Crystal Structure of Aenigmatite

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Summary The crystal structure of aenigmatite, related to that of sapphirine, consists of "octahedral walls" connected by $[Si_6O_{18}]_\infty$ chains and by octahedra between walls.

AENIGMATITE (cossyrite) is a common constituent of many sodium-rich peralkaline igneous rocks, both of volcanic and plutonic parageneses. Its structure has for a long time presented an interesting crystallochemical problem.

The *X*-ray crystallography of aenigmatite has recently been studied by Kelsey and McKie,[1] who, on the basis of published and new analyses, suggested the idealized formula $Na_4Fe_{10}Ti_2Si_{12}O_{40}$ for the contents of the unit cell, and gave the following crystal data: $a = 10{\cdot}406$, $b = 10{\cdot}813$, $c = 8{\cdot}926$ Å, $\alpha = 104°56'$, $\beta = 96°52'$, $\gamma = 125°19'$.

Atomic co-ordinates and cation distribution in aenigmatite

Atom		*x*	*y*	*z*
M(1)	Fe	0·320	0·351	−0·317
M(2)	Fe	0·765	0·320	−0·349
M(3)	Fe	0·597	0·443	−0·435
M(4)	Fe	0·096	0·438	−0·450
M(5)	Na	0·207	0·126	−0·110
M(6)	Na	0·663	0·114	−0·130
M(7)	Ti	0·996	0·241	−0·245
M(8)	Fe	0	1/2	0
M(9)	Fe	0	0	1/2
T(1)	Si	0·208	0·157	0·254
T(2)	Si	0·721	0·162	0·271
T(3)	Si	0·521	0·265	0·168
T(4)	Si	0·015	0·264	0·150
T(5)	Si	0·647	−0·060	0·448
T(6)	Si	0·647	0·446	−0·058
O(1)		0·237	0·380	−0·117
O(2)		0·758	0·387	−0·115
O(3)		0·360	0·565	−0·338
O(4)		0·863	0·565	−0·340
O(5)		0·564	0·449	−0·256
O(6)		0·018	0·424	−0·226
O(7)		0·662	0·666	−0·460
O(8)		0·165	0·663	−0·419
O(9)		0·762	−0·107	0·362
O(10)		0·248	−0·102	0·375
O(11)		0·834	0·136	0·175
O(12)		0·326	0·136	0·168
O(13)		0·478	−0·210	0·472
O(14)		−0·067	−0·234	0·429
O(15)		0·602	0·002	0·306
O(16)		0·064	−0·012	0·240
O(17)		0·094	0·174	0·116
O(18)		0·593	0·161	0·148
O(19)		0·511	0·308	−0·009
O(20)		0·965	0·278	−0·019

The way to the solution of the crystal structure of aenigmatite was opened by the publication of the crystal structure of sapphirine by Moore.[2] In fact, notwithstanding their very different chemistry, there are profound crystallochemical similarities between these two minerals. For sapphirine, Moore gave the following crystal data: $a = 11{\cdot}266$, $b = 14{\cdot}401$, $c = 9{\cdot}923$ Å, $\beta = 125°28'$, space group $P2_1/a$, with an asymmetric unit formula $M_8T_6O_{20}$, where M represents octahedral cations (Mg and Al) and T tetrahedral cations (Al and Si). This formula reveals a close analogy with that of aenigmatite, which contains sixteen octahedral and twelve tetrahedral cations for forty oxygen anions.

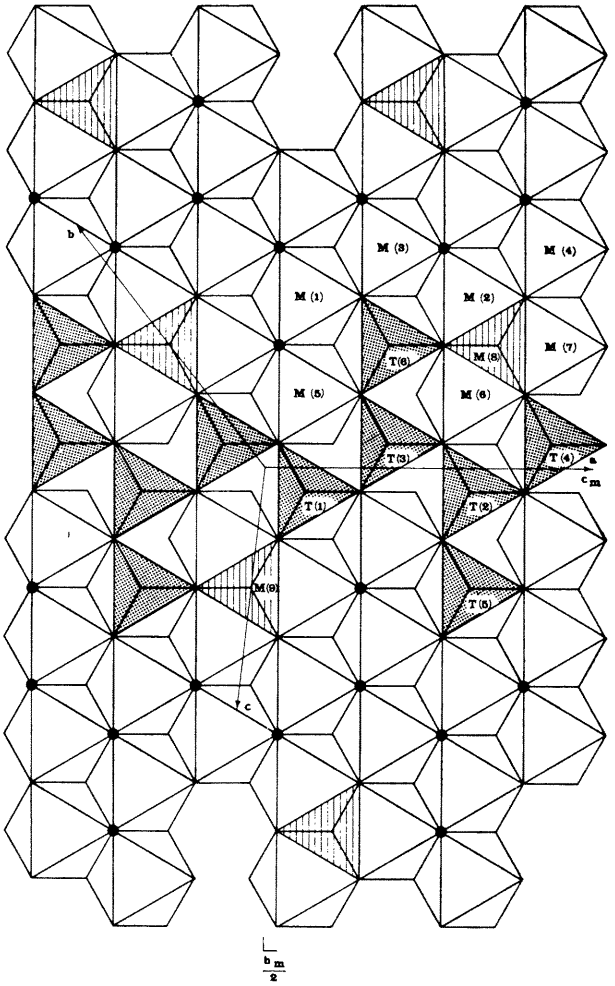

FIGURE. *Idealised polyhedral diagram of the aenigmatite structure down* a_m^*. *Octahedra in the walls are white, tetrahedra of the* $[Si_6O_{18}]_\infty$ *chain are dotted, and the ruled regions indicate the edges shared with the octahedra between the walls. Filled circles denote junction of octahedra with the tetrahedral vertices above the walls. Tetrahedral chains running below the walls are not shown. Triclinic and pseudomonoclinic cells are indicated*: b *and* c *vectors end at height* $\frac{1}{2}(d_{100})_m$.

Moreover the triclinic aenigmatite cell can be described in terms of a multiple (fourfold) pseudomonoclinic cell with parameters: $a_m = 12{\cdot}118$, $b_m/2 = 14{\cdot}814$, $c_m = 10{\cdot}406$ Å, $\beta_m = 127°9'$, which show a close relationship to the corresponding parameters of the sapphirine cell. The triclinic cell is transformed by $[011/\bar{1}22/100]$ to obtain the pseudomonoclinic cell; the letter *m* indicates quantities which refer to the pseudomonoclinic cell.

On the basis of these considerations a trial model for the crystal structure of aenigmatite was derived: in the trial model the asymmetric unit, apart from its chemical composition, was the same as that in sapphirine. In aenigmatite, two octahedral cations M(8) and M(9) in special positions on inversion centres corresponded to the M(8) octahedral cation in a general position in sapphirine. As regards the chemistry, the tetrahedral sites were occupied by silicon atoms; among the octahedral cations, M(5) and M(6), which share oxygen atoms with two silicon atoms, had to be sodium cations to satisfy Pauling's electrostatic valence rule. It was assumed at this stage that the remaining octahedral sites were all occupied by iron cations.

To test the model, intensity data were collected from a small fragment cut from a specimen of aenigmatite from Naujakasik, Greenland, donated by Prof. E. Onorato. Three layers with c as precessing axis ($l = 0$, 1, and 2) were recorded by integrated Buerger precession photographs. The intensities, measured with a Nonius microdensitometer, were corrected for Lorentz and polarization factors; no transmission factor correction was applied. Three cycles of full-matrix least-squares refinement applied to the co-ordinates of the trial model gave a reliability index $R_{hkl} = 0{\cdot}136$ for the 908 observed reflections.

The chemistry of aenigmatite strongly suggests that a titanium cation is ordered on a particular octahedral site, and bond-length calculations indicated M(7) as the titanium site. Then two more refinement cycles brought R_{hkl} to 0·119. Unit weights were attributed to all reflections and form factors for the neutral atoms were used throughout. Positional co-ordinates at the present stage of refinement are given in the Table. A refinement with full three-dimensional data is in preparation, so the errors and the thermal parameters are not included.

The crystal structure of aenigmatite is represented, following Moore,[2] as an idealized polyhedral diagram in the Figure which clearly shows the close relationship with the crystal structure of sapphirine: also the structure of aenigmatite can be considered as constructed from the three structural components found by Moore in sapphirine: (i) octahedral walls which run parallel to the a-axis (or c_m axis) and oriented parallel to {011} (or $\{100\}_m$) plane; (ii) tetrahedral chains $[Si_6O_{18}]_\infty$ which run parallel to the a (or c_m) axis; (iii) octahedra between walls, sharing edges with the walls above and below.

The two structures differ in the chemical nature of the three structural components and in the way in which the structural components are joined to form the three-dimensional arrangement.

The aenigmatite crystallochemical formula can be written as $Na_2Fe_4^{VI}Ti^{VI}(Fe^{VI})O_2[Si_6O_{18}]$, where, following Moore, the parentheses include the octahedral iron atom placed between walls. Thus, in the conventional classification of silicates, aenigmatite should be placed among the chain silicates.

The results of refinement with full three-dimensional data must be awaited before the cation distribution can be definitively confirmed and the precise deviations from ideality of the polyhedral arrangements can be established.

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Added in proof. The crystal structure of aenigmatite has been simultaneously and independently obtained by Camillo and Mazzi, of the Institute of Mineralogy, University of Pavia.

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[1] C. H. Kelsey and D. McKie, *Mineral. Mag.*, 1964, **33**, 986.
[2] P. B. Moore, *Nature*, 1968, **218**, 81; *Amer. Mineralogist*, 1969, **54**, 31.