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Derivative structures based on the alunite octahedral sheet: mitridatite and englishite

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SUMMARY. It is proposed that mitridatite and englishite contain octahedral sheets of the alunite type and that their formulae are $[Ca_6(H_2O)_3(PO_4)_2][Fe_3(OH)_6(PO_4)(PO_3OH)]_3$ and $[K_2Na(H_2O)_4Ca_{4\cdot5}(PO_3OH)_3][Al_3(OH)_6(PO_4)(PO_3OH)]_3$ respectively.

DURING the course of compiling new single crystal data on basic iron and aluminium phosphates, a striking relationship was noted between two very complex structures—mitridatite and englishite—and the relatively simple alunite structure type. The alunite structure is based on a network of corner-linked Me^{3+}–oxygen octahedra whose cation centres reside on the nodes of the familiar Kagomé net. An orthohexagonal unit of this net includes six octahedra (fig. 1). Many compounds, both natural and synthetic, are based on the alunite structure, including crandallite, $Ca[Al_3(OH)_6(PO_4)(PO_3OH)]$, a species recently investigated in detail by Blount (1974).

The relationship was noted during a three-dimensional crystal structure analysis on mitridatite. Despite the large cell with an estimated 40 atoms in the asymmetric unit, it was hoped that the chemistry of this important phase could be rationalized. Presently, we have located the Fe^{3+} atoms, the associated PO_4 tetrahedra, and the hydroxyl groups; these define the components of an alunite-like sheet, $[Fe_3^{3+}(OH)_6(PO_4)(PO_3OH)]^{2-}$, parallel to {100} and located at intervals $x = 1/4$ and $3/4$. Unfortunately, progress on the rest of this structure is slow owing to difficulty in assigning correct phases associated with weak superstructure reflexions. A single crystal study on englishite shows that reflexions in the b^*c^* plane are related to those of mitridatite and that both compounds reveal a strong pseudohexagonal intensity distribution in this plane (cf. Moore, 1974).

Cell parameters for englishite, mitridatite, and crandallite appear in Table I. The data for englishite, heretofore unpublished, were obtained from a single crystal fragment of Fairfield, Utah, material. Owing to the large cell, it was not possible to refine the full three-dimensional cell based on the powder data since ambiguities exist in indexing. The mineral exhibits perfect micaceous cleavage parallel to {100}; preferential orientation of flakes crushed with glass and placed on a slide afforded the enhanced *h*00 reflexions, which were utilized to refine the *a*-axial dimension (Table II). The remaining data were obtained from calibrated precession photographs and probably have associated errors of 0·3 %. Streaks appeared on the photographs indicating

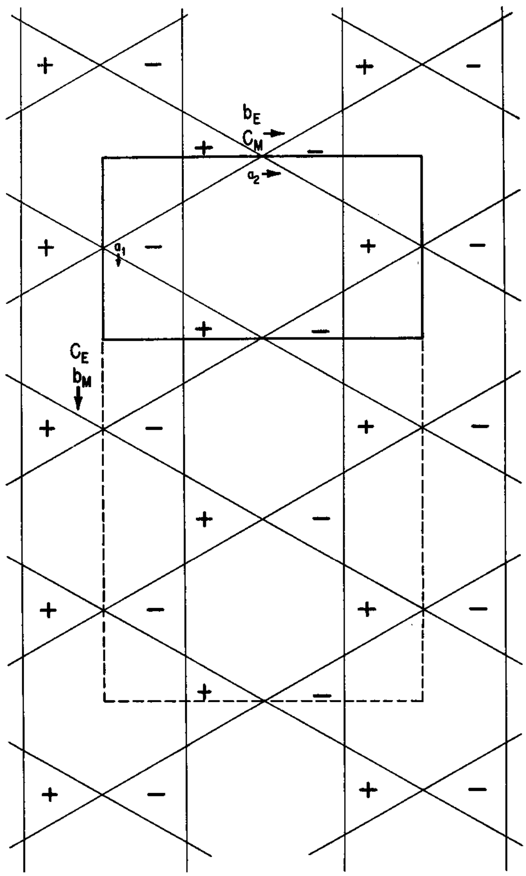

FIG. 1. The Kagomé net whose nodes are the octahedral centres in sheets of the alunite type. Associated tetrahedra above (+) or below (—) the sheets are indicated. The axes a_1 and a_2 refer to the orthohexagonal unit in Table IV; b_E and c_E, and b_M and c_M are the crystal cell coordinates for englishite and mitridatite in Table I.

TABLE I. *Cell data for englishite, mitridatite, and crandallite*

		Englishite*	Mitridatite†	Crandallite‡
a		38.43(2) Å	17.52(2)	7.00(1)
b		11.86 Å	19.35(4)	
c		20.67 Å	11.25(2)	16.19
β		111°16′	95°55′	
Space group		A2/a or Aa	A2/a or Aa	R$\bar{3}$m
Density	obs.	2.65 g.cm^{-3}	3.24	2.95
	calc.	2.67	3.27	3.00
Z		8	4	1

* Errors in b, c, and β are uncertain since the results were computed from precession films

† Data from Moore (1974)

‡ Data from Blount (1974)

Observed densities are from Larsen and Shannon (1930) for englishite and crandallite, and from Moore (1974) for mitridatite.

a small degree of disorder in the crystal. Powder data, obtained from a single crystal Gandolfi camera, are presented in Table III. No attempt was made to index these data since a full three-dimensional single crystal data set is not yet at hand.

The crucial information appears in Table IV. Here, the cell data have been transformed into the orthohexagonal equivalent of the alunite cell, with $a_1 = a_{\text{hex}}$, $a_2 = a_{\text{hex}}\sqrt{3}$ and $c' = c_{\text{hex}}$. It is noted that a, $c/3$, and $b/3$; $a\sqrt{3}$, b, and c; and c, $\frac{1}{2}a \sin\beta$, $a \sin\beta$ for alunite, englishite, and mitridatite respectively are related according to the orthohexagonal unit. Crandallite is included for purposes of comparison since it is a phosphate and since 'acid' phosphate tetrahedra occur in the structure.

TABLE II

Englishite; the h00 reflexions

I	d	hkl	a sin β
75	17.89 Å	200	35.78 Å
100	8.96	400	35.84
45	5.965	600	35.79
40	3.581	10.0.0	35.81
75	2.983	12.0.0	35.80
70	2.558	14.0.0	35.81
20	2.240	16.0.0	35.84
15	1.9897	18.0.0	35.82
5	1.7911	20.0.0	35.82
15	1.6295	22.0.0	35.85

Flakes crushed with glass; Si internal standard (a 5.4301 Å). Chart diffractogram, Cu-Kα radiation, ½° per min.

TABLE III

Englishite; X-ray powder data

I	d	I	d	I	d	I	d
9	17.66Å	1	3.18 Å	4	2.34 Å	1	1.62 Å
10	8.94	3	3.08	1	2.22	3	1.58
1	7.01	6	2.96	1	2.19	2	1.42
2	5.86	8	2.84	2	2.09	3	1.36
6	5.57	2	2.77	2	1.97	2	1.16
1	5.25	6	2.68	2	1.93	2	1.13
4	3.85	2	2.62	2	1.84	3	1.08
1	3.58	2	2.58	5	1.71	2	1.03
1	3.40	3	2.54	2	1.68	3	0.98
2	3.35	1	2.46	1	1.65		

114.6 mm diam. camera, single-crystal Gandolfi technique, Fe-Kα radiation, Mn filter

TABLE IV. *Alunite sheet structures: orthohexagonal unit*

	Alunite		Englishite		Mitridatite		Crandallite	
a_1	a	6.97 Å	c/3	6.89 Å	b/3	6.45 Å	a	7.00 Å
a_2	a√3	12.07	b	11.86	c	11.25	a√3	12.11
c'	c	17.38	½a sin β	17.90	a sin β	17.43	c	16.19
Vol. per O^{2-}	17.4 Å^3		18.9 Å^3		17.9 Å^3		16.2 Å^3	
No. of sheets	3		2		3		3	

To relate their crystal chemistry further, it is assumed that mitridatite contains $[Fe^{3+}_3(OH)_6(PO_4)(PO_3OH)]^{2-}$ sheets, and englishite (and crandallite) $[Al^{3+}_3(OH)_6(PO_4)(PO_3OH)]^{2-}$ sheets of the alunite type. The chemical analysis for englishite in Larsen and Shannon (1930) and for mitridatite in Moore (1974) were recomputed on the basis of this interpretation. It is seen that in the c'-repeat, alunite and crandallite possess three sheets, and englishite and mitridatite two sheets each. The remaining ions are assumed to reside between these sheets. In this manner, the distributions between the sheets and in the sheets can be assigned (Table V). Presumably, these complexes of ions between the sheets contribute to the complexity of the mitridatite and englishite crystal cells. Further analysis of their structures should provide an answer for the distribution of these inter-sheet ions.

Further support for this interpretation comes from calculations on the oxygen packing. The volumes per oxygen are 17·4, 18·9, 17·9, and 16·2 Å^3 for alunite, englishite, mitridatite, and crandallite respectively (Table IV). Finally, the calculated compositions for englishite and mitridatite are in good agreement with the published analyses (Table VI) as are the computed densities and observed specific gravities (Table I).

TABLE V. *Proposed crystal-chemical formulae for crandallite, mitridatite, and englishite*

	Between sheets	In sheets
Crandallite	$[Ca_3]^{6+}$	$[Al_3(OH)_6(PO_4)(PO_3OH)]_3^{6-}$
Mitridatite	$[Ca_6(H_2O)_3(PO_4)_2]^{6+}$	$[Fe_3(OH)_6(PO_4)(PO_3OH)]_3^{6-}$
Englishite	$[K_2Na(H_2O)_4Ca_{4.5}(PO_3OH)_3]^{6+}$	$[Al_3(OH)_6(PO_4)(PO_3OH)]_3^{6-}$

TABLE VI. *Chemical analyses of mitridatite and englishite, compared with theory for the formulae of Table IV*

	Englishite		Mitridatite	
	1	2	3	4
K_2O	5.4	5.34	-	-
Na_2O	1.6	1.75	-	-
CaO	14.1	14.31	17.4	18.03
Al_2O_3	24.7	26.03	-	-
Fe_2O_3	-	-	38.3*	38.51
P_2O_5	37.8	36.24	31.5	30.44
H_2O	16.5	16.33	12.8	13.02
Sum	100.1	100.00	100.0	100.00

1. Larsen and Shannon, 1930
2. Theoretical composition
3. Ito anal. in Moore, 1974.
4. Theoretical composition

* Includes 2.7% Mn_2O_3

These interpretations shed new light on the complex mineral chemistry of mitridatite and englishite. The common appearance of mitridatite as a low-temperature product in phosphate-bearing pegmatites has been noted by Moore (1974) and englishite occurs associated with crandallite and related phosphates (Larsen and Shannon, 1930). As the alunite sheet is a stable moiety over a wide range of conditions, it is not unreasonable that its octahedral basis can be utilized in a variety of more complicated structures.

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