fluoborite, $B_3[Mg_9(F, OH)_9O_9]$

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Abstract

Painite—$CaZrB[Al_9O_{18}]$, hexagonal $P6_3$, $a = 8.715(2)$, $c = 8.472(2)$Å, $Z = 2$—possesses a rigid and dense $[Al_9O_{18}]^{9-}$ octahedral framework, topologically identical to those found in jeremejevite, $B_5[\square_3Al_6(OH)_3O_{15}]$ and fluoborite, $B_3[Mg_9(F,OH)_9O_9]$. $R = 0.071$ for 1618 independent reflections.

The octahedral framework is linked to $[BO_3]^{3-}$ triangles and $[ZrO_6]^{8-}$ trigonal prisms at $\frac{1}{3}\frac{2}{3}z$ and a large pipe at $0\,0\,z$ is clogged with compressed $[CaO_6]^{10-}$ octahedra. Average interatomic distances are Ca–O = 2.398, Zr–O = 2.126, B–O = 1.380, Al(1)–O = 1.915, Al(2)–O = 1.918, and Al(3)–O = 1.914Å.

The octahedral framework in painite, resistant to attack by acids and bases, suggests a highly refractory phase and the possibility of other equally resistant compounds, hypothetical examples being $NaNb^{5+}B[Al_9O_{18}]$ and $\square U^{6+}B[Al_9O_{18}]$. In the latter, the pipe would be free from obstructions.

Introduction

Painite is a curious mineral species, first reported by Claringbull, Hey and Payne (1957) from the ruby mines of Mogok, Burma. It was found as a garnet-red 1.7 gram single hexagonal crystal of hardness 8. They proposed a formula $Ca_4SiBAl_{20}O_{38}$, the slight imbalance in charge due either to non-integral oxygen or total cations.

We continue to express interest in dense oxide structures, especially those of the aluminates. In addition, a structural relationship was suggested in the crystal cell data for jeremejevite, $Al_6(OH)_3(BO_3)_5$. Our findings reveal an elegant structure for painite, the aluminate framework of which is related to jeremejevite and to the octahedral framework of fluoborite, $Mg_3(F,OH)_3(BO_3)$. Finally, we demonstrate that the correct formula for painite is $CaZrB[Al_9O_{18}]$.

Experimental

A thin sawn plate of the type crystal (B.M. 1954, 192) from near Ohngaing village, Mogok, upper Burma, was kindly provided by Mr. Peter Embrey of the British Museum of Natural History. The chip selected for structure analysis was a flat fragment, measuring 0.31 × 0.22 × 0.10 mm along a_1, a_2^*, and c, respectively. Calibrated precession photographs established the cell data in Table 1.

Three-dimensional single-crystal X-ray diffraction intensities about the a_2-rotation axis were collected on a PAILRED semi-automated diffractometer with graphite monochromatized Mo$K\alpha_1$ ($\lambda = 0.70926$Å) radiation. With $2\theta_{\max} = 69.5°$, data were gathered through the k = 0- to 11-levels. Other salient details: scan speed 1°min^{-1}, aperture 2.0°, 20 second background measurements, half-scan range of 2.0° widening to 2.5° at higher levels. Reflection pairs of the type $I(hkl)$ and $I(hk\bar{l})$ were collected. An absorption correction was applied to the crystal using $u = 22.8$ cm^{-1}; approximating the shape of the chip by selecting seven facets, we employed the Gaussian integration method, described by Burnham (1966). This correction was small since maximum difference in transmission factors was about 5%. Additional corrections were made for Lorentz and polarization effects. Weights applied to the processed reflections included an uncertainty for the ν-angle maximum mis-setting of 0.1°, tilting error of 0.05°, average crystal size error of 0.008 mm, and the counting statistics. Two sets of Fo were available: those which were based on an average of $F(hkl)$ and $F(hk\bar{l})$ (centrosymmetric case) and separate $F(hkl)$ and $F(hk\bar{l})$ (noncentrosymmetric case).

During the crystal structure analysis, it was necessary to challenge the chemical composition of painite proposed by Claringbull *et al* (1957), and we submitted a fragment to electron probe analysis, performed by Dr. I. M. Steele. The crystal was homogeneous throughout and revealed major Ca, Zr, and Al with all other elements of atomic number greater than Na not detected. The standards selected were diopside (Ca), synthetic ZrO_2(Zr), and corundum (Al). Correction of the data utilized the ABFAN-2 program of Hadidiacos, Finger, and Boyd (1969). The results in Table 2 depart seriously fróm the original chemical analysis, with poor agreement for all the elements reported. We suspect that ZrO_2 (not reported in the earlier study) was in part coprecipitated with CaO and Al_2O_3, and in part reported as the contribution to SiO_2 which we found to be absent in the crystal (< 0.01%). Although we could not analyze boron, the structure analysis clearly revealed the presence of fully occupied $[BO_3]^{3-}$ triangles. The probe analysis is in satisfactory agreement with the proposed formula $CaZrBAl_9O_{18}$, which yields ρ = 4.01 gm cm^{-3}, in excellent agreement with the specific gravity of 4.01 reported by Claringbull *et al* (1957).

TABLE 1. Crystal Cell Parameters for Painite, Fluoborite, and Jeremejevite*

	Painite	Fluoborite	Jeremejevite
a(Å)	8.715(2)	9.06	8.56
c(Å)	8.472(2)	3.06	8.18
Z	2	2	2
space group	$P6_3$	$P6_3/m$	$P6_3/m$ (?)
formula unit	$CaZrAl_9O_{15}[BO_3]$	$Mg_3(F,OH)_3[BO_3]$	$Al_6(OH)_3[BO_3]_5$
axial ratios	0.970 (c/a)	1.013 (3c/a)	0.956 (c/a)
specific gravity[1]	4.01	2.89	3.28
density, gm cm^{-3}	4.01	2.82	3.24

*Cell parameters for fluoborite from Takéuchi (1950) and for jeremejevite from Golovastikov *et al.* (1955).

[1] Claringbull *et al.* (1957), for painite. The data for fluoborite and jeremejevite are from Geijer and Damour respectively, quoted in Palache *et al.* (1951).

Structure analysis and refinement

One of the reasons we investigated painite was due to an apparent relationship with jeremejevite, $Al_6(OH)_3(BO_3)_5$. Golovastikov, Belova, and Belov (1955), who approximately determined the crystal structure, established that for jeremejevite, $Z = 2$, $a = 8.56$, $c = 8.18$ Å, space group $P6_3/m$. We proposed that painite and jeremejevite possessed similar structures and that Al^{3+} in the former isomorphically replaced some of the B^{3+} in the latter compound. A three-dimensional Patterson synthesis $P(uvw)$, supported the isomorphism for the octahedral Al^{3+} and the anion frame, but the remaining cations were not clearly deciphered.

The $N(z)$ test on special reflections (see Howells, Phillips, and Rogers, 1950) and the $P(y)$ test on general reflections (see Srikrishnan and Parthasarathy, 1970) supported the centric group $P6_3/m$. A trial β-synthesis (Ramachandran and Srinivasan, 1970) yielded unexpected results: no isomorphism between B^{3+} and Al^{3+} was noted and, in addition, a strong density appeared at $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{4}$ and a weaker density at 000. We tentatively ascribed Ca(1) 0 0 0; Ca(2) $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{4}$; Al(1) $\frac{1}{3}$ 0 $\frac{1}{4}$ and Al(2) $\frac{1}{3}\,\frac{1}{3}$ 0.09. The anion frame agreed well with the jeremejevite model. Further β'-syntheses led to $R = 0.33$, and at this stage it was apparent that "Ca(2)" was some other more dense ionic species. Allowing its occupancy to vary, a trial least-squares refinement led to $R = 0.17$, whereupon B^{3+} was unambiguously located at $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{4}$. Further refinement converged to $R = 0.16$ and did not reduce further, despite a rather sharp and clean electron density map. We noted, however, that the Al^{3+} temperature factors were unexpectedly large (1.5 to 3.0Å^{-2}) and decided that the structure was in fact noncentrosymmetric, based on space group $P6_3$, and that the actual structure departed only slightly from centrosymmetry. Since correlations in parameters were high, two blocked matrices were refined in alternate sequence. We also concluded that the formula unit was in fact $CaZrBAl_9O_{18}$ and substituted the scattering curve for Zr in place of Ca at "Ca(2)". This conclusion was forced on the basis of site multiplicity refinement and inspection of interatomic distances. The parameters refined smoothly until R became 0.071 for all 1618 non-equivalent reflections, including $F(hkl)$ and $F(hk\bar{l})$ pairs. Inversion of the atomic coordinates did not materially affect the reliability index and it was not possible to select unambiguously the proper polar orientation of the structure. This study provides yet another example for which a crystal structure analy-

TABLE 2. Chemical Composition of Painite

	1	2	3
CaO	7.17	15.7	8.33
Al_2O_3	69.02	76.2	68.19
B_2O_3	n.d.	2.2.	5.17
ZrO_2	18.77	n.d.	18.31
SiO_2	absent	5.6	-
H_2O	n.d.	0.7	-
	94.96	100.4	100.00

[1] Electron probe analysis, this study (I. M. Steele, analyst).

[2] Claringbull *et al.* (1957).

[3] Computed for $CaZrB[Al_9O_{18}]$.

TABLE 3. Painite. Atomic Coordinates and Isotropic Thermal Vibration Parameters*

Atom	x	y	z	B(Å^2)
Zr	2/3	1/3	1/4	0.57(1)
Ca	0	0	0.4929(2)	1.23(2)
Al(1)	0.3329(1)	0.3373(1)	.7490(3)	.61(2)
Al(2)	.3425(2)	.3625(2)	.0791(1)	.63(2)
Al(3)	.3437(2)	.3596(2)	.4224(1)	.54(2)
B	1/3	2/3	.2495(4)	.84(8)
O(1)	.3992(3)	.5518(3)	.2495(4)	.81(3)
O(3)	.4052(3)	.5237(3)	.5919(3)	.69(4)
O(4)	.4060(4)	.5235(4)	.9070(3)	.54(3)
O(2)	.3281(3)	.2186(3)	.2503(5)	.69(3)
O(5)	.3019(3)	.1935(4)	.5807(3)	.58(3)
O(6)	.2983(4)	.1912(4)	.9165(3)	.73(4)

*Estimated standard errors refer to the last digit.

sis establishes the correct formula, and it is gratifying to note that the electron probe analysis supports our deduced formula. The lesson to be learned is that no wet chemical analysis should be trusted in the absence of some thorough qualitative results such as can be obtained from an emission spectrogram.

Programs used in this study included a locally modified version of the familiar ORFLS program of Busing, Martin, and Levy (1962). It has options for varying the proportionate contribution of two scattering curves at any site, multiple blocked refinements, retrieval of bond distances at any stage and options for β- and γ'-syntheses. The scattering curves for Ca^{2+}, Zr^{4+}, Al^{3+}, B^{0}, and O^{1-} derive from Cromer and Mann (1968), and the anomalous dispersion corrections for Ca, Zr and Al from Cromer and Liberman (1970). The secondary extinction correction (Zachariasen, 1968) converged to $c_0 = 3.0(3) \times 10^{-5}$ and the scale factor, $s = 6.31(4)$ where $F_o = sF_c$.

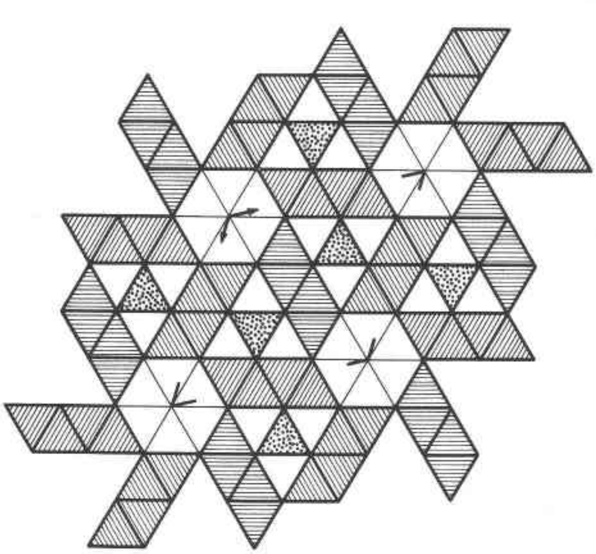

FIG. 1. Idealized fluoborite structure projected on the regular triangular net {3,6}. The $MgO_3(F,OH)_3$ octahedra are ruled and the $[BO_3]$ triangles are stippled. Note the missing anion at the origin and the resulting large pipelike channel.

The polar nature of the structure must be accepted as fact and obtains from slight deviations of the $[Al_9O_{18}]^{9-}$ framework from centrosymmetry. Golovastikov *et al.* (1955) proposed the centric group, $P6_3/m$, for the structurally related jeremejevite, but their data and refinement are crude. We suspect that a more precise refinement of the jeremejevite structure will reveal the space group $P6_3$; this is supported by a positive piezoelectric test reported in Palache, Berman, and Frondel (1951) obtained by the oscilloscope method on a sawn plate.

The atomic coordinates and isotropic thermal vibration parameters appear in Table 3, and Table 4 lists the structure factor data.[1] Owing to high correlations, we did not attempt an anisotropic thermal vibration parameter refinement.

Description of the structure

Painite possesses a rather elegant and aesthetically pleasing structure which can be directly compared with the octahedral framework structure of fluoborite, $Mg_3(F, OH)_3(BO_3)$. Fluoborite was investigated by Takéuchi (1950) who established its structural motif. It is based on a framework of corner-linked octahedral edge-sharing bands, two octahedra in width, which run parallel to the *c* axis. The corner links relate symmetry-equivalent bands by the 3-fold rotation at $\frac{1}{3}\,\frac{2}{3}\,z$ and $0\ 0\ z$. The resulting framework has composition $[Mg_3(F,OH)_3O_3]^{3-}$. Since three octahedral centers coordinate to each anion, the ratio of octahedral populations to anions is exactly 1:2. Open hexagonal channels at the origin prompted the term "pipe structure" by Takéuchi (1950); and Moore (1972), and Moore and Araki (1974) have exploited the octahedral edge distance as an example of a wallpaper-type structure. This term appears natural since the *c*-axial repeat is not only parallel to octahedral edges but is itself the octahedral edge distance. Thus, no nonequivalent atoms overlap in this projection. The $[BO_3]$ triangles are oriented perpendicular to the trigonal axes and complete the structure, an idealized diagram of which appears in Figure 1.

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[1] For a copy of the structure factor data, Table 4, order Document AM-75-010-B from the Business Office, Mineralogical Society of America, 1909 K Street, N.W. 20006. Please remit in advance $1.00 for the microfiche.

Painite possesses the identical framework topology with formula $[Al_3O_6]^{3-}$. The *c*-axial repeat, however, is three times that of fluoborite (Table 1), a consequence of a rather remarkable ordering of the remaining cationic species. The structural differences can be discerned at the positions 0 0 *z* and $\frac{1}{3}\,\frac{2}{3}\,z$ with respect to the painite cell. At 0 0 *z*, the sites are all empty in fluoborite but in painite they are occupied at $z \sim 0$ and $\frac{1}{2}$ by Ca^{2+} cations in compressed octahedral coordination by the O(5) and O(6) framework oxygens. At $\frac{1}{3}\,\frac{2}{3}\,z$, fluoborite has B^{3+} populations at $z = \frac{3}{12}$, $\frac{7}{12}$, and $\frac{11}{12}$ with respect to the painite cell. Painite has a B^{3+} cation at $z = \frac{3}{12}$ and in addition Zr^4, at $\frac{9}{12}$, the latter cation in trigonal prismatic coordination with respect to the O(3) and O(4) framework oxygens at $\frac{7}{12}$ and $\frac{11}{12}$. Thus, Zr^{4+} achieves the role of the two B^{3+}–O triangles. The assembled painite structure is featured in Figure 2.

Perhaps even more remarkable is a curious structural relationship between fluoborite and jeremejevite, $Al_6(OH)_3(BO_3)_3(BO_3)_2$. As in painite, the *c*-axial repeat is trebled that of fluoborite (Table 1) and all three structures have 36 anions in the painite-shaped cell. The jeremejevite structure parameters, obtained from Golovastikov *et al* (1955), were inverted to establish the same orientation of anions as those of fluoborite and painite. The framework composition is $[\square Al_2(OH)O_5]$, where $\square$ = vacancy, and it is seen in Figure 3 that only two-thirds of the octahedra are occupied along the columns such that every third framework position along *c* is empty. As in fluoborite, the sites at 0 0 *z* are empty but the sites

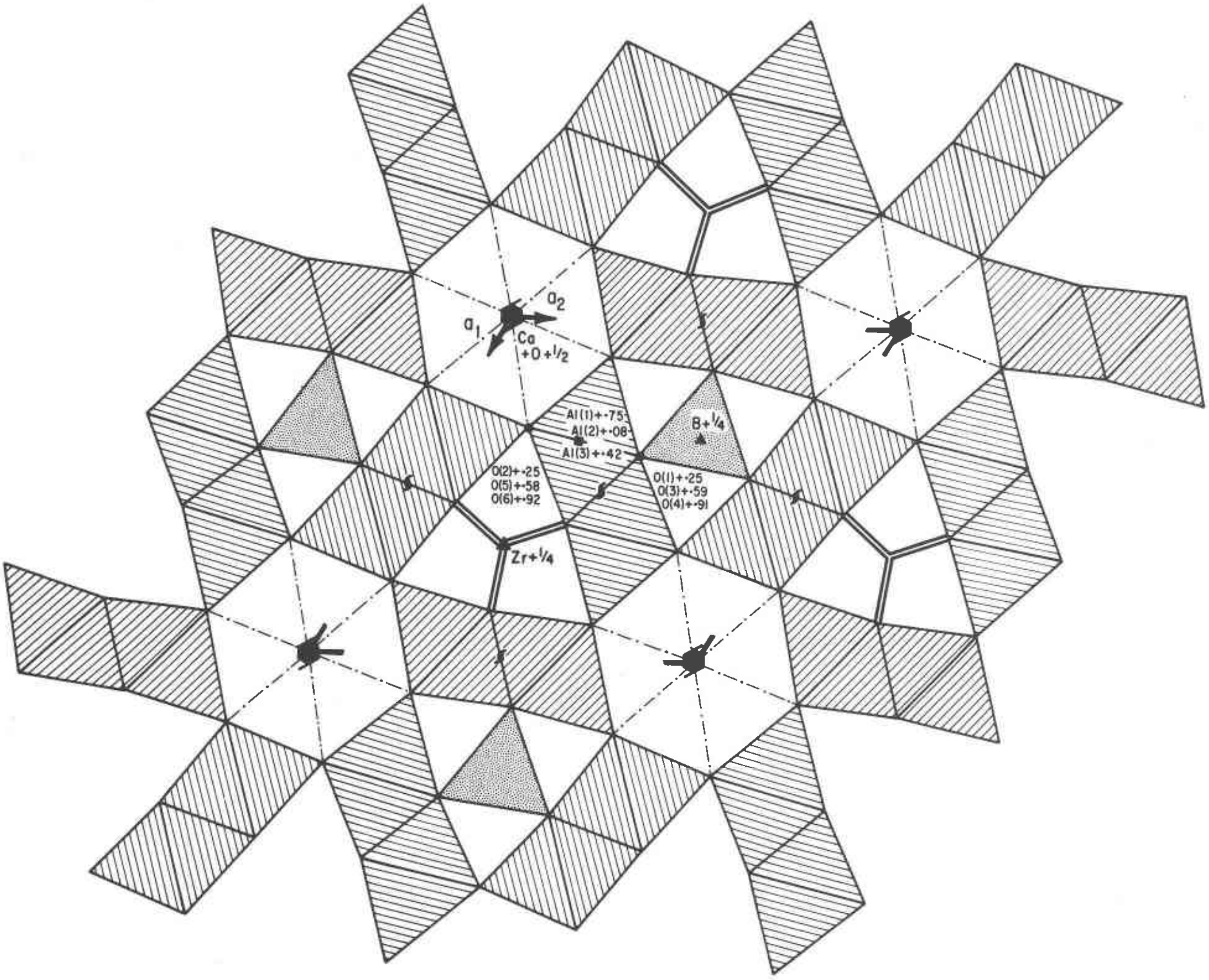

FIG. 2. Polyhedral diagram of the painite structure showing symmetry elements, the $[Al_9O_{18}]^{9-}$ framework (ruled) and the $[BO_3]$ triangles at $z = \frac{1}{4}$. The Zr–O bonds at $z = \frac{1}{4}$ are drawn as solid lines and the Ca–O bonds as dot-dash lines. The B^{3+} and Zr^{4+} positions at $z = \frac{3}{4}$ are not shown. The loci of the atoms correspond to the coordinates in Table 3.

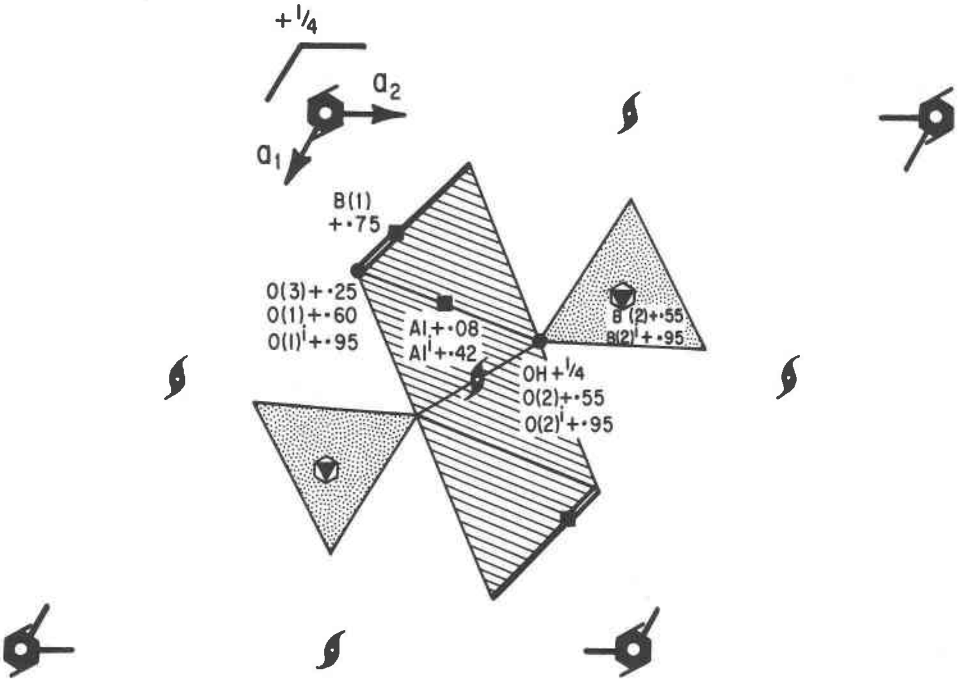

FIG. 3. A section of the jeremejevite structure showing symmetry elements and polyhedral projections. The $B(2)O_3$ triangles are stippled and the B(1)–O bonds are drawn bold. This diagram can be directly compared with Figure 2. The coordinates were obtained from Golovastikov *et al* (1955) and inverted so that a direct correspondence to fluoborite and painite can be recognized.

at $\frac{1}{3}\,\frac{2}{3}\,z$ have B^{3+} populations at $\frac{7}{12}$ and $\frac{11}{12}$. Most curious of all is the additional corner-links of $[BO_3]$ triangles at $x\ y\ \frac{9}{12}$; $\bar{x}\ \bar{y}$, $\frac{3}{12}$, *etc*, between the empty octahedral positions in the framework. These $[BO_3]$ triangles have one edge parallel to the *c* axis, and these edges link the broken octahedral columns together. In effect, the $[BO_3]$ triangles are situated at the outer faces of the empty octahedra.

The structural relationships among fluoborite, painite, and jeremejevite are best compared crystal chemically by adopting a more unconventional (but more sensible!) expression for the formulae. In these formulae, the octahedral frameworks are bracketed as follows:

Fluoborite	B_3	$[Mg_9(F,OH)_9O_9]$
Painite	CaZrB	$[Al_9O_{18}]$
Jeremejevite	B_5	$[\square_3Al_6(OH)_3O_{15}]$

where, in jeremejevite, $\square$ = octahedral vacancy on the (pseudo-) mirror plane.

The geometrically idealized arrangements of all three structures belong to space group $P6_3/m$ and their cells have the same metrical properties, providing the *c* axis of fluoborite is trebled. In two of them (fluoborite and painite) the same framework stoichiometry obtains and exploits cations of two distinct charges, Mg^{2+} and Al^{3+}. Along the 3-fold axes, discrete ordering schemes are encountered. One structure, jeremejevite, exploits ordered vacancies in the octahedral framework such that only two-thirds of the sites are occupied, thus affording a new set of positions for additional $[BO_3]$ triangles.

All this suggests that the fluoborite-type framework is unusually adaptive and may be the basis of yet more related structure types. The kinds of ordering schemes encountered in the three structures reported herein open up mind-boggling possibilities for other hypothetical arrangements and compositions. It would appear that a search for other exotic structures related to the fluoborite framework would proceed with prime emphasis on phases having the following properties: (1) space group $P6_3$ or $P6_3/m$; (2) $a \sim 8.5$–9.2Å; (3) c/a ratio $\sim 0.33N$, where $N = 1,2,3, \cdots$; and (4) $12N$ anions in the cell.

Bond distances and distortions

Painite consists of Al(1)–O, Al(2)–O, and Al(3)–O octahedra; a B–O triangle; a slightly compressed Zr–O trigonal prism; and a highly compressed Ca–O octahedron. Although the anion framework and as-

TABLE 5. Painite. Polyhedral Interatomic Distances and Angles†

Al(1)		O–Me–O´ (degrees)
Al(1) -O(5)	1.827	
-O(6)	1.829	
-O(2)^{ii}	1.909	
-O(3)	1.945	
-O(4)	1.949	
-O(1)^{i}	2.032	
average	1.915	
O(1)^{i} -O(4)	2.492*	77.5
O(1)^{i} -O(3)	2.498*	77.8
O(3) -O(5)	2.551*	85.1
O(4) -O(6)	2.561*	85.3
O(2)^{ii}-O(4)	2.635	86.2
O(2)^{ii}-O(3)	2.638	86.4
O(3) -O(4)	2.671**	86.6
O(1)^{i} -O(6)	2.782	94.6
O(1)^{i}-O(5)	2.824	93.9
O(2)^{ii}-O(6)	2.842	99.0
O(5) -O(6)	2.845	102.2
O(2)^{ii}-O(5)	2.867	100.3
average	2.684	89.6

Al(2)		
Al(2) -O(5)^{ii}	1.834	
-O(2)	1.880	
-O(4)	1.903	
-O(3)^{i}	1.910	
-O(6)	1.924	
-O(1)	2.057	
average	1.918	
O(3)^{i} -O(4)	2.450*	79.9
O(1) -O(3)^{i}	2.498*	78.0
O(4) -O(6)	2.561*	84.0
O(1) -O(2)	2.648*	84.4
O(2) -O(3)^{i}	2.651	88.7
O(5)^{ii}-O(6)	2.683	91.1
O(4) -O(5)^{ii}	2.759	95.2
O(2) -O(5)^{ii}	2.765	96.2
O(1) -O(5)^{ii}	2.773	90.7
O(2) -O(6)	2.839	96.5
O(1) -O(4)	2.915	94.7
O(3)^{i} -O(6)	2.939	100.1
average	2.707	90.0

Al(3)		
Al(3) -O(6)^{ii}	1.854	
-O(2)	1.867	
-O(5)	1.870	
-O(4)^{i}	1.894	
-O(3)	1.905	
-O(1)	2.092	
average	1.914	
O(3) -O(4)^{i}	2.450*	80.3
O(1) -O(4)^{i}	2.492*	77.2
O(3) -O(5)	2.551*	85.0
O(2) -O(4)^{i}	2.641	89.2
O(1) -O(2)	2.648*	83.8
O(5) -O(6)^{ii}	2.683	92.2
O(2) -O(6)^{ii}	2.740	94.9
O(3) -O(6)^{ii}	2.778	95.2
O(2) -O(5)	2.808	97.4
O(1) -O(6)^{ii}	2.840	89.4
O(4)^{i} -O(5)	2.907	101.1
O(1) -O(3)	2.914	93.5
average	2.704	89.9

Ca		
3 Ca -O(6)	2.371	
3 -O(5)	2.425	
average	2.398	
6 O(5)^{ii}-O(6)	2.683	68.0
3 O(6)-O(6)^{iii}	3.951	112.8
3 O(5)^{ii}-O(5)^{i}	3.999	111.0
average	3.329	89.9

Zr		
3 Zr -O(3)^{i}	2.126	
3 -O(4)^{i}	2.126	
average	2.126	
3 O(3) -O(4)	2.670**	77.8
3 O(3) -O(3)^{iv}	2.860	84.5
3 O(4) -O(4)^{iv}	2.872	85.0
average	2.801	82.4

B	
3 B -O(1)	1.380
3 O(1)-O(1)^{iv}	2.391

†Estimated standard deviations do not exceed ±0.004Å for Me–O and ±0.006Å for O–O´.

*Shared oxygen edges between Al, **shared oxygen edges between Al and Zr.

i = -x, -y, 1/2+z; ii = x-y, x, 1/2+z; iii = -y, x-y, z, and iv = y-z, -x, z applied to coordinates in Table 3.

sociated cations are ideally centrosymmetric, the actual structure possesses slight distortions away from $P6_3/m$. This can be noticed in the interatomic distances in Table 5, where Al(2) and Al(3) would be equivalent for $P6_3/m$. The individual distances to the same anions not only vary well beyond the error limits, but the order of anions (the distances are tabulated as increasing magnitudes) is not the same. The distortions cannot be explained by anisotropic bonding behavior for the cations in special positions along $\frac{1}{3}\,\frac{2}{3}\,z$:$ZrO_6$ and BO_3 possess $\bar{6}$ symmetry within the limit of error in coordinates.

The real distortions appear to be a result of serious deviations from electrostatic neutrality for some of the anions. Table 6 presents the electrostatic bond strength sums as deviations, Δpx, from neutrality and the relationship of these deviations to those found in the Al–O bond distances. O(1) and O(2) seriously depart from local neutrality, with $\Delta px = +0.50$ and -0.50 e.s.u. respectively. Thus, the Al–O(1) average distance is 0.14Å longer than the polyhedral average. The Al–O (2) average distance is shorter than the polyhedral average but the difference is not as great as anticipated. O(5) and O(6), with $\Delta px = -0.17$ e.s.u., show ΔAl–O between 0.05 and 0.07Å less than the polyhedral average, with O(3) and O(4) ($\Delta px = +0.17$ e.s.u.) within the range of the average value. It appears that the contributions of the Ca^{2+}–O bonds do not greatly affect the framework and that those bonds are weak. The B^{III}–O 1.38 and Zr^{VI}–O 2.13Å averages are exactly those predicted from ionic radii tables. These observations suggest that the $[Al_9O_{18}]^{9-}$ framework adjusts to accommodate deviations from electrostatic neutrality but in a way that is not immediately obvious. In many respects, the framework averages out the distance distortions such that the ideal symmetry of $P6_3/m$ is lowered to $P6_3$. Another adjustment in the framework results from Al–Al repulsions across shared edges: these are among the shortest distances for their polyhedra.

An interesting aspect of the painite structure is the

TABLE 6. Painite. Electrostatic Bond Strength Sum Calculations*

Anion	Coordinating cations	Δp_x	ΔAl–O
O(1)	B + Al(1) + Al(2) + Al(3)	+0.50	+0.144Å
O(2)	Al(1) + Al(2) + Al(3)	-0.50	-0.031
O(3)	Zr + Al(1) + Al(2) + Al(3)	+0.17	+0.004
O(4)	Zr + Al(1) + Al(2) + Al(3)	+0.17	-0.001
O(5)	Ca + Al(1) + Al(2) + Al(3)	-0.17	-0.072
O(6)	Ca + Al(1) + Al(2) + Al(3)	-0.17	-0.047

*Δp_x = deviations from electrostatic neutrality (p_x = 2.00), ΔAl–O = deviations from Al–O 1.916Å average.

large pipelike channel at 0 0 *z*. This is clogged by Ca^{2+} which bonds to O(5) and O(6), resulting in a highly compressed octahedron. If the ideal fluoborite framework is inspected (Fig. 1) it is seen that the center of the pipe is actually represented by a missing anion position. Consequently, the pore diameter of the pipe is about the same as that of an O^{2-} anion. Thus, cations like Li^{1+}, Na^{1+}, K^{1+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} should accommodate themselves within the pipe. In painite, there are no other obstructions beyond the Ca^{2+} cations. In many respects, the aperture in the painite framework resembles that in β-Al_2O_3, which also results from a missing anion. Like painite, the position may be occupied by Ca^{2+}, as in hibonite ($CaAl_{12}O_{19}$) or by any of a number of alkalis, depending on the charge of the residual framework.

The relationship of painite to β-Al_2O_3 adds interest to its structure. An appealing feature is the one-dimensional quality of the pipe which is surrounded in turn by a rigid tightly bound aluminate framework. Such a pipe, like the sheets of missing anions in β-Al_2O_3, may provide a good medium for conduction of intermediate-sized alkalis through a solid crystal, even at very high temperatures where aluminosilicate structures such as the zeolites disintegrate. The existence of a large natural single crystal of painite as well as its extreme resistance to acid and base attack ("Painite is a highly resistant mineral, insoluble in acids, and only slowly attacked by fusion with sodium carbonate or with sodium pyrosulfate"; *cf* Claringbull *et al,* 1957) suggests that the structure type is not only thermochemically stable but also that the framework is that of a highly refractory compound, capable of withstanding thermal and chemical abuse. For these reasons, our interest and attention are now being drawn toward its synthesis and the synthesis of possible analogs such as $NaNb^{5+}B[Al_9O_{18}]$ and $U^{6+}B[Al_9O_{18}]$. The latter composition is especially appealing since the pipelike channel would be free from any obstructions. On this note, we speculate that the open pipe may selectively sieve He but not the other inert gases at high temperature.

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