Crystal structure of muirite $Ba_9(Ca, Ba)(Ca, Ti)_4(OH)_8[Si_8O_{24}](Cl, OH)_8$

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The present paper continues the crystallochemical study[1] of natural and synthetic barium minerals. Crystals of the present Ba silicate were kindly provided by Professor A. Pabst of the University of California, this being one of seven new barium minerals observed in barium-rich gneisses near Mount Fresno.[2]

The mineral $Ba_9(Ca, Ba)(Ca, Ti)_4(OH)_8[Si_8O_{24}](Cl, OH)_8$ is essentially a Ba silicate of complex composition:

SiO_2	Al_2O_3	TiO_2	FeO	CaO	K_2O	BaO	SrO	(O≡Cl)	Σ
21.60	0.70	4.20	2.06	4.70	0.10	60.10	0.13	1.00	100

and it consists of small orange to brown grains of size up to 0.3 mm. The crystals had faces of {100} prism and {001} pinakoid, with clear cleavage on these planes. It has been reported[2] that the parameters of the tetragonal cell are a = 13.942; c = 5.590 Å, ρmea = 3.86 g/cm³, Z = 1, and the possible space groups are P4/mmm, P4mm, P422, P$\bar{4}$m2, and P$\bar{4}$2m. We selected for x-ray examination a single crystal of irregular form (0.20 × 0.20 × 0.10 mm³); we found a = 14.000 ± 0.003; c = 5.625 ± 0.002 Å, as refined with a P$\bar{1}$ Syntex diffractometer, and these values agree satisfactorily with those found previously.

The available evidence consisted of 956 independent nonzero reflections, and this was obtained with the same diffractometer (Mo radiation, graphite monochromator, $2\theta - \theta$ method, variable scan range of 6-24 deg/min, $0 \le h \le 18$, $h \ge k$, $0 \le l \le 10$). The intensities were converted to $|F_{hkl}|$, and the subsequent operations were performed as well, at the computing center at Moscow University using a BÉSM-4M computer with the Kristall programs.[3] No absorption correction was applied.

There were no systematic absences, so the mineral belongs to one of the above symmorphic space groups. The structure was elucidated within the framework of the holohedral group by the heavy-atom method. The model was refined by least squares in the isotropic approximation to R = 0.075 using all 956 reflections (R = 0.069 from 934 $|F_{hkl}|$). The OH groups were distinguished by means of the valency balances. Tables 1 and 2 give the coordinates of the basal atoms with individual temperature corrections and also the interatomic distances. A characteristic feature of the structure is that there are isolated eight-sided silicon–oxygen rings $[Si_8O_{24}]$ (Fig. 1a, in center) around a four-fold axis; the symmetry of a ring is P4/mmm.

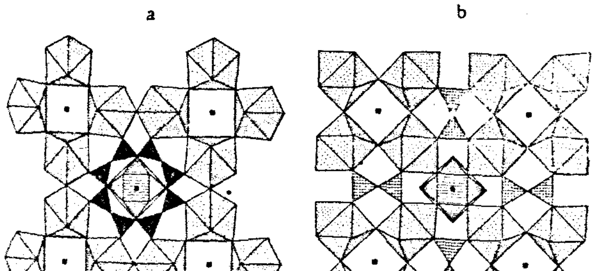

Fig. 1. Projection on the xy plane for the muirite structure: a) structure at the level of the Ba_2 polyhedra (z_{Ba_2} = 0.5) and $[Si_8O_{24}]$ ring, with the Ba, Ca cubooctahedron shown hatched; b) structure at the level of the Ba_3 polyhedra (z_{Ba_3} = 0) showing Ca, Ti prisms with cross-hatching.

The structure may be described as a massive framework of large cation polyhedra (Fig. 1). Along the z axis there run columns of very much flattened Thomson cubes filled to 50% by Ba_1 atoms, the vertices of some being Cl and OH. A column is held in accordance with an 8_4 screw axis by Ba_2 and Ba_3 polyhedra. Both types of polyhedron are halves of cubooctahedra, bits of a close packing. The outer halves are replaced by a trigonal prism in the Ba_2 polyhedron (on the x and y axes) and by semioctahedra in the case of Ba_3 (on diagonals). The columns are linked via vertical O–O edges of the trigonal prisms, and they produce a three-dimensional Ba–O framework. Rows of Ba, Ca cubooctahedra lie at the centers of the square channels, these being linked by square faces. Around these columns there are highly symmetrical insular eight-sided $[Si_8O_{24}]$ rings, which are also attached to the main framework of Ba polyhedra within. There are Ca, Ti trigonal prisms between the rings and the framework at the points where the dentate Ba columns link up, and these accommodate the additional Mn and Fe cations.

The bright color of the crystals indicates that the titanium is trivalent and has an ionic radius close to that of Ca, which was confirmed from the valency calculation. Another interesting point is that the color is lost when the crystal melts, probably because the titanium becomes tetravalent.

The cubooctahedra are filled in a 1 : 1 ratio by barium and calcium atoms.

There is 60 wt.% BaO, which determines the special

TABLE 1. Coordinates of Basal Atoms in the Muirite Structure

Atom	Multiplicity	x/a	y/b	z/c	u_j
Ba_1	2(1)	0	0	0.255	0.69
Ba_2	4	0.334	0	0.5	0.88
Ba_3	4	0.233	0.233	0	0.87
(Ca, Ba)	1	0.5	0.5	0.5	1.38
(Ca, Ti)	4	0.5	0.136	0	0.79
Si	8	0.397	0.236	0.5	0.84
$(Cl, OH)_1$	4	0.223	0	0	0.63
$(Cl, OH)_2$	4	0.147	0.147	0.5	0.62
$(OH)_3$	4	0	0.5	0.253	2.47
$(OH)_4$	4	0.403	0.403	0	2.84
O_1	16	0.386	0.171	0.267	1.69
O_2	4	0.320	0.320	0.5	3.88
O_3	4	0.5	0.292	0.5	1.37

Note: The numbers in parentheses are the numbers of distances.

TABLE 2. Interatomic Distances (Å) in Muirite

Ca, Ba polyhedron		Ca, Ti polyhedron		Ba_1 polyhedron	
Ca, Ba—O_3	2.91(4)	Ca, Ti—O_1	2.24(4)	Ba_1—$(Cl, OH)_2$	3.22(4)
$(OH)_4$	3.41(8)	$(OH)_3$	2.38(2)	$(Cl, OH)_1$	3.43(4)
Ba polyhedra				SiO_4 tetrahedron	
				Si—O_1	1.60(2)
Ba_2—$(OH)_3$	2.71(2)			O_2	1.60
O_1	2.83(4)	Ba_3—O_1	2.76(4)	O_3	1.64
$(Cl, OH)_1$	3.22(2)	$(Cl, OH)_1$	3.26(2)	O_2—O_3	2.55
$(Cl, OH)_2$	3.33(2)	$(Cl, OH)_2$	3.29(2)	O_1—O_1	2.62
		$(OH)_4$	3.36	O_2	2.63
				O_3	2.67

symmetry of the structure, which appears as though it had an eight-fold axis. The structure arises from the Ba polyhedra and the silicon–oxygen pattern. In previously elucidated silicate structures, an eight-fold ring is a component of the Si–O radical, and cannot have such high symmetry. Highly deformed eight-fold rings occur in the chain structure of xonotlite,[4] and there are rings flattened into ovals in scapolite[5] and danburite.[6] The clear cleavage on (001) and (100) is due to the separate silicon–oxygen rings, together with the weak layers of OH groups and Cl atoms in the first case, or the layers of Ba–OH (Cl, O) in the second. This Ba silicate resembles a zeolite. The Ba_2 and Ba_3 positions are fourfold, so their polyhedra form a three-dimensional framework having two channels, where the four-fold axes contain an incomplete set of Ba_1 ions and central Ba alternating with Ca.

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