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THE CRYSTAL STRUCTURE OF BØGGILDITE

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ABSTRACT

The crystal structure of bøggildite, $\mathrm{Sr_2Na_2[Al_2(PO_4)F_9]}$, *a* 5.251(3), *b* 10.464(5), *c* 18.577(9) Å, β 107.53(3)°, *V* 973.3(2) Å^3, $Z = 4$, space group $P2_1/c$ has been solved by Patterson and Fourier methods and refined by a full-matrix least-squares method to an *R* index of 5.5% for 1736 observed (3σ) reflections. Each $(\mathrm{PO_4})$ tetrahedron corner-links to two $\mathrm{Al}\phi_6$ octahedra to form an $\mathrm{Al_2(PO_4)}\phi_{10}$ unit (ϕ: unspecified anion); these units link by corner-sharing between octahedra and tetrahedra to form an infinite chain of composition $(\mathrm{Al_2(PO_4)F_9})$ that is the fundamental basis of the structure. This chain extends parallel to the *Y* axis, and adjacent chains nestle closely together to form a sheet in the (100) plane. Bonding within the sheet and between adjacent sheets is by the Sr and Na cations that have co-ordination numbers [7], [8] and [9]. Bøggildite, with its mixed corner-linked octahedral-tetrahedral chains, is radically different from the other aluminofluoride minerals containing tetrahedral oxyanions. In creedite, $\mathrm{Ca_3Al_2(SO_4)F_8(OH)_2{\cdot}2H_2O}$, and chukhrovite, $\mathrm{Ca_3(Y,Ce)Al_2(SO_4)F_{13}{\cdot}10H_2O}$, there is no linkage between the $\mathrm{Al}\phi_6$ octahedra and the tetrahedra. This is the result of the different bond-valence requirement of the oxygen atoms co-ordinating the P and S in different structures.

Keywords: bøggildite, crystal structure, aluminofluoride, phosphate.

SOMMAIRE

La structure cristalline de la bøggildite, $\mathrm{Sr_2Na_2[Al_2(PO_4)F_9]}$, *a* 5.251(3), *b* 10.464(5), *c* 18.577(9) Å, β 107.53(3)°, *V* 973.3(2) Å^3, $Z = 4$, de groupe spatial $P2_1/c$, a été établie par les méthodes Patterson et Fourier, et affinée par la méthode des moindres carrés à matrice entière, sur 1736 réflexions observées (3σ), jusqu'à un résidu de 5.5%. Chaque tétraèdre $\mathrm{PO_4}$ s'unit à deux octaèdres $\mathrm{Al}\phi_6$ (ϕ: groupe anionique non-spécifié) en mettant un atome d'oxygène en commun avec chacun d'eux, de façon à former un groupe $\mathrm{Al_2(PO_4)}\phi_{10}$. De tels groupes s'unissent, par le même processus de partage d'atome d'oxygène entre octaèdre et tétraèdre, pour donner une chaîne infinie de composition $\mathrm{Al_2(PO_4)F_9}$, élément structural fondamental, parallèle à l'axe des *y*. Un ensemble de pareilles chaînes proches l'une de l'autre forme un feuillet structural d'orientation (100). Les liaisons, tant à l'intérieur des feuillets qu'entre feuillets contigus, sont assurées par les cations Sr et Na en coordinence 7, 8 ou 9. Par ses chaînes mixtes d'octaèdres et tétraèdres à coins communs, la bøggildite diffère radicalement des autres aluminofluorures naturels à oxy-anions tétraédriques. Dans la créedite $\mathrm{Ca_3Al_2(SO_4)F_8(OH)_2{\cdot}2H_2O}$ et la tchoukhrovite $\mathrm{Ca_3(Y,Ce)Al_2(SO_4)F_{13}{\cdot}10H_2O}$, on n'observe pas d'assemblage entre octaèdres $\mathrm{Al}\phi_6$ et tétraèdres, fait qui résulte des différences entre les exigences des valences de liaison des atomes d'oxygène coordonnés à P et à S dans des structures différentes.

(Traduit par la Rédaction)

Mots-clés: bøggildite. structure cristalline, aluminofluorure, phosphate.

INTRODUCTION

Bøggildite is a rare flesh-red phosphate aluminofluoride mineral, $\mathrm{Sr_2Na_2Al_2(PO_4)F_9}$, found at the Ivigtut cryolite locality, Greenland, where it occurs together with siderite, fluorite, black cryolite, quartz, green mica and sphalerite at the contact of the cryolite body with adjacent greisen (Bøgvad 1951, Nielsen 1954, Pauly 1956). Møller (1956) showed bøggildite to be monoclinic, with space group $P2_1/c$. Møller's orientation is retained here.

As part of a continuing study of the structures of the aluminofluoride minerals (Hawthorne & Ferguson 1975, 1981, in prep.), the structure of bøggildite has been solved to determine its structural relationship to the other aluminofluorides. Although there are no other phosphate aluminofluorides, there are sulfate aluminofluorides, namely creedite, $\mathrm{Ca_3Al_2(SO_4)F_8(OH)_2{\cdot}2H_2O}$, and chukhrovite, $\mathrm{Ca_3(Y,Ce)Al_2(SO_4)F_{13}{\cdot}10H_2O}$, the structures of which are known. Consideration of bond valences in these three minerals suggested that the structure of bøggildite would be based on $(\mathrm{PO_4})-(\mathrm{Al}\phi_6)$ linkages and that the structures of creedite and chukhrovite should be based on $(\mathrm{SO_4})-(\mathrm{Ca}\phi_{8,9})$ linkages (ϕ: unspecified anion). As this is the case for creedite and chukhrovite, solution of the bøggildite structure acquired added interest.

EXPERIMENTAL

Single-crystal X-ray precession photographs display monoclinic symmetry with systematic absences $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$, uniquely determining the space group as $P2_1/c$. Precession photographs of several crystals were characterized by large spots, indicative of a considerable degree of mosaicity. Cell dimensions were determined by least-squares refinement of 15 reflections automatically aligned on a Syntex P2₁ automatic 4-circle diffractometer.

An equidimensional fragment of ~0.18 mm 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 2383 reflections were measured over one asymmetric unit to a maximum 2θ of 60° ($\sin\theta/\lambda = 0.704$). The data were corrected for Lorentz, polarization, absorption and background effects, and 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 2383 unique reflections, 1736 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 three-dimensional Patterson synthesis, $P(uvw)$, suggested atoms at the Wykoff positions $2a$ and $2c$. These were assumed to be Al, and a successful solution for the two Sr positions was subsequently derived. The remaining atoms were found by successive difference Fourier synthesis, and full-matrix least-squares refinement of all positional variables and individual isotropic temperature-factors converged to an R index of 9.1%. Temperature factors were converted to an anisotropic form as given in Table 1, and full-matrix refinement of all variables, together with an isotropic extinction correction (final value $1.0(2) \times 10^{-6}$), resulted in convergence at an R index of 5.5%. This value is somewhat higher than that normally obtained in this laboratory; this may result from the fact the bøggildite is not as perfectly

TABLE 1. MISCELLANEOUS INFORMATION: BØGGILDITE

a	5.251(3)Å	Crystal size	∼0.20 mm
b	10.464(5)	Rad/Mono	Mo/C
c	18.577(9)	Total No. of $\lvert F_o \rvert$	2383
β	107.53(3)	No. of $\lvert F_o \rvert > 3\sigma$	1736
V	973.3(2)	Final R (obs)	5.5%
Space group	$P2_1/c$	Final R_w (obs)	6.5%
Unit cell contents		$4[Sr_2Na_2Al_2(PO_4)F_9]$	

$D_{calc} = 3.692\text{g cm}^{-3}$

Temperature factor form used: $\exp[-\Sigma\Sigma h_i h_j \beta_{ij}]$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1$

TABLE 2. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR BØGGILDITE

	x	y	z	B^*_{equiv} (Å^2)
Sr(1)	0.3393(2)	0.0396(1)	0.33111(5)	0.96(2)
Sr(2)	0.3566(2)	0.4632(1)	0.35754(5)	1.04(2)
P	0.9466(6)	0.2500(3)	0.9092(2)	0.88(4)
Al(1)	0	0	0	0.77(7)
Al(2)	0	0	½	0.82(8)
Al(3)	0.6951(7)	0.2469(3)	0.2404(2)	0.86(5)
Na(1)	0.1105(11)	0.2425(6)	0.6310(3)	2.5(1)
Na(2)	0.5408(10)	0.2194(5)	0.5194(3)	1.7(1)
O(1)	0.2226(16)	0.2435(8)	0.3990(4)	1.3(1)
O(2)	0.8644(17)	0.1121(8)	0.9189(4)	1.2(1)
O(3)	0.9347(18)	0.1730(8)	0.4784(4)	1.3(1)
O(4)	0.7299(18)	0.3031(8)	0.8390(4)	4.4(2)
F(1)	0.3030(14)	0.0913(7)	0.0365(4)	1.5(1)
F(2)	0.4397(14)	0.1243(7)	0.2111(3)	1.1(1)
F(3)	0.8513(15)	0.0919(7)	0.0604(4)	1.5(1)
F(4)	0.9380(14)	0.1315(7)	0.2324(4)	1.3(1)
F(5)	0.9332(14)	0.1261(7)	0.7629(3)	1.3(1)
F(6)	0.6396(15)	0.2141(7)	0.6431(3)	1.5(1)
F(7)	0.3431(14)	0.0339(8)	0.5480(4)	1.5(1)
F(8)	0.4413(15)	0.1359(7)	0.7395(4)	1.4(1)
F(9)	0.0709(14)	0.9663(7)	0.4117(3)	1.3(1)

$^*B_{equiv} = 4/3 \sum_i \sum_j g_{ij}\beta_{ij}$; g_{ij}: real-space metric tensor

TABLE 3. ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$)* FOR BØGGILDITE

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sr(1)	1294(45)	244(9)	27(2)	-15(16)	-8(7)	1(4)
Sr(2)	1358(47)	249(9)	35(3)	-16(17)	-17(7)	7(4)
P	132(11)	20(2)	2(1)	-1(4)	-3(2)	0(1)
Al(1)	88(19)	24(4)	2(1)	0	-1(3)	0
Al(2)	117(20)	25(4)	1(1)	0	1(3)	0
Al(3)	110(13)	21(3)	2(1)	2(5)	-7(3)	-1(1)
Na(1)	193(23)	50(5)	19(1)	1(9)	-25(5)	-4(2)
Na(2)	176(22)	63(5)	4(1)	2(8)	0(4)	3(2)
O(1)	143(33)	28(7)	5(2)	-5(13)	-9(7)	2(3)
O(2)	204(37)	19(7)	3(2)	-2(12)	-6(7)	3(3)
O(3)	214(39)	31(7)	3(2)	0(13)	5(7)	1(3)
O(4)	579(44)	87(8)	23(2)	27(16)	7(8)	4(4)
F(1)	123(30)	33(6)	10(2)	-17(11)	-16(6)	5(3)
F(2)	128(28)	33(6)	4(2)	-8(10)	0(5)	-2(3)
F(3)	208(33)	37(6)	6(2)	6(12)	13(6)	1(3)
F(4)	132(29)	27(6)	9(2)	20(11)	5(6)	-2(3)
F(5)	149(30)	29(6)	6(2)	20(11)	-5(5)	-1(3)
F(6)	166(30)	54(7)	2(2)	1(11)	6(6)	-3(3)
F(7)	119(28)	47(7)	7(2)	7(12)	-1(5)	6(3)
F(8)	173(32)	31(6)	8(2)	-16(11)	6(6)	2(3)
F(9)	189(30)	37(6)	2(2)	-3(12)	10(5)	1(3)

$^*\times 10^5$ for Sr(1) and Sr(2)

TABLE 4. INTERATOMIC DISTANCES AND ANGLES IN BØGGILDITE

Sr(1)-F(2)	2.596(6)	Sr(2)-F(1)	2.597(7)
Sr(1)-F(4)	2.530(7)	Sr(2)-F(2)	2.537(7)
Sr(1)-F(5)	2.569(7)	Sr(2)-F(3)	2.515(7)
Sr(1)-F(6)	2.693(8)	Sr(2)-F(4)	2.594(7)
Sr(1)-F(7)	2.481(6)	Sr(2)-F(5)	2.560(7)
Sr(1)-F(8)	2.707(8)	Sr(2)-F(8)	2.582(7)
Sr(1)-F(9)	2.468(6)	Sr(2)-O(1)	2.589(9)
Sr(1)-O(1)	2.643(9)	Sr(2)-O(2)	2.683(9)
Sr(1)-O(4)	2.599(9)	Mean	2.582
Mean	2.587	Al(2)-F(7)x2	1.789(7)
P-O(1)	1.519(9)	Al(2)-F(9)x2	1.822(6)
P-O(2)	1.532(8)	Al(2)-O(3)x2	1.863(8)
P-O(3)	1.535(8)		
P-O(4)	1.553(8)	Mean	1.825
Mean	1.535	Al(3)-F(2)	1.816(8)
Al(1)-F(1)x2	1.804(7)	Al(3)-F(4)	1.794(8)
Al(1)-F(3)x2	1.823(7)	Al(3)-F(5)	1.786(8)
Al(1)-O(2)x2	1.873(7)	Al(3)-F(6)	1.788(7)
Mean	1.833	Al(3)-F(8)	1.808(8)
Na(1)-F(1)	2.862(10)	Al(3)-O(4)	1.861(8)
Na(1)-F(2)	2.365(9)	Mean	1.809
Na(1)-F(3)	2.344(9)	Na(2)-F(1)	2.412(9)
Na(1)-F(4)	2.672(9)	Na(2)-F(3)	2.528(9)
Na(1)-F(6)	2.567(9)	Na(2)-F(6)	2.198(8)
Na(1)-F(6)'	2.735(9)	Na(2)-F(7)	2.336(9)
Na(1)-F(8)	2.493(9)	Na(2)-F(9)	2.828(9)
Na(1)-F(9)	2.419(9)	Na(2)-O(1)	2.368(9)
Na(1)-O(3)	2.800(9)	Na(2)-O(3)	2.459(10)
Mean	2.584	Mean	2.447
P tetrahedron			
O(1)-O(2)	2.525(12)	O(1)-P-O(2)	111.7(5)
O(1)-O(3)	2.520(12)	O(1)-P-O(3)	111.3(5)
O(1)-O(4)	2.537(12)	O(1)-P-O(4)	111.4(5)
O(2)-O(3)	2.484(11)	O(2)-P-O(3)	108.2(5)
O(2)-O(4)	2.463(11)	O(2)-P-O(4)	106.0(5)
O(3)-O(4)	2.500(10)	O(3)-P-O(4)	108.1(5)
Mean	2.505	Mean	109.5
Al(1) octahedron			
F(1)-F(3)x2	2.542(11)	F(1)-Al(1)-F(3)x2	89.0(4)
F(1)-F(3)'x2	2.588(10)	F(1)-Al(1)-F(3)'x2	91.0(4)
F(1)-O(2)x2	2.663(10)	F(1)-Al(1)-O(2)x2	92.8(3)
F(1)-O(2)'x2	2.536(11)	F(1)-Al(1)-O(2)'x2	87.2(3)
F(3)-O(2)x2	2.659(10)	F(3)-Al(1)-O(2)x2	92.0(3)
F(3)-O(2)'x2	2.567(11)	F(3)-Al(1)-O(2)'x2	88.0(3)
Mean	2.593	Mean	90.0
Al(2) octahedron			
F(7)-F(9)x2	2.503(10)	F(7)-Al(2)-F(9)x2	87.8(3)
F(7)-F(9)'x2	2.603(9)	F(7)-Al(2)-F(9)'x2	92.2(3)
F(7)-O(3)x2	2.592(11)	F(7)-Al(2)-O(3)x2	90.4(4)
F(7)-O(3)'x2	2.573(12)	F(7)-Al(2)-O(3)'x2	89.6(4)
F(9)-O(3)x2	2.515(10)	F(9)-Al(2)-O(3)x2	86.1(3)
F(9)-O(3)'x2	2.694(11)	F(9)-Al(2)-O(3)'x2	93.9(3)
Mean	2.580	Mean	90.0
Al(3) octahedron			
F(2)-F(4)	2.527(10)	F(2)-Al(3)-F(4)	88.8(4)
F(2)-F(6)	2.521(10)	F(2)-Al(3)-F(6)	88.8(3)
F(2)-F(8)	2.563(10)	F(2)-Al(3)-F(8)	90.0(2)
F(2)-O(4)	2.522(9)	F(2)-Al(3)-O(4)	86.6(4)
F(4)-F(5)	2.600(9)	F(4)-Al(3)-F(5)	93.2(4)
F(4)-F(6)	2.500(10)	F(4)-Al(3)-F(6)	88.5(4)
F(4)-O(4)	2.624(11)	F(4)-Al(3)-O(4)	91.8(4)
F(5)-F(6)	2.472(9)	F(5)-Al(3)-F(6)	87.5(4)
F(5)-F(8)	2.489(10)	F(5)-Al(3)-F(8)	87.7(4)
F(5)-O(4)	2.734(11)	F(5)-Al(3)-O(4)	97.1(4)
F(6)-F(8)	2.466(10)	F(6)-Al(3)-F(8)	86.6(4)
F(8)-O(4)	2.662(11)	F(8)-Al(3)-O(4)	93.0(4)
Mean	2.557	Mean	90.0
Na(1) polyhedron			
F(1)-F(2)	3.123(9)	F(1)-Na(1)-F(2)	72.7(3)
F(1)-F(3)	2.541(11)	F(1)-Na(1)-F(3)	57.4(3)
F(1)-F(6)'	3.014(10)	F(1)-Na(1)-F(6)'	65.1(3)
F(1)-O(3)	3.120(11)	F(1)-Na(1)-O(3)	66.9(3)
F(2)-F(3)	3.505(12)	F(2)-Na(1)-F(3)	96.2(3)
F(2)-F(4)	2.780(10)	F(2)-Na(1)-F(4)	66.7(3)
F(2)-F(6)'	2.521(10)	F(2)-Na(1)-F(6)'	58.7(3)
F(2)-F(8)	2.563(10)	F(2)-Na(1)-F(8)	63.6(3)
F(3)-F(4)	3.116(9)	F(3)-Na(1)-F(4)	76.5(3)
F(3)-F(6)	2.957(10)	F(3)-Na(1)-F(6)	73.9(3)
F(3)-O(3)	2.995(11)	F(3)-Na(1)-O(3)	70.6(3)
F(4)-F(6)	2.500(10)	F(4)-Na(1)-F(6)	57.0(3)
F(4)-F(8)	3.564(12)	F(4)-Na(1)-F(8)	87.2(3)
F(6)-F(8)	4.130(13)	F(6)-Na(1)-F(8)	109.4(3)
F(6)-F(9)	2.801(10)	F(6)-Na(1)-F(9)	68.3(3)
F(6)-O(3)	3.848(12)	F(6)-Na(1)-O(3)	91.5(3)
F(6)'-F(8)	2.466(10)	F(6)'-Na(1)-F(8)	56.1(3)
F(6)'-O(3)	4.056(12)	F(6)'-Na(1)-O(3)	94.2(3)
F(8)-F(9)	3.423(9)	F(8)-Na(1)-F(9)	88.3(3)
F(9)-O(3)	2.515(10)	F(9)-Na(1)-O(3)	57.1(3)
Mean	3.077	Mean	73.9
Na(2) polyhedron			
F(1)-F(3)	2.778(11)	F(1)-Na(2)-F(3)	68.4(3)
F(1)-F(6)	3.014(10)	F(1)-Na(2)-F(6)	81.5(3)
F(1)-F(7)	3.930(12)	F(1)-Na(2)-F(7)	111.7(3)
F(1)-O(1)	3.007(11)	F(1)-Na(2)-O(1)	78.0(3)
F(3)-F(6)	2.957(10)	F(3)-Na(2)-F(6)	77.1(3)
F(3)-F(9)	3.957(11)	F(3)-Na(2)-F(9)	95.1(3)
F(3)-O(3)	2.995(11)	F(3)-Na(2)-O(3)	73.8(3)
F(6)-F(7)	2.729(10)	F(6)-Na(2)-F(7)	73.9(3)
F(6)-F(9)	2.801(10)	F(6)-Na(2)-F(9)	66.4(3)
F(7)-F(9)	2.940(10)	F(7)-Na(2)-F(9)	68.6(3)
F(7)-O(1)	3.437(10)	F(7)-Na(2)-O(1)	93.9(3)
F(9)-O(3)	2.515(10)	F(9)-Na(2)-O(3)	56.3(3)
O(1)-O(3)	3.657(11)	O(1)-Na(2)-O(3)	98.5(3)
Mean	3.132	Mean	80.2
Sr(1) polyhedron			
F(2)-F(4)	2.780(10)	F(2)-Sr(1)-F(4)	65.7(2)
F(2)-F(8)	2.882(10)	F(2)-Sr(1)-F(8)	65.8(2)
F(2)-O(4)	2.522(9)	F(2)-Sr(1)-O(4)	58.1(2)
F(4)-F(5)	2.775(9)	F(4)-Sr(1)-F(5)	65.9(2)
F(4)-F(9)	3.629(11)	F(4)-Sr(1)-F(9)	93.1(2)
F(4)-O(1)	3.224(10)	F(4)-Sr(1)-O(1)	77.1(2)
F(5)-F(6)	2.472(9)	F(5)-Sr(1)-F(6)	56.0(2)
F(5)-F(8)	2.489(10)	F(5)-Sr(1)-F(8)	56.2(2)
F(5)-F(9)	3.379(9)	F(5)-Sr(1)-F(9)	84.2(2)
F(6)-F(7)	2.729(10)	F(6)-Sr(1)-F(7)	63.5(2)
F(6)-F(8)	2.466(10)	F(6)-Sr(1)-F(8)	54.3(2)
F(6)-F(9)	2.801(10)	F(6)-Sr(1)-F(9)	65.6(2)
F(7)-F(8)	3.598(12)	F(7)-Sr(1)-F(8)	87.7(2)
F(7)-F(9)	2.940(10)	F(7)-Sr(1)-F(9)	72.9(2)
F(7)-O(1)	3.638(11)	F(7)-Sr(1)-O(1)	90.4(2)
F(7)-O(4)	3.297(11)	F(7)-Sr(1)-O(4)	80.9(2)
F(8)-O(4)	3.779(11)	F(8)-Sr(1)-O(4)	90.8(3)
F(9)-O(1)	3.036(11)	F(9)-Sr(1)-O(1)	72.8(3)
O(1)-O(4)	3.220(13)	O(1)-Sr(1)-O(4)	75.8(3)
Mean	3.033	Mean	72.5
Sr(2) polyhedron			
F(1)-F(2)	3.123(9)	F(1)-Sr(2)-F(2)	74.9(2)
F(1)-F(3)	2.778(11)	F(1)-Sr(2)-F(3)	65.8(2)
F(1)-O(1)	4.369(11)	F(1)-Sr(2)-O(1)	114.8(2)
F(1)-O(2)	2.536(11)	F(1)-Sr(2)-O(2)	57.4(2)
F(2)-F(4)	2.527(10)	F(2)-Sr(2)-F(4)	59.0(2)
F(2)-F(8)	2.882(10)	F(2)-Sr(2)-F(8)	68.5(2)
F(2)-O(2)	3.491(10)	F(2)-Sr(2)-O(2)	83.9(2)
F(3)-F(4)	3.116(9)	F(3)-Sr(2)-F(4)	75.1(2)
F(3)-F(5)	3.882(12)	F(3)-Sr(2)-F(5)	99.5(2)
F(3)-O(1)	3.766(11)	F(3)-Sr(2)-O(1)	95.1(3)
F(4)-F(5)	2.775(9)	F(4)-Sr(2)-F(5)	65.1(2)
F(4)-F(8)	3.563(10)	F(4)-Sr(2)-F(8)	87.0(2)
F(5)-F(8)	2.831(10)	F(5)-Sr(2)-F(8)	66.8(2)
F(5)-O(1)	2.872(10)	F(5)-Sr(2)-O(1)	67.8(2)
F(8)-O(1)	3.707(10)	F(8)-Sr(2)-O(1)	91.6(2)
F(8)-O(2)	3.413(9)	F(8)-Sr(2)-O(2)	80.8(2)
O(1)-O(2)	3.610(12)	O(1)-Sr(2)-O(2)	86.4(3)
Mean	3.249	Mean	78.8

monocrystalline as most of the previous minerals examined. Observed and calculated structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Final atomic positions and equivalent isotropic temperature-factors are presented in Table 2, and anisotropic temperature-factor coefficients are listed in Table 3. Interatomic distances and angles, and the magnitude and orientations of the principal axes of the thermal ellipsoids, calculated with the program ERRORS (L. W. Finger, pers. comm.), are presented in Tables 4 and 5.

DISCUSSION

Description of the structure

The bøggildite structure (Fig. 1) has one crystallographically unique PO_4 tetrahedron that shows typical variations in bond lengths and angles (Table 4). There are three unique Al positions with point symmetries $\bar{1}$, $\bar{1}$ and 1, respectively. Al(1) and Al(2) are each co-ordinated by four fluorine and two oxygen anions, arranged in a slightly distorted octahedral array; in each polyhedron, the two oxygens are in a *trans* configuration. Al(3) is octahedrally coordinated by five fluorine and one oxygen anions, and shows slightly greater angular distortion than the other Al octahedra. Co-ordination polyhedra for the Sr and Na cations are illustrated in Figure 2. Sr(1) is surrounded by seven fluorine and two oxygen atoms arranged in a distorted augmented square antiprism. Sr(2) is surrounded by six fluorine and two oxygen atoms, arranged in a distorted square antiprism. Na(1) is surrounded by eight fluorine atoms and one oxygen atom in an arrangement that does not closely resemble any of the regular nine-vertex polyhedra. Na(2) is surrounded by five fluorine and two oxygen atoms in an arrangement that is a distorted augmented trigonal prism. The variation in mean bond-lengths among these polyhedra can be explained reasonably well as a result of variations in co-ordination number of both the cations and anions. A comparison of the observed mean bond-lengths with the sum of the relevant cation and anion radii [Sr(1) 2.59(2.63), Sr(2) 2.58(2.58), Na(1) 2.58(2.56), Na(2) 2.45(2.45) Å] for observed (calculated) distances shows very close agreement, except for Sr(1).

The empirical bond-valence table for bøggildite (Table 6), calculated using the curves of Brown & Wu (1976), confirms the assignment of anions in this study. The bond-valence sums around the fluorine anions closely approach the ideal value of unity (except for F(2), perhaps), indicating no significant substitution of OH for F, which would tend to result in sums significantly less than 1.0 *v.u.*

Each (PO_4) tetrahedron corner-links to two Al octahedra to form an $Al_2(PO_4)OF_9$ unit; this links by corner-sharing between octahedra and tetrahedra to form an infinite chain of composition $[Al_2(PO_4)F_9]^{6-}$ that is illustrated in Figure 3. Three of the tetrahedral vertices link to octahedra, and the remaining tetra-

TABLE 5. VIBRATION ELLIPSOIDS FOR BOGGILDITE

	R.M.S. Displacement	Angle to X-axis	Angle to Y-axis	Angle to Z-axis
Sr(1)	0.064(3)Å	83(1)°	90(2)°	24(1)°
	0.116(2)	95(5)	175(5)	88(3)
	0.138(2)	8(3)	95(5)	114(1)
Sr(2)	0.071(3)	80(1)	93(3)	27(1)
	0.117(2)	97(4)	173(4)	90(3)
	0.143(2)	12(2)	96(4)	117(1)
P	0.051(11)	82(3)	91(6)	26(3)
	0.104(6)	92(7)	178(7)	90(7)
	0.141(5)	8(3)	92(8)	116(3)
Al(1)	0.056(16)	82(9)	90	26(9)
	0.114(11)	172(9)	90	64(9)
	0.115(9)	90	0	90
Al(2)	0.030(28)	90(6)	90	17(6)
	0.118(9)	90	0	90
	0.127(10)	0(6)	90	107(6)
Al(3)	0.043(16)	75(4)	87(6)	33(4)
	0.107(7)	81(10)	171(10)	92(8)
	0.139(7)	18(6)	81(10)	123(4)
Na(1)	0.110(11)	51(4)	83(8)	57(3)
	0.165(9)	80(6)	170(7)	92(7)
	0.236(8)	41(4)	83(6)	147(3)
Na(2)	0.075(13)	84(5)	96(4)	24(5)
	0.160(9)	173(10)	95(13)	67(6)
	0.187(8)	94(13)	8(9)	82(6)
O(1)	0.075(22)	69(9)	96(17)	39(8)
	0.122(15)	103(17)	167(16)	87(18)
	0.164(15)	25(11)	102(17)	129(8)
O(2)	0.061(25)	82(7)	109(20)	32(11)
	0.106(17)	98(10)	160(19)	105(18)
	0.178(14)	12(8)	95(9)	118(6)
O(3)	0.069(22)	92(7)	92(13)	15(7)
	0.131(15)	90(17)	178(14)	92(13)
	0.170(15)	2(7)	90(17)	105(7)
O(4)	0.184(10)	78(4)	110(12)	36(8)
	0.223(10)	86(7)	158(11)	112(11)
	0.292(11)	13(5)	82(7)	117(5)

F(1)	0.082(17)	53(9)	90(16)	54(9)
	0.122(14)	109(12)	156(8)	71(13)
	0.191(12)	43(7)	114(8)	138(6)
F(2)	0.073(18)	80(10)	79(10)	30(10)
	0.133(13)	130(73)	136(73)	63(22)
	0.141(13)	42(73)	132(73)	103(35)
F(3)	0.092(16)	100(8)	96(13)	9(11)
	0.142(13)	76(25)	166(24)	97(13)
	0.164(13)	17(21)	77(25)	96(9)
F(4)	0.102(16)	52(16)	141(20)	97(37)
	0.117(13)	100(30)	103(35)	149(18)
	0.154(13)	40(12)	55(12)	120(15)
F(5)	0.085(16)	69(12)	96(22)	39(15)
	0.113(15)	67(13)	153(12)	111(22)
	0.168(12)	32(9)	64(11)	121(8)
F(6)	0.055(24)	96(8)	83(5)	13(7)
	0.147(13)	170(16)	83(19)	79(8)
	0.175(12)	82(19)	10(14)	98(6)
F(7)	0.092(15)	68(13)	106(9)	43(12)
	0.140(13)	157(14)	104(21)	55(16)
	0.167(12)	97(21)	22(15)	68(14)
F(8)	0.110(14)	95(27)	116(40)	29(27)
	0.123(14)	121(15)	138(35)	105(44)
	0.164(13)	31(15)	120(14)	114(11)
F(9)	0.054(22)	99(6)	94(8)	9(6)
	0.143(12)	101(41)	168(39)	92(10)
	0.157(13)	14(32)	102(41)	99(6)

hedral vertex does not; consequently, this remaining oxygen must bond to both Sr cations at least, in order to satisfy its bond-valence requirements. These $[\mathrm{Al_2(PO_4)F_9}]^{6-}$ chains intercalate together in the (100) plane to form a sheet of parallel chains that is linked to adjacent sheets above and below by the Sr and Na cations (Fig. 4).

Related structures

Two other aluminofluoride minerals contain $(X\mathrm{O_4})$ oxyanions: the structures of creedite $\mathrm{Ca_3Al_2(SO_4)F_8(OH)_2{\cdot}2H_2O}$ and chukhrovite $\mathrm{Ca_3(Y,Ce)Al_2(SO_4)F_{13}{\cdot}10H_2O}$, have been solved by Borisov *et al.* (1965) and Bokiy & Gorogotskaya (1965), respectively. However, these two structures differ radically from the bøggildite structure. As shown above, the $(X\mathrm{O_4})$ group in bøggildite links to three $\mathrm{Al}\phi_6$ octahedra to form a tetrahedral/octahedral polymer that is the fundamental unit of the structure. In the creedite and chukhrovite structures, the $(X\mathrm{O_4})$ groups do not link to $\mathrm{Al}\phi_6$ octahedra at all, but only to the Ca (and Y) polyhedra; in addition, in the creedite structure there is polymerization of the $\mathrm{Al}\phi_6$ octahedra that does not occur in bøggildite.

These major structural differences can be simply explained using bond-valence theory (Brown 1978), together with the supposition that the major imperative of a structure is the satisfaction of ion bond-valences. In the case of the bøggildite structure, the P–ϕ and Al–ϕ bonds have average bond valences of 1.25 and 0.50 valence units (*v.u.*), respectively, and the other cations have bond-valences of 0.13–

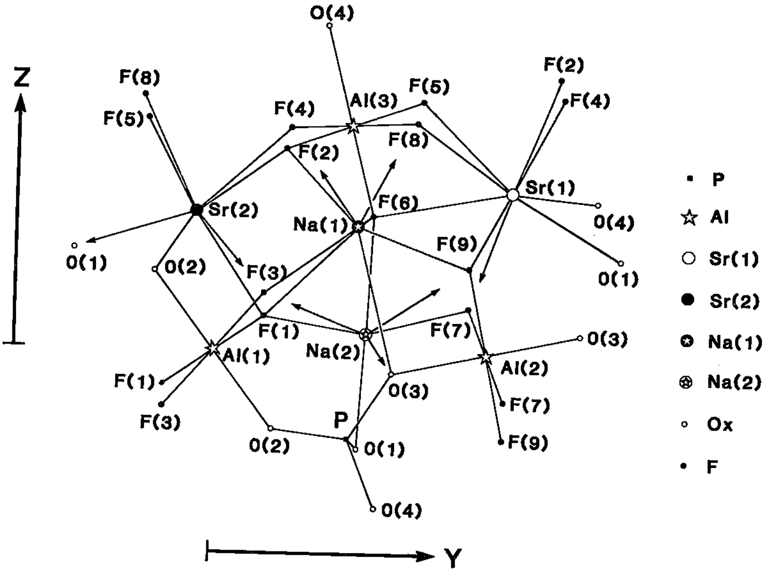

FIG. 1. The crystal structure of bøggildite projected down *X*.

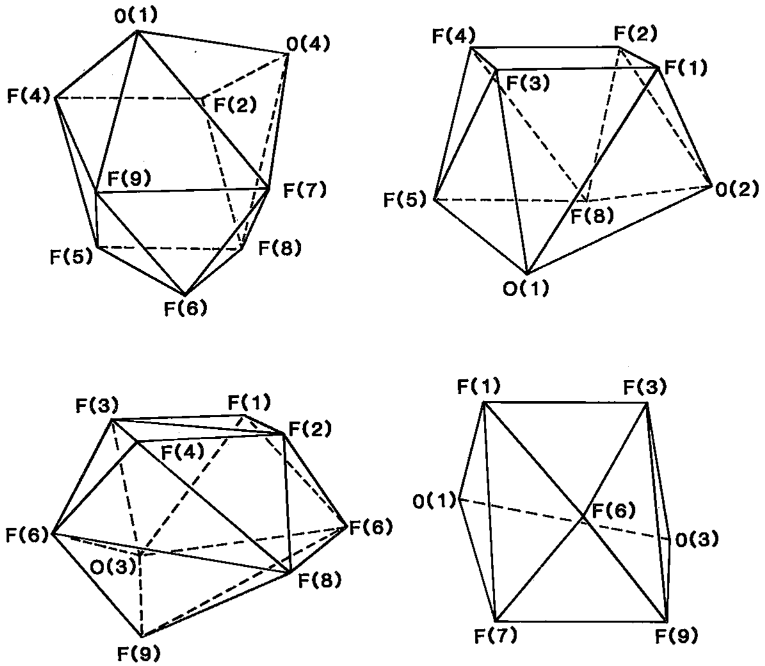

FIG. 2. Co-ordination polyhedra in the bøggildite structure. Sr (1) in top left, Sr(2) in top right, Na(1) in bottom left, and Na(2) in bottom right.

TABLE 6. EMPIRICAL BOND-VALENCE TABLE FOR BØGGILDITE

	Sr(1)	Sr(2)	Na(1)	Na(2)	Al(1)	Al(2)	Al(3)	P	Σ
O(1)	0.230	0.266		0.197				1.325	2.018
O(2)		0.207			$0.539^{\times2}_{\downarrow}$			1.277	2.023
O(3)			0.096	0.168		$0.552^{\times2}_{\downarrow}$		1.267	2.083
O(4)	0.259						0.555	1.205	2.019
F(1)		0.236	0.068	0.143	$0.496^{\times2}_{\downarrow}$				0.943
F(2)	0.207	0.271	0.155				0.482		1.115
F(3)		0.286	0.161	0.117	$0.474^{\times2}_{\downarrow}$				1.038
F(4)	0.242	0.237	0.092				0.508		1.079
F(5)	0.221	0.257					0.518		0.996
F(6)	0.166		0.083 0.109	0.213			0.515		1.086
F(7)	0.271			0.164		$0.514^{\times2}_{\downarrow}$			0.949
F(8)	0.161	0.244	0.124				0.491		1.020
F(9)	0.281		0.141	0.072		$0.475^{\times2}_{\downarrow}$			0.969
Σ	2.038	2.004	1.029	1.074	3.018	3.082	3.069	5.074	

0.25 *v.u.* The oxygen atoms of the $(PO_4)^{3-}$ tetrahedron have the largest bond-valence deficiency, one that 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 1.75 *v.u.*, and the remaining bond-valence requirements can be satisfied by further bonding to the alkali and alkaline earth cations. The stoichiometry of bøggildite does not allow the (PO_4) group to link to four $Al\varnothing_6$ octahedra. In the case of the creedite and chukhrovite structures, the S–Ø and Al–Ø bonds have average bond-valences of 1.50 and 0.50 *v.u.*, respectively, and the other cations have bond-valences of ~0.25 *v.u.* If there were linkage between the (SO_4) and $(Al\varnothing_6)$ polyhedra, the linking atoms would have ideal bond-valence sums and could not participate further in the bonding. This would leave fewer anions to co-ordinate such large cations as Ca (and Y), which prefer larger co-ordination numbers. If the (SO_4) and $Al\varnothing_6$ polyhedra do not link to-

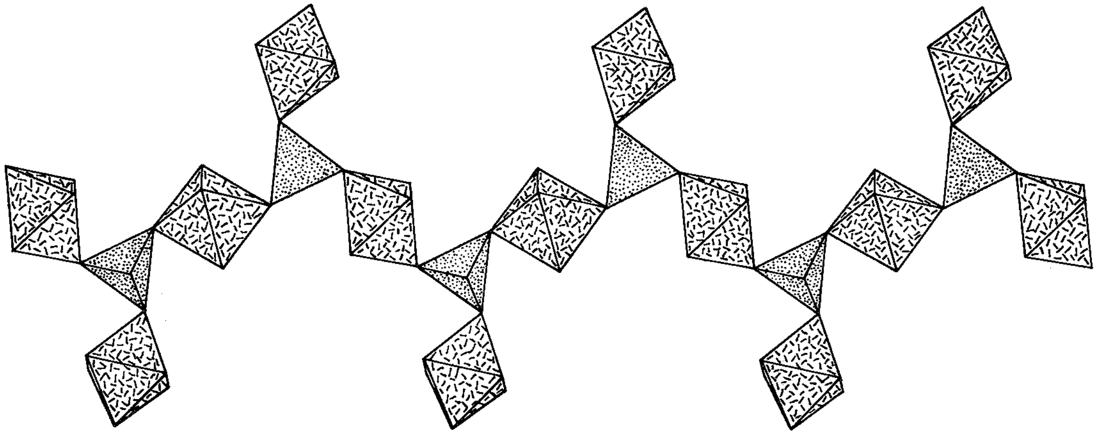

FIG. 3. The $[Al_2(PO_4)F_9]$ infinite chain that is the fundamental basis of the bøggildite structure.

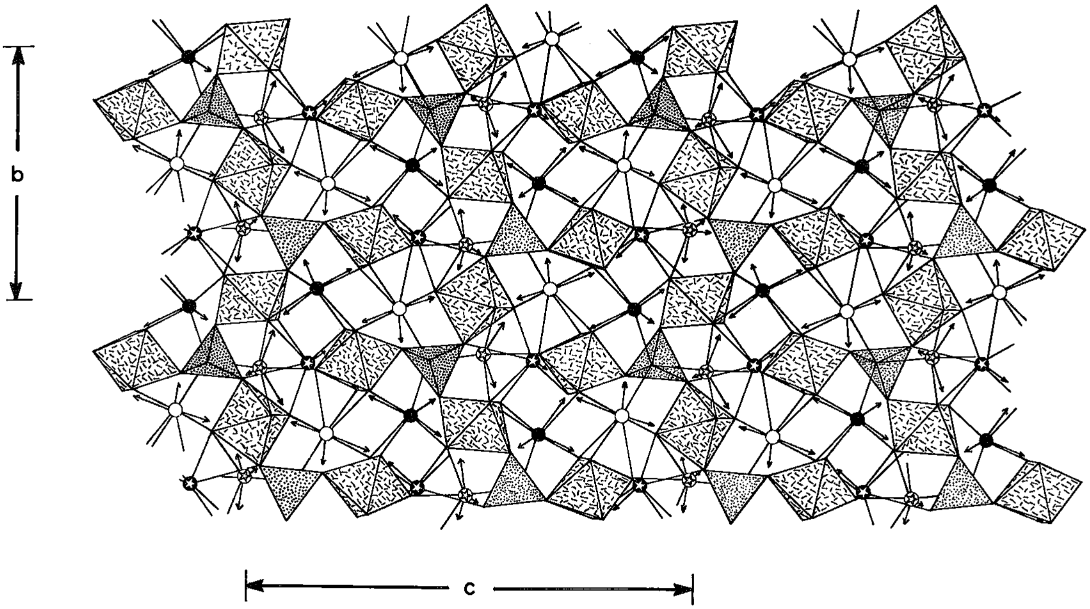

FIG. 4. Polyhedral representation of the bøggildite structure; legend as in Figure 1. Intercalation of the $[Al_2(PO_4)F_9]$ chains forms a sheet parallel to (100), that is illustrated here. Bonding within and between (indicated by bonds ending in arrows) sheets is from the Sr and Na cations as shown.

gether, this leaves far more anions free to participate in the co-ordination of Ca, allowing it to assume the co-ordination number it prefers, while still satisfying the bond-valence requirements of each anion. There are no other aluminofluorite minerals containing $(PO_4)^{3-}$ oxyanions to see if this argument holds true for other structures. However, the same argument can be applied to the mineral stenonite $Sr_2Al(CO_3)F_5$, which should thus have linked carbonate and aluminofluoride polyhedra. A structural study of stenonite is planned to test this argument.

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