

THE CRYSTAL STRUCTURE OF JØRGENSENITE

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ABSTRACT

The crystal structure of jørgensenite, $\text{Na}_2(\text{Sr,Ba})_{14}\text{Na}_2\text{Al}_{12}\text{F}_{64}(\text{OH})_4$, a 16.059(7), b 10.974(4), c 7.277(3) Å, β 101.70(3)°, monoclinic, $C2/m$, $Z = 1$, has been solved and refined to an R index of 7.4% using 1632 observed reflections recorded with $\text{MoK}\alpha$ X-rays. The structure is very similar to that of jarlilite, $\text{Na}_2(\text{Sr,Na},\square)_{14}\text{Al}_{12}(\text{Mg},\square)_2\text{F}_{64}(\text{OH},\text{H}_2\text{O})_4$. Sheets of corner-sharing AlF_6 and NaF_6 octahedra are intercalated with slabs of edge- and face-sharing $\text{Sr}\phi_9$, $(\text{Sr,Ba})\phi_9$ and $\text{Sr}\phi_{10}$ polyhedra. The following site-occupancies were obtained: $X(1) = X(3) = \text{Sr}$, $X(2) = 0.40 \text{ Sr} + 0.60 \text{ Ba}$, $\text{Al}(1) = \text{Al}(2) = \text{Al}$, $\text{Na}(1) = \text{Na}(2) = \text{Na}$. The principal differences from the jarlilite structure are (1) the occupancy of $X(2)$ by Ba rather than Na (as in jarlilite) and (2) the occupancy of $\text{Na}(2)$ by Na rather than Mg (as for the Mg site in jarlilite). Natural compositions show considerable solid-solution between end-members.

Keywords: jørgensenite, crystal structure, aluminofluoride mineral, jarlilite.

SOMMAIRE

Nous avons affiné la structure cristalline de la jørgensenite, $\text{Na}_2(\text{Sr,Ba})_{14}\text{Na}_2\text{Al}_{12}\text{F}_{64}(\text{OH})_4$, a 16.059(7), b 10.974(4), c 7.277(3) Å, β 101.70(3)°, monoclinique, $C2/m$, $Z = 1$, jusqu'à un résidu R de 7.4% en utilisant 1632 réflexions observées et enregistrées avec rayonnement $\text{MoK}\alpha$. La structure ressemble beaucoup à celle de la jarlilite, $\text{Na}_2(\text{Sr,Na},\square)_{14}\text{Al}_{12}(\text{Mg},\square)_2\text{F}_{64}(\text{OH},\text{H}_2\text{O})_4$. Des feuillettes d'octaèdres AlF_6 et NaF_6 à coins partagés sont intercalés avec des panneaux de polyèdres $\text{Sr}\phi_9$, $(\text{Sr,Ba})\phi_9$ et $\text{Sr}\phi_{10}$ partageant arêtes et faces. Nous avons trouvé les populations suivantes dans les sites: $X(1) = X(3) = \text{Sr}$, $X(2) = 0.40 \text{ Sr} + 0.60 \text{ Ba}$, $\text{Al}(1) = \text{Al}(2) = \text{Al}$, $\text{Na}(1) = \text{Na}(2) = \text{Na}$. La jørgensenite se distingue de la jarlilite surtout par (1) la présence de Ba dans le site $X(2)$ plutôt que par Na, et la présence de Na dans le site $\text{Na}(2)$ plutôt que par Mg (comme c'est le cas pour le site Mg dans la jarlilite). Dans la nature, il y a une solution solide importante entre les deux pôles.

(Traduit par la Rédaction)

Mots-clés: jørgensenite, structure cristalline, aluminofluorure, jarlilite.

INTRODUCTION

Jarlilite is a strontium-bearing aluminofluoride mineral first described by Bøggvad (1933) from the Ivigtut cryolite deposit, Greenland. Bøggvad (1933) also reported another mineral, which he named "meta-jarlilite", very similar to jarlilite in composition, appearance and occurrence. Brosset (1942) and Ferguson (1947, 1949) proposed that "meta-jarlilite" is the same species as jarlilite, the former being at most a compositional variety of the latter. Both Brosset (1942) and Ferguson (1949) noted the major discrepancy between the observed (3.87) and calculated (3.61 g/cm³) specific gravities of jarlilite, and concluded that the formula of jarlilite, $\text{NaSr}_3\text{Al}_3\text{F}_{16}$, was wrong. Hawthorne

(1983) solved the crystal structure of jarlilite and proposed a new formula: $\text{Na}_2(\text{Sr,Na},\square)_{14}\text{Al}_{12}(\text{Mg},\square)_2\text{F}_{64}(\text{OH},\text{H}_2\text{O})_4$. Detailed work on the chemical composition and paragenesis (Pauly 1992, Pauly & Nielsen 1992) showed that the situation is more complicated than was previously realized. Specifically, there are significant chemical and paragenetic differences between jarlilite and "meta-jarlilite"; these are summarized in detail by Pauly *et al.* (1997), who showed that "meta-jarlilite" is a distinct mineral species, which they named jørgensenite, $\text{Na}_2(\text{Sr,Ba})_{14}\text{Na}_2\text{Al}_{12}\text{F}_{64}(\text{OH})_4$. In order to fully characterize the structural and chemical relationships between jørgensenite and jarlilite, we here present the results of a crystal-structure study of jørgensenite.

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EXPERIMENTAL

The crystals examined here are from the stemonite paragenesis (Pauly 1962, Pauly & Nielsen 1992). Precession photographs show the cell and space group (Table 1) to be conformable with that of jarlite (Hawthorne 1983). An equidimensional crystal was

TABLE 1. MISCELLANEOUS INFORMATION FOR JØRGENSENITE

<i>a</i> (Å)	16.059(7)	Crystal size	-0.20 mm
<i>b</i>	10.974(4)	Rad/Monochr.	Mo/Gr
<i>c</i>	7.277(3)	Total <i>F</i>	4001
β (°)	101.70(3)	Unique <i>F</i>	1940
<i>V</i> (Å ³)	1256.0(9)	<i>F</i> ₀ > 5σ	1632
Space group	<i>C2/m</i>	<i>R</i> (azimuthal) %	10.3 - 3.9
		<i>R</i> (obs) %	7.4
		<i>wR</i> (obs) %	9.2

Unit cell contents: [Na₂(Sr,Ba)₁₄Al₁₂F₆₆(OH)₄]
 $R = \sum(|F_o| - |F_c|) / \sum |F_o|$
 $wR = \sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2$, $w = 1/\sigma^2(F)$

mounted on a Nicolet R3m automated four-circle diffractometer equipped with a Mo X-ray tube. Twenty-five reflections were aligned automatically; from the resulting setting angles, a least-squares refinement gave the cell dimensions listed in Table 1. Intensity data were collected according to the method of Hawthorne & Groat (1985). A total of 4001 reflections were measured over two asymmetric units to a maximum 2θ angle of 60°. Absorption corrections were done by the psi-scan method, modeling the crystal shape as an

ellipsoid. Data were corrected for Lorentz, polarization and background effects, and reduced to structure factors. A reflection was considered as observed if its magnitude exceeded that of 5σ based on counting statistics. Miscellaneous information pertinent to data collection and refinement is given in Table 1.

STRUCTURE REFINEMENT

Scattering curves 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. All calculations were done using the SHELXTL PLUS system of programs.

The atom positions for jarlite (Hawthorne 1983), appropriately modified for differences in chemical composition, were used as a starting model for the jørgensenite structure. Refinement eventually converged to an *R* index of 7.5% for an anisotropic displacement model. As this value of *R* index is significantly higher than we usually obtain, another set of intensity data was collected on this crystal and gave the same result. Intensity data were collected on a second crystal, and refinement converged to an *R* index of 7.4%. We conclude that the high *R* index is a consequence of the material rather than any deficiency in the data-collection procedure. The results of the last refinement are given in Table 2, selected interatomic distances are listed in Table 3, and an empirical bond-valence table is given in Table 4. Observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 2. ATOMIC PARAMETERS FOR JØRGENSENITE

	<i>x</i>	<i>y</i>	<i>z</i>	* <i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
X(1)	0	0	0	35(1)	31(1)	39(2)	33(2)	0	4(1)	0
X(2)	0.2615(1)	0	0.1291(2)	33(1)	34(1)	32(1)	34(1)	0	8(1)	0
X(3)	0.3513(1)	0.1947(1)	0.6952(2)	34(1)	33(1)	36(1)	32(1)	0(1)	6(1)	1(1)
Al(1)	0.1631(4)	0	0.5408(9)	28(2)	31(3)	29(3)	25(3)	0	5(2)	0
Al(2)	0.1080(3)	0.2430(4)	0.7973(6)	29(1)	31(2)	28(2)	27(2)	0(2)	7(2)	0(2)
Na(1)	0	1/2	0	34(5)	32(8)	42(9)	25(7)	0	0(1)	0
Na(2)	0	1/2	1/2	30(4)	29(6)	37(7)	26(6)	0	10(4)	0
OH(1)	0.4225(9)	0	0.7158(18)	24(4)	28(6)	22(6)	20(6)	0	1(5)	0
F(2)	0.2429(9)	0	0.7533(17)	39(4)	44(7)	49(8)	22(6)	0	2(5)	0
F(3)	0.0951(8)	0	0.3136(17)	40(4)	35(7)	56(8)	25(6)	0	-1(5)	0
F(4)	0.1151(6)	0.3660(9)	0.9670(12)	36(3)	44(5)	37(5)	26(4)	-5(4)	6(3)	2(4)
F(5)	0.2265(5)	0.1163(8)	0.4512(12)	34(3)	36(4)	33(4)	35(4)	3(4)	8(3)	-4(4)
F(6)	0.2202(5)	0.2535(9)	0.8104(12)	35(3)	33(4)	40(5)	32(4)	-1(4)	8(3)	0(4)
F(7)	0.0025(5)	0.2282(9)	0.2101(13)	41(3)	32(4)	50(6)	39(5)	-1(4)	8(4)	-6(4)
F(8)	0.0948(6)	0.3556(9)	0.6135(14)	45(3)	52(6)	49(6)	34(5)	12(4)	12(4)	7(5)
F(9)	0.0998(6)	0.1182(9)	0.6225(16)	50(4)	45(5)	48(6)	56(6)	-21(5)	9(5)	-1(5)
F(10)	0.1260(6)	0.1352(8)	0.9910(12)	36(3)	40(4)	34(5)	33(4)	8(4)	6(3)	0(4)

* $U_i = U_i \times 10^{-3}$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN JØRGENSENITE

X(1)-F(3)	x2	2.48(1)	X(3)-OH(1)	2.413(8)
X(1)-F(7)	x4	2.93(1)	X(3)-F(2)	2.84(1)
X(1)-F(10)a	x4	2.52(1)	X(3)-F(4)d	2.50(1)
<X(1)-F>		2.68	X(3)-F(5)	2.54(1)
X(2)-F(2)a		2.69(1)	X(3)-F(5)b	2.54(1)
X(2)-F(4)b	x2	2.67(1)	X(3)-F(6)	2.50(1)
X(2)-F(5)	x2	2.82(1)	X(3)-F(7)b	2.46(1)
X(2)-F(6)b	x2	2.75(1)	X(3)-F(8)b	2.63(1)
X(2)-F(10)a	x2	2.66(1)	X(3)-F(10)d	2.92(1)
<X(2)-F>		2.72	<X(3)-O,F>	2.59
Al(1)-F(2)		1.80(1)	Al(2)-F(4)	1.82(1)
Al(1)-F(3)		1.79(1)	Al(2)-F(6)	1.79(1)
Al(1)-F(5)	x2	1.83(1)	Al(2)-F(7)e	1.77(1)
Al(1)-F(9)	x2	1.82(1)	Al(2)-F(8)	1.80(1)
<Al(1)-F>		1.82	Al(2)-F(9)	1.86(1)
			Al(2)-F(10)	1.82(1)
			<Al(2)-F>	1.81
Na(1)-OH(1)c	x2	2.19(1)	Na(2)-OH(1)f	x2 2.19(1)
Na(1)-F(4)a	x4	2.41(1)	Na(2)-F(8)	x4 2.24(1)
<Na(1)-OH,F>		2.34	<Na(2)-OH,F>	2.22

a: x, y, z-1; b: 1/2-x, 1/2-y, 1-z; c: -1/2+x, 1/2+y, z-1;
d: 1/2-x, 1/2-y, 2-z; e: -x, y, 1-z; f: -1/2+x, 1/2+y, z.

TABLE 4. EMPIRICAL BOND-VALENCE TABLE* FOR JØRGENSENITE

X(1)	X(2)	X(3)	Al(1)	Al(2)	Na(1)	Na(2)	Σ
OH(1)		0.44			0.22 ^{2d}	0.22 ^{2d}	0.88
F(2)	0.20	0.13	0.50				0.83
F(3)	0.24 ^{2d}		0.51				0.75
F(4)	0.20 ^{2d}	0.24		0.48	0.14 ^{2d}		1.06
F(5)	0.16 ^{2d}	0.22	0.47 ^{2d}				1.07
F(6)	0.16 ^{2d}	0.24	0.51				0.93
F(7)	0.12 ^{2d}	0.25	0.54				0.91
F(8)		0.19	0.50		0.20 ^{2d}		0.89
F(9)			0.48 ^{2d}	0.44			0.92
F(10)	0.23 ^{2d}	0.21 ^{2d}	0.12	0.48			1.04
Σ	1.88	1.70	2.05	2.91	2.95	1.00	1.24

* calculated from the curves of Brown (1981)

DISCUSSION

Cation occupancies

Chemical analysis of jørgensenite from the stononite paragenesis indicates that the X-site occupancies are dominated by Sr and Ba. This is in accord with the refined site-scattering values for the X sites in jørgensenite, which indicate the occupancies X(1) = X(3) = Sr, X(2) = Sr_{0.40}Ba_{0.60}; these differ significantly from the analogous site-occupancies found for jarlite (Table 5) by Hawthorne (1983).

There are two distinct Al sites in this structure type, with a total content of 12 Al sites per cell. The scattering from each site is compatible with full occupancy of

both Al(1) and Al(2) by Al in both jørgensenite and jarlite, and this is in excellent accord with the Al content of each mineral (Pauly & Nielsen 1992). This is further indicated by the <Al(1)-F> and <Al(2)-F> distances in each structure: 1.81 and 1.82 Å in jørgensenite, 1.81 and 1.81 Å in jarlite.

The Na(1) site in jørgensenite is occupied by Na; the observed <Na(1)-φ> distance (φ: unspecified anion) of 2.34 Å is completely compatible with this occupancy, and is close to the analogous value of 2.31 Å in jarlite. The Na(2) site has a site-scattering value compatible with occupancy by Na (Z = 11) or Mg (Z = 12), and we must rely on other factors to identify the constituent cation(s). The <Na(2)-φ> distance in jørgensenite is 2.22 Å, and the analogous value in jarlite (for the Mgφ₆ octahedron) is 2.08 Å. These two values, together with the chemical composition of jørgensenite, suggest that Na(2) is occupied by a mixture of Na and Mg. We cannot simply use the difference in mean bond-length at the two sites as an indication of the relative amounts of Na and Mg, as the Mgφ₆ octahedron in jarlite contains Mg, vacancy and possibly a small amount of Na. An ideal <Mg-F> distance may be obtained by summing the relevant ionic radii from Shannon (1976): 0.72 + 1.30 = 2.02 Å. This suggests that Na(2) contains approximately 0.7 Na and 0.3 Mg, in reasonable agreement with the results of chemical analysis of jørgensenite (Pauly & Nielsen 1992) and the incident bond-valence sum (1.24 valence units, *vu*) at the Na(2) site in jørgensenite (Table 4).

TABLE 5. EMPIRICAL BOND-VALENCE TABLE* FOR JARLITE

X(1)	X(2)	X(3)	Al(1)	Al(2)	Na(1)	Mg	Σ
OH(1)		0.399			0.279 ^{2d}	0.359 ^{2d}	0.977*
F(2)	0.174	0.130	0.507				0.811
F(3)	0.238 ^{2d}		0.549				0.787
F(4)	0.179 ^{2d}	0.228		0.482	0.154 ^{2d}		1.037
F(5)	0.119 ^{2d}	0.220	0.486 ^{2d}				1.044
F(6)	0.161 ^{2d}	0.222		0.549			0.932
F(7)	0.119 ^{2d}	0.247		0.549			0.915
F(8)		0.157		0.469		0.283 ^{2d}	0.889
F(9)			0.455 ^{2d}	0.446			0.901
F(10)	0.223 ^{2d}	0.183 ^{2d}	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)

Description of the structure

Jørgensenite is essentially isostructural with jarlite; the sheet of octahedra within the structure is illustrated in Figure 1. An array of AlF₆ octahedra is linked into a sheet by chains of corner-sharing Naφ₆ octahedra. It is here that one of the principal differences from the jarlite structure is apparent. Jørgensenite has the Na(2) position occupied by Na, whereas the analogous site in jarlite contains Mg and □. These sheets of octahedra are interleaved with thick slabs of Xφ_n polyhedra

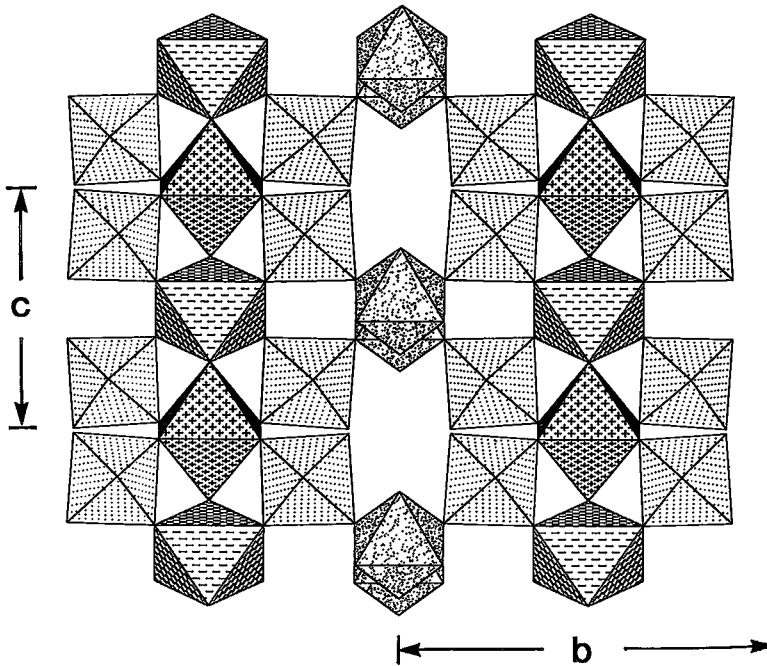


FIG. 1. Part of the crystal structure of jørgensenite viewed perpendicular to (100); $Al(1)\phi_6$ octahedra are regular-dot shaded, $Al(2)\phi_6$ octahedra are random-dot shaded, $Na(1)\phi_6$ octahedra are cross-shaded, and $Na(2)\phi_6$ octahedra are broken-line shaded.

(Hawthorne 1983) to form a dense and fairly isodesmic structure.

The bond-valence arrangement in jørgensenite is shown in Table 4, and can be compared with that of jarlrite (Table 5). There are two principal differences between the two structures: (1) the $X(2)$ site is occupied by $0.81Sr + 0.19Na$ in jarlrite, and by $0.40Sr + 0.60Ba$ in jørgensenite, and hence the bond valences involving the $X(2)$ cation are systematically larger in jørgensenite than in jarlrite; (2) the Mg site in jarlrite corresponds to the $Na(2)$ site in jørgensenite, and hence the corresponding bond-valences are smaller in jørgensenite than in jarlrite. Indeed, simple comparison of the ideal end-member formulae of jørgensenite and jarlrite shows that they should have bond-valence sums of 1.0 and 2.0 vu , respectively, at the $Na(2)$ and Mg sites; the observed values of 1.24 vu (Table 4) and 1.77 vu (Table 5) illustrate the essential difference between the two structures, and show that each observed composition has about 25% of the other end-member in solid solution.

CONCLUSIONS

Jørgensenite, $Na_2(Sr,Ba)_{14}Na_2Al_{12}F_{64}(OH)_4$, is isostructural with jarlrite, $Na_2(Mg,\square)_2(Sr,Na,\square)_{14}Al_{12}F_{64}(OH,H_2O)_4$. The ideal end-member compositions are related by the substitution $Na_2 \rightleftharpoons Mg + \square$, and natural compositions show significant solid-solution between these two end members.

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