

The atomic arrangement of pellyite: $\text{Ba}_2\text{Ca}(\text{Fe},\text{Mg})_2\text{Si}_6\text{O}_{17}$

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Abstract

Pellyite, $\text{Ba}_2\text{Ca}(\text{Fe},\text{Mg})_2\text{Si}_6\text{O}_{17}$, is orthorhombic, with $a = 15.677(4)$, $b = 7.15(2)$, $c = 14.209(6)$ Å and $Z = 4$. The structure was solved with Patterson and Fourier syntheses and refinement on 648 independent reflections in space group *Cmcm*, employing anisotropic temperature factors, resulted in a final R factor of 0.032. Ferrous iron (and minor substituting Mg, Zn, and Mn) occurs in tetrahedral coordination while Ca is octahedrally coordinated. The structure is a nearly continuous framework of Si- and Fe-tetrahedra with Ba occupying a large void of ten coordination within the tetrahedral framework. The tetrahedral-cation: oxygen ratio in pellyite is 8:17.

Introduction

Pellyite is a new mineral recently discovered in a contact metasomatic deposit adjacent to a porphyritic quartz monzonite stock in the Yukon Territory (Montgomery, Thompson, and Meagher, 1972). These authors determined the cell parameters: $a = 15.677(4)$ Å, $b = 7.15(2)$ Å, and $c = 14.209(6)$ Å for the orthorhombic mineral. The reported density is 3.51 gm/cm³. In the present study an electron-probe microanalysis has been undertaken which is believed to be more accurate than the gravimetric analysis reported by Montgomery *et al* (1972) due to the presence, on a fine scale, of a second Ba-silicate phase which occurs with the pellyite. An ARL-SEM-Q automated electron microprobe was used for the quantitative analysis utilizing the data correction routine of Bence and Albee (1968). The results of the analysis in weight percents are: BaO 36.00, CaO 6.62, FeO 12.18, MgO 0.98, ZnO 1.20, MnO 1.54, Al₂O₃ 0.28, SiO₂ 40.86, total 99.66 percent. This yields the following chemical formula based on 17 oxygens: $\text{Ba}_{2.04}\text{Ca}_{1.02}\text{Fe}_{1.47}\text{Mg}_{0.21}\text{Zn}_{0.13}\text{Mn}_{0.19}\text{Al}_{0.05}\text{Si}_{5.90}\text{O}_{17}$ with $Z = 4$.

A preliminary discussion of the crystal structure of pellyite was presented in an abstract (Meagher, 1971); however, positional parameters were not published at that time. Subsequent to that report, a second crystal was selected and a set of intensities recorded which constitute the data for this study. The reason for collection of a second data set stemmed from a dissatisfaction with the absorption correction

applied to the first data set because of difficulty in approximating the shape of the irregular crystal. Although there is a general reduction in errors associated with the second data set, the positional parameters are statistically equivalent to those determined from the first data set.

Experimental

Single crystal Weissenberg photographs revealed the systematic absences: hkl , $h + k = 2n + 1$; and $h0l$, $l = 2n + 1$ which confirm the space group possibilities *Cmcm*, *Cmc2₁*, and *C2cm* as stated by Montgomery *et al* (1972).

A single crystal, tabular in shape, with dimensions $0.04 \times 0.07 \times 0.08$ mm was selected for intensity collection. Three dimensional intensity data was collected utilizing equi-inclination geometry on a manual Weissenberg scintillation-counter diffractometer. Zr-filtered Mo radiation was used along with a pulse-height discriminator. Symmetrically non-equivalent reflections were scanned within $\sin \theta \leq 0.5$ and traced on a strip chart recorder. Relative intensities were determined with a planimeter and corrected for Lorentz and polarization factors. The 648 independent intensities were corrected for absorption using a linear absorption coefficient of 68.8 cm^{-1} .

Structure determination

Because of the presence of a heavy atom, the Patterson function was employed for solution of the structure. A three-dimensional Patterson map clearly

revealed the positions of the barium and iron. Statistical tests for the presence of a center of symmetry were inconclusive; however, vector-set peak concentrations of the type $P(x00)$ indicated space groups $Cmcm$ and $Cmc2_1$ were the most likely candidates. Furthermore, vector-set peak concentrations of the type $P(00z)$ favored space group $Cmcm$; hence this space group symmetry was assumed during the structure determination. Successive three-dimensional Fourier maps, computed with the phases given initially by the heavier atoms, revealed the entire structure.

To evaluate the nature of the iron in the structure, a Mössbauer spectroscopic analysis was carried out on a constant acceleration spectrometer. A 10 m.c. source of Co^{57} in palladium was used for the spectra, and the doppler velocity scale was calibrated against the quadrupole splitting of a NBS standard nitroprusside absorber. A single doublet was observed for iron with an isomer shift and quadrupole splitting of 1.12 mm/sec and 2.00 mm/sec, respectively (FWHM = 0.29 mm/sec) at room temperature relative to Fe in stainless steel. At liquid nitrogen temperatures, the isomer shift and quadrupole splitting is 1.22 and 2.13 mm/sec, respectively (FWHM = 0.30 mm/sec). The isomer shift indicates essentially all the iron is Fe^{2+} and the sharp doublet suggests the Fe^{2+} occupies a single structural site.

A full-matrix least-squares refinement was carried out on an IBM 360/67 computer using the program BUCILS, a modified version of ORFLS (Busing, Martin, and Levy, 1962). The scattering curves were taken from the *International Tables for X-ray Crystallography* (1962) and were corrected for the real part of the anomalous dispersion. The weighting scheme of Cruickshank (1965) was applied. Initial refinements were carried out on multiple scale factors, positional parameters, and isotropic temperature factors which resulted in a residual (R) factor of 0.065. It was observed that oxygen O(1), occupying the center of symmetry at the origin, had an abnormally high isotropic temperature factor; therefore, an attempt was made at this point to refine the structure in each of the acentric space group symmetries $C2cm$ and $Cmc2_1$. In the initial model all atoms related by the center of symmetry were arbitrarily moved from their refined positions. The isotropic refinements resulted in very high correlation coefficients between the positional parameters of those atoms which would be related by symmetry in space group $Cmcm$. The refined parameters were not significantly different from those determined in

$Cmcm$ and after several attempts to improve upon the results of the centric refinement the acentric refinements were abandoned.

The isotropic thermal parameters were converted to the anisotropic form, and the refinement in space group $Cmcm$ was continued to convergence with a resulting weighted R factor of 0.032. Observed and calculated structure factors are listed in Table 1. The final positional and anisotropic thermal parameters are listed in Tables 2 and 3, respectively.

Discussion of the structure

Five and six-membered rings of Si(1), Si(2), and Fe tetrahedra are linked alternately along the c axis to form chains of the type shown in Figure 1. These chains are, in turn, linked through the Si(1) and Fe tetrahedra to adjacent chains in a C -face-centered arrangement. The resulting structure (Fig. 2) is a nearly continuous tetrahedral framework structure. Oxygen O(6) is the only non-bridging oxygen in pellylite, which possesses a Zoltai sharing coefficient (Zoltai, 1960) of 1.94 compared to 2.0 for a framework structure. Figure 2 illustrates the layered arrangement of both the Ca octahedra, which share opposite edges with Fe tetrahedra, and the Ba atoms which occupy sites on the mirror planes at $z = 1/4$ and $3/4$.

Si(1) tetrahedron

The Si(1) tetrahedron shares two corners with adjacent Fe tetrahedra and the remaining two with an Si(1) and Si(2) tetrahedron, respectively. As indicated in Table 4, two edges are shared with Ba polyhedra with shared edge O(4)–O(5) being the shortest in the tetrahedron, corresponding to the closest Ba–Si approach of 3.649 Å.

The Si ion is displaced from the tetrahedron centroid by 0.09 Å in a direction away from oxygen O(5), resulting in two short and one long Si–O bond length. Oxygen O(5) is coordinated by two Si(1) and two Ba ions resulting in the greatest degree of overbonding among the oxygens (refer to Table 7), and the Si(1)–O(5) distance of 1.662 Å is the longest Si–O distance in the structure. Aluminum was assigned to the Si(1) site because of its larger mean T –O distance of 1.622 Å and because of the overbonding associated with Si(1).

Si(2) tetrahedron

Figure 1 illustrates the tetrahedral linkage about Si(2). The Si(2) tetrahedron shares two corners with adjacent Si(1) tetrahedra through O(3) and one cor-

TABLE 2. Refined Atomic Parameters for Pellyite

ATOM	SITE OCCUPANCY**	x	y	z	B(Å ²)*
Ba	1.00 Ba	0.1374(1)***	0.3326(1)	0.25	0.95(1)
Ca	1.00 Ca	0.50	0.0	0.0	0.76(5)
Fe	0.74 Fe ²⁺ 0.11 Mg 0.09 Mn 0.06 Zn	0.2922(1)	0.0	0.0	0.59(3)
Si(1)	0.95 Si 0.05 Al	0.3477(1)	0.2982(3)	0.1413(1)	0.60(4)
Si(2)	1.00 Si	0.0	0.0612(4)	0.1080(2)	0.53(5)
O(1)	0.0	0.0	0.0	0.0	2.58(33)
O(2)	0.3853(4)	0.1303(8)	0.0798(4)	1.24(9)	
O(3)	0.0867(4)	-0.0264(8)	0.1521(4)	1.95(12)	
O(4)	0.2559(4)	0.3690(8)	0.1079(4)	1.74(11)	
O(5)	0.3330(6)	0.2189(11)	0.25	1.38(14)	
O(6)	0.0	0.2804(9)	0.1286(6)	1.02(13)	

* Isotropic equivalent of the anisotropic temperature factor (Hamilton, 1959).
 ** Assumed from electron microprobe analysis and structural consideration.
 *** Number in parentheses refers to one estimated standard deviation.

ner with an adjacent Si(2) tetrahedron through O(1). The non-bridging oxygen O(6) is coordinated by two Ba and one Ca in addition to Si(2). The Si(2)-O(6) interatomic distance of 1.595 Å is the shortest Si-O distance in the structure and the Si(2) tetrahedron, which also shares two of its edges with neighboring Ba polyhedra, is the smaller of the two silica tetrahedra.

The fact that O(1) occupies a center of symmetry requires an Si(2)-O(1)-Si(2) bond angle of 180°. Liebau (1961) has presented arguments that 180° Si-O-Si angles are unlikely in silicates because of the considerable covalent character of the Si-O bond. Others support the idea that a 180° Si-O-Si angle does, in fact, occur in silicates (Shannon and Katz, 1970). Nevertheless, it is frequently found that in structures where a T-O-T angle of 180° is forced by

TABLE 3. Anisotropic Temperature Factor Tensor Values for Pellyite*

ATOM	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	77(2)	480(10)	138(42)	-54(5)	0	0
Fe	55(7)	442(28)	42(41)	0	0	39(13)
Si(1)	85(9)	235(34)	58(42)	-12(12)	26(6)	11(14)
Si(2)	61(11)	264(49)	57(44)	0	0	-7(22)
Ca	76(11)	405(49)	86(41)	0	0	-32(22)
O(1)	412(75)	1663(331)	37(73)	0	0	15(121)
O(2)	113(21)	602(93)	172(59)	75(40)	42(22)	-82(46)
O(3)	266(28)	663(102)	234(52)	181(42)	-134(24)	-156(47)
O(4)	184(24)	1004(122)	168(49)	92(44)	20(22)	199(48)
O(5)	187(35)	465(129)	168(52)	-30(63)	0	0
O(6)	130(37)	165(125)	197(64)	0	0	69(63)

* Values are reported $\times 10^5$. The coefficients are of the form $(\beta_{11} h^2 + \dots + 2 \beta_{12} h k + \dots)$.

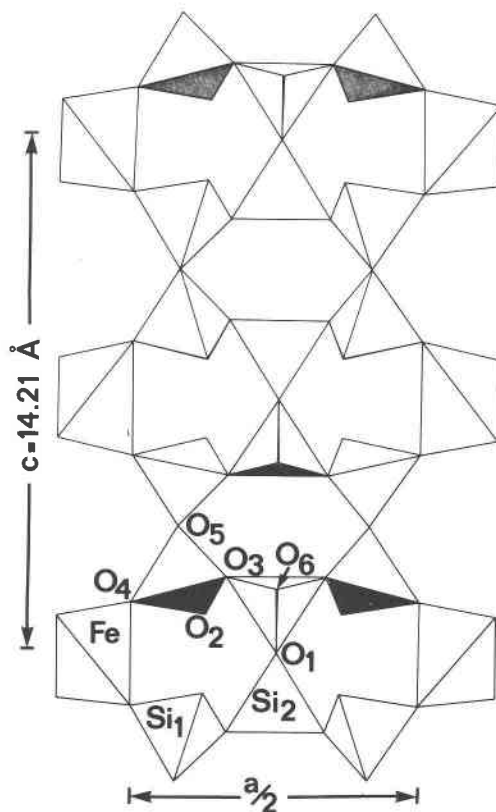


FIG. 1. A portion of the pellyite structure illustrating the tetrahedral linkage. Chains of this type are linked together through the Fe tetrahedra along the periphery of the chain and oxygen O(2) of tetrahedron Si(1). Oxygen O(6) is the only non-bridging oxygen in the structure.

space-group symmetry, high apparent thermal vibration of the bridging oxygen exists (*cf* Calvo, 1965; Cannillo, Giuseppetti, and Tadini, 1969; Smolin and Shepelev, 1970). As mentioned previously, the apparent thermal vibration of O(1) is anomalously high and possesses a high degree of anisotropy (Table 6). The shape of the thermal vibration ellipsoid is that of an oblate spheroid flattened in the direction of the *c* axis as illustrated in Figure 3.

It is quite probable that positional disorder of O(1) contributes to the magnitude of this apparent thermal vibration. To evaluate this possibility a least-squares refinement was carried out with O(1) deleted from the model, and a three dimensional difference Fourier was calculated using the resulting structure factors. This resulted in a positive electron-density anomaly about the O(1) position in the shape of an oblate spheroid of the same orientation as the anisotropic thermal vibration ellipsoid and indicated that a split atom model for O(1) was not reasonable. If O(1)

possesses a random positional disorder about the origin, then the Si-O-Si linkage cannot be linear. It is difficult to estimate the Si-O-Si angle under these circumstances; however, the thermal vibration ellipsoid would reflect, in part, the positional displacement of O(1).

The Si(2)-O(1) interatomic distance of 1.596 Å is uncorrected for thermal displacement. Lacking a complete understanding of the correlations between the thermal displacements of the silicon and oxygen in pellyite, one can only calculate the lower bounds of the thermally corrected bond lengths (Busing, Martin, and Levy, 1964). A calculated lower limit for the Si(2)-O(1) distance is 1.605 Å, which is listed in Table 4 along with the uncorrected distance. A simple geometric calculation assuming a 1.605 Å bond length non-collinear with the Si-Si vector yields an Si(2)-O(1)-Si(2) angle of approximately 167.9°. This bond angle is offered only as an "order of magnitude" approximation.

Fe tetrahedron

The Fe-tetrahedron links the chain of Si-tetrahedra shown in Figure 1 to adjacent chains by sharing all four corners with neighboring Si(1) tetrahedra. The tetrahedron shares an O(2)-O(2A) edge with a Ca octahedron and two O(2)-O(4) edges with Ba polyhedra. The shared edges are considerably shorter

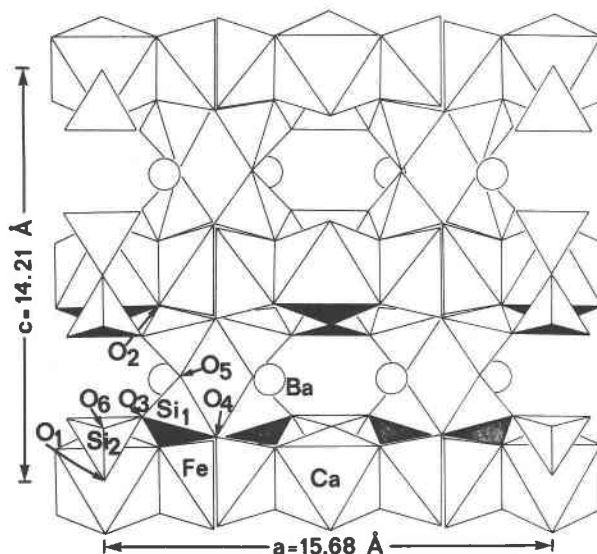


FIG. 2. A perspective drawing of 1/2 the pellyite unit cell looking down the *b* axis. A mirror plane perpendicular to the *c* axis passes through the Ba and O(5) atoms at $z = 1/4$ and $3/4$, respectively. A second mirror passes through the origin at O(1) and is perpendicular to the *a* axis.

than the unshared edges, resulting in a highly distorted tetrahedron. The O-T-O tetrahedral angles vary from 90.3° to 134.5° with a mean value of 108.3°.

Although this tetrahedron is occupied

TABLE 4. Interatomic Distances in Pellyite

Si(1) Tetrahedron				Si(2) Tetrahedron			
Si(1)-O(2)	1.598(6) Å	O(2)-O(3)	2.697(8) Å	Si(2)-O(1)	1.596(3) Å	O(1)-O(3) [2] ^{††}	2.560(6) Å
Si(1)-O(3)	1.629(6)	O(2)-O(4)	2.681(8)		1.605 [†]		
Si(1)-O(4)	1.598(6)	O(2)-O(5)**	2.631(7)	Si(2)-O(3) [2]	1.623(6)	O(1)-O(6)	2.713(8)
Si(1)-O(5)	1.662(3)	O(3)-O(4)	2.654(9)	Si(2)-O(6)	1.595(7)	O(3)-O(3A)	2.719(12)
		O(3)-O(5)	2.615(9)			O(3)-O(6)** [2]	2.602(8)
		O(4)-O(5)**	2.587(8)				
Mean	1.622 Å	Mean	2.644 Å	Mean	1.609 Å	Mean	2.626 Å
					1.612 Å*†		
Fe Tetrahedron				Ca Octahedron			
Fe-O(2) [2]	2.070(6)	O(2)-O(2A)**	2.935(11)	Ca-O(2) [4]	2.321(6)	O(2)-O(2A)** [2]	2.935(11)
Fe-O(4) [2]	1.949(6)	O(2)-O(4)** [2]	2.924(8)	Ca-O(6) [2]	2.410(8)	O(2)-O(2B) [2]	3.597(12)
		O(2)-O(4A)	3.466(9)			O(2)-O(6) [4]	3.158(8)
		O(4)-O(4A)	3.594(10)			O(2)-O(6A) [4]	3.523(12)
Mean	2.010 Å	Mean	3.218 Å	Mean	2.351 Å	Mean	3.316 Å
Ba Polyhedron							
		Ba-O(2) [2]	3.242(6)	Ba-O(5)	3.173(10)		
		Ba-O(3) [2]	3.026(6)	Ba-O(5A)	2.801(8)		
		Ba-O(4) [2]	2.756(6)	Ba-O(6) [2]	2.785(5)		
		Mean	2.959 Å				

* Number in parentheses refers to one estimated standard deviation.

** Shared polyhedral edge.

† Lower limit for the thermally corrected interatomic distance.

†† Number in brackets refers to multiplicity of bond length.

*† Lower limit for Si(2)-O(1) used in calculation of the mean.

TABLE 5. Interatomic Angles in Pellyite

Si(1) Tetrahedron			
O - T - O Angles		T - O - T Angles	
O(2)-Si(1)-O(3)	113.4(3) ^o	Si(1)-O(2)-Fe	112.2(3) ^o
O(2)-Si(1)-O(4)	114.1(3)	Si(1)-O(4)-Fe	137.3(4)
O(2)-Si(1)-O(5)*	107.6(4)	Si(1)-O(5)-Si(1)	136.8(5)
O(3)-Si(1)-O(4)	110.6(3)	Si(1)-O(3)-Si(2)	142.2(4)
O(3)-Si(1)-O(5)	105.2(4)		
O(4)-Si(1)-O(5)*	105.0(4)		
Mean	109.3 ^o		
Si(2) Tetrahedron			
O - T - O Angles		T - O - T Angles	
O(1)-Si(2)-O(3)[2]**	105.4(2)	Si(2)-O(1)-Si(2)	180.0
O(1)-Si(2)-O(6)	116.5(4)		167.9 [†]
O(3)-Si(2)-O(3)	113.8(5)	Si(2)-O(3)-Si(1)[2]	142.2(4)
O(3)-Si(2)-O(6)*[2]	108.0(3)		
Mean	109.5 ^o		
Fe Tetrahedron			
O(2)-Fe-O(2A)*	90.3(3)	Fe-O(2)-Si(1)[2]	112.2(3)
O(2)-Fe-O(4)*[2]	93.3(2)	Fe-O(4)-Si(1)[2]	137.3(4)
O(2)-Fe-O(4A)[2]	119.2(2)		
O(4)-Fe-O(4A)	134.5(4)		
Mean	108.3 ^o		
Ca Octahedron			
O(2)-Ca-O(2A)*[2]	78.4(3)	O(2)-Ca-O(6)[4]	83.8(2)
O(2)-Ca-O(2B)[2]	101.6(3)	O(2)-Ca-O(6A)[4]	96.2(2)
Mean	90 ^o		

* Shared edge.
 ** Number in brackets refers to multiplicity of bond angle.
 † Calculated T-O-T angle assuming thermally corrected Si(2)-O(1) distance of 1.605Å.

TABLE 6. Thermal Ellipsoid Data for Pellyite

Atom	Axis	rms displacement Å(σ)	Angle, in degrees, with respect to		
			+a(σ)	+b(σ)	+c(σ)
Ba	1	0.087(2)	32(2)	58(2)	90
	2	0.119(18)	90	90	180
	3	0.120(1)	57(2)	148(2)	90
Fe	1	0.061(32)	90	105(8)	15(8)
	2	0.083(5)	180	90	90
	3	0.110(4)	90	15(8)	75(8)
Si(1)	1	0.064(23)	115(9)	112(37)	34(32)
	2	0.080(7)	84(23)	157(36)	112(31)
	3	0.110(6)	26(13)	94(7)	65(14)
Si(2)	1	0.076(27)	90	73(76)	17(76)
	2	0.083(8)	90	163(76)	73(76)
	3	0.087(8)	0	90	90
Ca	1	0.088(18)	90	59(32)	31(32)
	2	0.097(7)	180	90	90
	3	0.107(8)	90	149(32)	59(32)
O(1)	1	0.061(60)	90	91(9)	1(9)
	2	0.208(21)	90	179(9)	91(9)
	3	0.227(21)	0	90	90
O(2)	1	0.082(19)	49(11)	124(9)	120(14)
	2	0.138(11)	133(28)	137(35)	94(51)
	3	0.146(16)	71(43)	113(48)	31(16)
O(3)	1	0.109(13)	95(95)	29(91)	61(112)
	2	0.113(16)	132(16)	72(132)	133(92)
	3	0.223(10)	42(5)	69(4)	124(5)
O(4)	1	0.102(19)	85(13)	124(9)	35(10)
	2	0.143(10)	155(10)	73(12)	73(13)
	3	0.188(10)	66(10)	40(7)	61(8)
O(5)	1	0.109(15)	82(17)	8(17)	90
	2	0.131(20)	90	90	180
	3	0.153(15)	8(17)	98(17)	90
O(6)	1	0.059(28)	90	12(11)	102(11)
	2	0.127(18)	180	90	90
	3	0.145(22)	90	78(11)	12(11)

predominately by Fe²⁺, minor amounts of Mg, Zn, and Mn have been assigned to this site on the basis of the electron microprobe analysis as indicated in Table 2. The rather unusual occurrence of Mn in

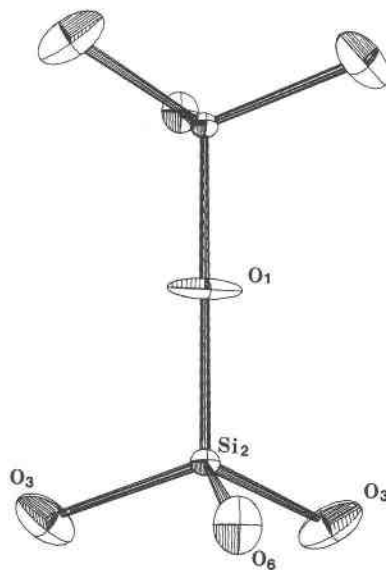


FIG. 3. Thermal vibration ellipsoids of the atoms associated with tetrahedron Si(2). The vibration ellipsoid of oxygen O(1) has the shape of an oblate spheroid flattened perpendicular to the *c* axis. Ellipsoids are drawn at 50 percent probability.

TABLE 7. Electrostatic Valence Balance in Pellyite

	Si (1)	Si (2)	Ba	Ca	Fe	Σ
O (1)		2x1.02				2.04
O (2)	1.02		0.11	0.33	0.38	1.84
O (3)	0.94	0.96	0.16			2.06
O (4)	1.02		0.29		0.51	1.82
O (5)	2x0.87		0.26+0.12			2.12
O (6)		1.03	2x0.27	0.27		1.84

tetrahedral coordination is not without precedence (*cf* Bakakin *et al*, 1970). The two symmetrically non-equivalent Fe–O interatomic distances show a wide variation with the Fe–O(2) distance of 2.070 Å to the edge shared with the Ca octahedron being significantly longer than the Fe–O(4) distance of 1.949 Å. The mean Fe–O bond length of 2.010 Å compares with the mean tetrahedral Fe–O distance of 2.00 Å in tuhualite (Merlino, 1969), although a small difference in site chemistry exists.

Ca and Ba polyhedra

The Ca ion occupies a site of point symmetry $2/m$ and is octahedrally coordinated by four bridging and two non-bridging oxygens. The Ca–O(6) interatomic distance of 2.410 Å to the non-bridging oxygen is significantly longer than the Ca–O(3) distance of 2.321 Å to the bridging oxygen. The resulting mean Ca–O distance is 2.351 Å. The octahedron is distorted as a result of sharing of opposite edges with Fe tetrahedra (Fig. 2.) The shared O(2)–O(2A) edge is shortened to 2.935 Å compared to the mean octahedral edge distance of 3.316 Å.

The Ba ions are positioned along the mirror planes at $z = 1/4$ and $3/4$ within large voids in the tetrahedral framework. The Ba can be considered ten-coordinated with a range of Ba–O distances between 2.756 and 3.242 Å and a mean distance of 2.959 Å.

Table 7 lists the empirical bond strengths calculated from the universal curves presented by Brown and Shannon (1973). The curve for Ba has been taken from Brown and Wu (private communication). Summation of these bond strengths indicates reasonable valence balance considering the parameters defining the Ba curve are not well defined.

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