REFINEMENT OF THE CRYSTAL STRUCTURE OF OSUMILITE

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ABSTRACT

The crystal structure of osumilite, $a = 10.155(1)$, $c = 14.284(4)$ Å; $P6/mcc$, $2[(Ca_{0.005}Na_{0.31}K_{0.78})^{XII}(Mg_{0.92}Fe_{0.92}Mn_{0.16})^{VI}(Si_{10.22}Al_{4.41}Fe_{0.37}{}^{3+})^{IV}O_{30} \cdot H_2O]$ was refined to $R = 0.066$ using 259 nonequivalent reflections recorded with a Weissenberg counter-diffractometer.

Mean T1–O (1.627[2] Å) and T2–O (1.762[2] Å) bond lengths indicate that 10.22 Si plus 1.78 Al are restricted to the 12 tetrahedra [T1] in the double hexagonal rings and that 2.63 Al plus 0.37 Fe^{3+} occupy the three tetrahedra [T2] outside the rings. Edges shared between (Mg,Fe^{2+},Mn)-containing octahedra and T2 tetrahedra are significantly shorter (2.568[11] Å) than unshared ones (3.155[10] Å, 2.879[8] Å). K,Ca,Na atoms are coordinated between the double six-membered rings in a hexagonal antiprism which shares an edge (2.601[5] Å) with the T1 tetrahedron.

The water molecule is randomly distributed within each cavity formed by the double hexagonal rings in one of six symmetrically identical positions at $x = 0.031$, $y = 0.114$, $z = 0.0$. A short H_2O-O distance of 2.6[1] Å indicates hydrogen bonding between H_2O and the cavity-wall oxygens.

Because of structural and physical similarities with cordierite and beryl, osumilite is classified with the framework rather than with the ring silicates in agreement with Zoltai's (1960) classification of the mineral.

INTRODUCTION

Osumilite $(Na,K,Ca)^{XII}(Fe^{2+},Mg,Mn)_2^{VI}(Si,Al,Fe^{3+})_{15}^{IV}O_{30} \cdot H_2O$, is a rare mineral found in acid volcanic rocks as anhedral phenocrysts in the groundmass and as terminated, prismatic crystals lining cavities together with quartz and tridymite. It has also been reported to occur in the Colomera iron meteorite (Bunch and Olsen, 1968). It is optically positive and of low birefringence resembling such framework silicates as smoky quartz and cordierite. In fact, Miyashiro (1956) suggests that much of the optically positive cordierite described in the literature is osumilite. Despite these similarities, however, osumilite is readily distinguished from these minerals by its X-ray powder diffraction pattern.

The crystal structure of osumilite was deduced by Miyashiro in 1956 who, on the basis of the mineral's double six-membered ring of tetrahedra and its close structural similarity with cordierite and beryl, described it as a ring silicate. On the other hand, Zoltai (1960) has classified osumilite as well as cordierite and beryl with the framework silicates because each tetrahedral corner in these structures is shared by two tetrahedra. Nonetheless, several current mineralogy texts (Bragg and Claringbull, 1965; Deer, Howie and Zussman, 1962) classify

these minerals as ring silicates. Recent structural refinements of cordierite (Gibbs, 1966; Meagher and Gibbs, 1967) and beryl (Gibbs et al., 1968) yielded mean Si-O bond lengths that are statistically identical with those recorded for other framework structures (Smith and Bailey, 1963), thus confirming Zoltai's classification of these minerals. A similar structural study of osumilite was undertaken to test the validity of Zoltai's classification of this mineral and to provide such structural details as precise bond distances and angles, polyhedral distortions, the cation distribution, and the orientation and location of the water molecule in the structure.

HISTORICAL BACKGROUND

Osumilite, named after the province of Osumi, was first recognized as a new mineral by Miyashiro (1953) following an examination of a specimen collected from a hypersthene-rhyodacite in Sakkabira, Japan. Natural and synthetic samples have been studied by several investigators (Morimoto, 1948; Morimoto and Minato, 1949; Rossi, 1963; Schreyer and Schairer, 1962; Schreyer and Seifert, 1967) who have described its physical properties, chemistry and paragenesis. Miyashiro (1956) undertook the first X-ray investigation of osumilite utilizing single crystal and powder methods. Weissenberg photographs displayed symmetry and systematic presences of reflections consistent with the alternate space groups $P6/mcc = D_{6h}^2$ and $P6cc = C_{6v}^2$ and gave the unit-cell dimensions $a = 10.17$ Å and $c = 14.34$ Å, which are similar to those reported for milarite (Ito et al., 1952). Observing spot-for-spot similarities in the X-ray diffraction records of the two minerals and closely similar chemistry, Miyashiro recognized the possibility of an isostructural relationship between osumilite and milarite.

Accordingly, he proposed a structural model for osumilite, based on the structure of milarite, consisting of double hexagonal rings composed of $(Si,Al)O_4$ tetrahedra linked by Al, Fe^{3+}, and Fe^{2+} atoms in four-fold coordination, Mg and Fe^{2+} atoms in six-fold coordination and K, Na and Ca atoms in twelve-fold coordination. The water molecules were assumed to center the large cavities formed by the double rings. Based on this model a qualitative structure analysis was made using about 45 intensities which verified the proposed isostructural relationship between milarite and osumilite.

EXPERIMENTAL DETAILS

Three small crystals of osumilite were prepared for microprobe examination (see Keil, 1967). All probe analyses were run at 15kV and 0.25 μA beam current on an Applied Research Laboratories electron microprobe analyzer which uses normal electron incidence and a take-off angle of 52.5°. Scans through the respective wavelength ranges of the moving

TABLE 1. CALCULATION OF UNIT CELL CONTENT OF OSUMILITE

Oxide	Wt. %	Oxide units[a]	No. ions
SiO_2	56.85	20.45	10.22
Al_2O_3	20.79	4.41	4.41
TiO_2	0.02	0.005	0.002
FeO	8.57	2.58	1.29
MgO	3.45	1.85	0.92
MnO	1.07	0.33	0.16
CaO	0.04	0.01	0.005
Na_2O	0.88	0.31	0.31
K_2O	3.40	0.78	0.78
H_2O	2.00	2.00	2.00

$ZM = \rho V/1.6602 = (2.64 \text{ g cm}^{-3})(1275.638 \text{ Å}^3)/1.6602 \times 10^{-24} = 2028.48$

[a] The number of oxygens normalized to 60.

crystal spectrometers (LiF, ADP and KAP) indicated detectable amounts of Fe, Si, Mg, Mn, Ca, Al, Ti, K and Na. Quantitative microprobe data were collected for the osumilite sample and the appropriate standards of known composition. Deadtime and backg(ound corrections were applied to the raw data followed by two applications of Smith's (1965) modification of Philibert's absorption correction. Due to the choice of standards, atomic number and fluorescence corrections were considered unnecessary.

The results of the probe analysis are listed in Table 1. The oxide weight percent total (97.11%) falls below 100 percent resulting in 56.31 oxygens per formula unit. A second probe analysis yielded essentially the same result; thus this total was accepted. Since the theoretical formula unit contains 60 oxygens, the number of oxide units per unit cell was normalized on the basis of 60 oxygens before calculation of the atomic proportions. The resultant formula unit is

$$2[(Ca_{0.005}Na_{0.31}K_{0.78})^{XII}(Fe_{0.92}Mg_{0.92}Mn_{0.16})^{VI}(Si_{10.22}Al_{4.41}Fe_{0.37}^{3+})^{IV}O_{30} \cdot H_2O]$$

Zero- and higher-level precession and Weissenberg photographs recorded from a crystal measuring $0.2 \times 0.3 \times 0.4$ mm indicated that the space group $P6/mcc$ originally assigned by Miyashiro (1956) is correct. Cell dimensions ($a = 10.155[1]$, $c = 14.284[4]$ Å) were obtained by a least-squares refinement of precision back-reflection Weissenberg data.

Intensity data for the crystal were collected on an equi-inclination Weissenberg diffractometer employing a scintillation counter and a pulse height analyzer set to accept 95 percent of the diffracted, Nb-filtered, Mo radiation. Υ and ϕ settings were calculated on an IBM 7040 with Prewitt's D-Set 4 equi-inclination diffractometer settings program. To utilize the C_{6v} symmetry about z, the c-axis was oriented parallel to the camera axis. Some 450 intensities were recorded as peaks on a strip chart, and their areas were integrated with a planimeter, the background of each being estimated according to the method described by Young (1965). Symmetry equivalent intensities were averaged to give 259 nonequivalent observations which were corrected for Lorentz-polarization factors and converted to $|F_{obs}|$.

The linear absorption coefficient was calculated to be $\mu = 17.02$ cm^{-1} and $\mu R = 0.26$ assuming a cylindrical crystal of radius $R = 0.155$ mm. This indicates that the intensities are in systematic error by about 2 percent due to differential absorption of the diffracted beam. Accordingly, no absorption correction was made. The $|F_{obs}|$ were weighted accord-

ing to a scheme (Hanson, 1965) designed to give maximum weight to intermediate $|F_{obs}|$ and less weight to small and large $|F_{obs}|$. The weighting factor, w, is given as

$$w = \frac{1}{\sigma^2 |F_{obs}|} = \frac{1}{1 + \{(|F_{obs}| - 5F_t)/1.67F_t\}^2}$$

where F_t is of the order of magnitude of the minimum $|F_{obs}|$, in this case 6.0.

A least-squares refinement of the resulting data was then calculated with the IBM 7040 (Busing *et al.*, 1962) starting with the positional parameters reported by Miyashiro (1956), scattering factor curves normalized on the basis of the reported chemistry and individual isotropic temperature factors of 1.5 for Na, K and Ca atoms; 0.9 for Fe^{2+}, Mg and Mn atoms; 0.9 for both tetrahedral atoms; 1.5 for oxygen atoms and 7.0 for H_2O. The atomic scattering curves were constructed from data provided by Volume III of the *International Tables for X-ray Crystallography* and arbitrarily modified to half-ionized values. Eight cycles of refinement, during which atomic coordinates, isotropic temperature factors and one overall scale factor were allowed to vary, resulted in a final unweighted R-factor of 6.6 percent. The refined positional and thermal parameters with their estimated standard errors are listed in Table 2.

During the early stages of refinement with the water molecule at the origin, an anomalously large temperature factor ($B=68[12]$ $Å^2$) was calculated for the molecule in the third cycle of refinement. Reduction of the multiplicity of water from 0.0833 to 0.0104 also yielded a large temperature factor ($B=19[7]$ $Å^2$), leading to the alternative conclusions that the water is present at the origin in very small amounts, or that it does not occupy this special position. A set of difference maps, computed to evaluate these conclusions, was found to have a statistically featureless distribution except for a negative region of electron density at the origin and positive regions symmetrically disposed about the six-fold axis at (0.028, 0.096, 0). Accordingly, a refinement of the water position was attempted in which 1/6 of a water molecule was placed at (0.028, 0.096, 0). The water position refined to (0.031[23], 0.114[10], 0) in three additional cycles of refinement and the isotropic temperature factor converged to $B=9[3]$ $Å^2$. A listing of the observed and calculated structure factors is given by Brown (1968).

Bond length, bond angle and error calculations were made with the Busing, Martin and Levy (1964) Function and Error Program. The results of these calculations are listed in Table 3.

TABLE 2. REFINED POSITIONAL PARAMETERS USING MODIFIED VERSION
OF HANSON'S WEIGHTING SCHEME

Atom	x	y	z	B
C1(K,Na,Ca)	0	0	1/4	3.6[2]
H_2O	0.031[23][a]	0.114[10]	0	9[3]
M(Mg,Fe^{2+})	1/3	2/3	1/4	0.90[6]
T2(Al,Fe^{3+})	1/2	0	1/4	1.31[7]
T1(Si,Al)	0.1037[1]	0.3513[1]	0.1085[1]	1.25[6]
O1	0.1216[7]	0.4046[8]	0	2.5[2]
O2	0.2142[5]	0.2837[5]	0.1316[5]	2.4[1]
O3	0.1372[4]	0.4913[4]	0.1789[4]	1.8[1]

[a] The values in square brackets are the estimated standard errors and refer to the last decimal place.

DISCUSSION

In many instances the physical properties of a compound are determined primarily by its structure and to a lesser extent by its chemistry. For example, SiO_2 and $AlPO_4$ both adopt the same structures and exhibit very similar physical properties and phase relationships despite their different chemistry (Schwarzenbach, 1966). In agreement with these empirical facts, Zoltai (1960), has proposed a classification of tetrahedral structures based on the degree of polymerization of the tetrahedral units irrespective of their chemistry. Such a classification has the advantage of grouping together minerals of similar physical properties. In contrast, the classification followed in several mineralogical texts separates, for example, such minerals as quartz, cordierite, beryl, and osumilite in spite of their physical and structural similarities.

As mentioned earlier, recent structural analyses of cordierite and beryl have confirmed Zoltai's classification of these minerals with the framework silicates. Since osumilite is physically and structurally similar to these minerals (Table 4) and to framework structures in general, it is inconsistent to include the mineral with any group other than the framework structures. Additional evidence in support of Zoltai's classification is that the chemistry of the T1 tetrahedron in osumilite is predicted exactly using a linear regression plot of Al content versus $(\overline{T-O})$ distance for framework structures (Ribbe and Gibbs, 1967).

Drawings of the tetrahedral framework in osumilite are given in Figures 1 and 2 where it can be seen that the structure consists of double hexagonal rings of $(Si,Al)O_4$ tetrahedra (T1) linked laterally and vertically by $(Al,Fe^{3+})O_4$ tetrahedra (T2) into a tetrahedral framework. Each T1 tetrahedron shares three of its corners with adjacent T1 tetrahedra to form double hexagonal rings of $Si_{10.2}Al_{1.8}O_{30}$ composition; the fourth corner is shared with a T2 tetrahedron and a (Mg,Fe^{2+},Mn)-containing octahedron (M). Each T2 tetrahedron shares corners with T1 tetrahedra of four different double hexagonal rings, linking them to form a series of adjoining cavities that run parallel to c. The cavity centered at $(0,0,\frac{1}{4})$ between adjoining double hexagonal rings accommodates the (K,Na,Ca) atoms at its center whereas the one centered at the origin houses the water molecule which is hydrogen-bonded to the cavity wall in one of six symmetrically identical positions. Each double hexagonal ring, rotated approximately 32° with respect to the double rings directly above and below it, is puckered with a T1-O2-T1 angle of 154.3[5]° and a T1-O1-T1 angle of 145.8[5]°. These angles suggest that the orbital hybridization of O1 and O2 is intermediate in character between sp and sp^2 (Moore, 1965). However, the T1-O3-T2 angle (125.0[3]°) indicates that the orbital hybridization of O3 is almost

pure sp^2 in character. Despite the fact that the T2 tetrahedron contains 12% Fe^{3+}, the mean of the three T-O-T angles (141°) agrees well with the value (138°) obtained by Liebau (1961) in a review of (Si,Al)-O-(Si,Al) angles for a number of carefully refined silicates.

The cordierite and beryl structures have been described as framework structures consisting of chains of four-membered rings linked laterally to form six-membered rings (Gibbs, 1966; Gibbs *et al.*, 1968). A similar description can be made of the osumilite structure except that the

TABLE 3. INTERATOMIC DISTANCES (Å) AND ANGLES (DEGREES)

Bond Distances and Angles in the T1 Tetrahedron			
T–O Bonds			
T1(24)–O1(24)	(1)[a]	1.621[3][b]	
T1(24)–O2(24)	(1)	1.616[5]	
T1(24)–O3(24)	(1)	1.632[5]	
T1(24)–O2(19)	(1)	1.640[5]	
Mean T1–O		1.627[2]	

O–O Bonds			Bond Angles	
O2(24)–O2(19)	(1)	2.601[5]	O2(24)–T1–O2(19)	106.0[4]
O2(24)–O3(24)	(1)	2.676[7]	O2(24)–T1–O3(24)	111.0[3]
O2(24)–O1(24)	(1)	2.661[8]	O2(24)–T1–O1(24)	110.6[4]
O2(19)–O1(24)	(1)	2.699[8]	O2(19)–T1–O1(24)	111.7[4]
O2(19)–O3(24)	(1)	2.622[7]	O2(19)–T1–O3(24)	106.5[3]
O3(24)–O1(24)	(1)	2.681[6]	O3(24)–T1–O1(24)	111.0[3]
Mean O–O		2.657[3]	Mean O–T1–O	109.4[1]

Bond Distances and Angles in the T2 Tetrahedron			
T–O Bonds			
T2(9)–O3(8)	(4)	1.762[5]	
Mean T2–O		1.762[5]	

O–O Bonds			Bond Angles		
O3(8)–O3(24)	(2)	3.155[10]	O3(8)–T2(9)–O3(24)	(2)	127.1[3]
O3(8)–O3(21)′	(2)	2.568[11]	O3(8)–T2(9)–O3(21)′	(2)	93.5[3]
O3(8)–O3(2)′	(2)	2.879[9]	O3(8)–T2(9)–O3(2)′	(2)	109.6[4]
Mean O–O		2.867[6]	Mean O–T2–O		110.1[2]

TABLE 3. (*Continued*)

Bond Distances and Angles in the M Octahedron

M–O Bonds

M(1)–O2(23)′	(6)	2.150[5]
Mean M–O		2.150[5]

O–O Bonds			Bond Angles		
O3(23)′–O3(3)′	(3)	2.997[11]	O3(23)′–M(1)–O3(3)′	(3)	88.4[3]
O3(24) –O3(2)′	(3)	2.568[11]	O3(24) –M(1)–O3(2)′	(3)	73.3[3]
O3(24) –O3(22)′	(6)	3.282[7]	O3(24) –M(1)–O3(22)′	(6)	99.5[2]
Mean O–O		3.032[5]	Mean O–M–O		90.4[1]

Nearest Neighbor Cation-Cation Distances

T1(24)–T1(20)	3.175[2]
M(1)–T2(9)	2.931
M(1)–M(8)	5.863

Cavity Dimensions

O2(24)–O2(21)	5.202[11]
C(1)–O2(24)	3.102[6]
C(1)–O3(24)	4.573[5]
C(1)–T2(9)	5.077
C(1)–O1(24)	5.107[7]

[a] Multiplicity.
[b] Estimated standard errors in brackets.

chains paralleling c are six-membered and linked laterally to form double six-membered rings (Fig. 3).

The bond lengths and angles in the T1 tetrahedron are listed in Table 3 and depicted in Figure 4A. The mean T1-O bond length (1.627[5] Å) indicates that each T1 tetrahedron in the double hexagonal rings contains, on the average, 0.85 Si and 0.15 Al in excellent agreement with the reported chemistry ($Si_{0.852}Al_{0.148}$). The tetrahedron is moderately distorted with T1-O bond lengths ranging from 1.616 to 1.640 Å and tetrahedral angles ranging from 106.0 to 111.7°. The oxygen-oxygen contact along the cavity wall of the double hexagonal rings (the edge shared with the hexagonal antiprism) is significantly shorter (2.601[5] Å) than the other oxygen-oxygen distances in the tetrahedron. The mean

TABLE 4. COMPARISON OF SOME PHYSICAL PROPERTIES OF BERYL, LOW
CORDIERITE AND OSUMILITE

	Beryl	Low Cordierite	Osumilite
Cleavage	(001) Imperfect	(010) Moderate	None
Specific Gravity	2.64	2.632	2.64
Refractive Indices	ϵ 1.565 ω 1.569	α 1.539 β 1.546 γ 1.549	ϵ 1.546 ω 1.550
Birefringence	0.004	0.010	0.004

O-T1-O bond angle (109.4[3]°) is statistically identical to the ideal tetrahedral angle (109.47°).

The T2 tetrahedron is more highly distorted due to the sharing of edges (Table 3 and Fig. 4B). It occupies positions at the periphery of the double hexagonal rings, linking the rings laterally and vertically into a framework. The tetrahedron shares two edges with M octahedra (Fig. 2) which exhibit a typically short oxygen-oxygen contact (2.568[11] Å) along three of their edges in agreement with Pauling's rules (Pauling, 1928). Miyashiro (1956) assigned $(Al_{2.21}Fe^{3+}_{0.26}Fe^{2+}_{0.53})$ to the T2 site. However, the mean T2-O bond length (1.762[2] Å) indicates that the site contains only Al and Fe^{3+} and not Fe^{2+}. A calculation made on the basis of 1.756 Å for an Al^{IV}-O bond and 1.86 Å for $Fe^{(3+)IV}$-O yielded a mean T2-O bond length of 1.76 Å in close agreement with the one experimentally determined.

The $(Mg^{2+}_{2.46}Fe_{0.46}Mn_{0.08})$ octahedron is markedly flattened, sharing one quarter of its edges with T2 tetrahedra (Fig. 4C). As described above the edges shared with the T2 tetrahedra measure 2.568[11] Å; the unshared edges measure 2.997[11] and 3.282[7] Å. The mean M-O distance (2.150[2] Å) is statistically identical to the one predicted on the basis of a plot of mean M-O distance versus average radius of octahedral cation for two cordierites (Meagher, 1967), emerald and beryl (Gibbs et al., 1968) (Figure 5). Although the distortion of O-M-O angles is large (Table 3), the mean O-M-O angle closely approaches 90° in agreement with McDonald and Cruickshank's (1967a) observation that angular distortions tend to average to regular values in silicates.

The O3 oxygen atom in osumilite is coordinated, on the average, by $(Si_{0.85}Al_{0.15})$,^{IV} $(Al_{0.88}Fe^{3+}_{0.12})^{IV}$ and $(Mg_{0.46}Fe^{2+}_{0.46}Mn_{0.08})^{VI}$ which almost perfectly satisfies the classic electrostatic charge of O3 (Pauling,
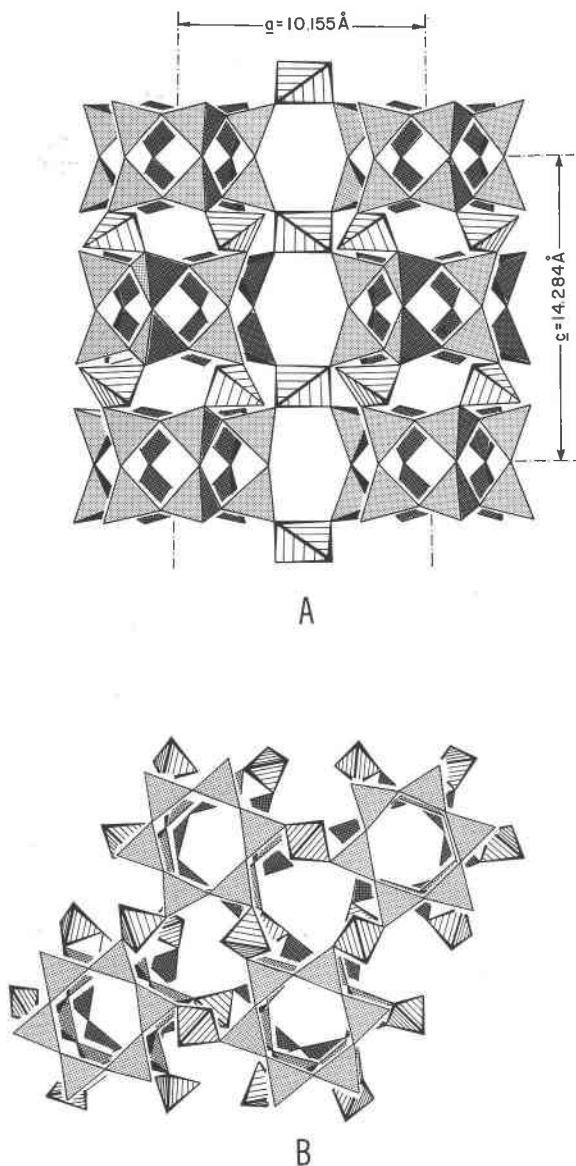
FIG. 1. The tetrahedral framework of osumilite viewed along [110] (A) and [001] (B). The (Al, Fe) tetrahedra (hatched) join the (Si, Al) tetrahedra (stippled) to form a framework structure.
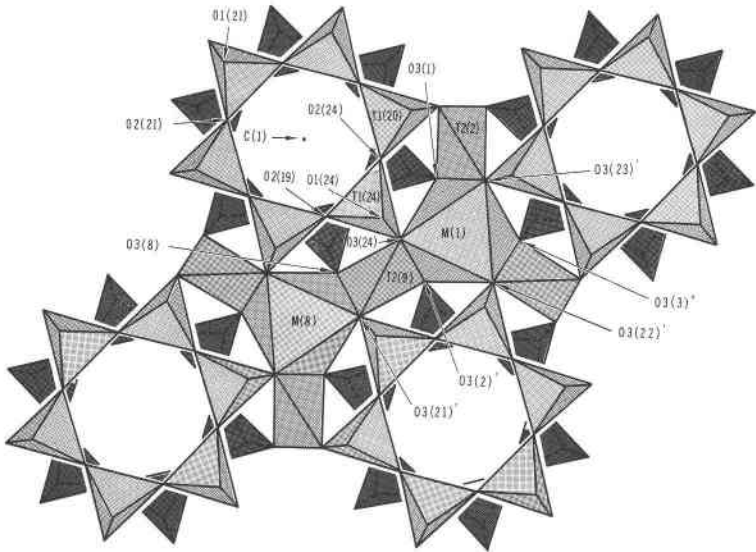
FIG. 2. Drawing of the osumilite structure projected on (001). Atoms are labeled according to the symmetry transformation of the initial starting positions.

1960). The coordination spheres about O2 and O1 are less well defined consisting of two $(Si_{0.85}Al_{0.15})^{VI}$ and $(K,Na,Ca)^{XII}$ about O2 and two $(Si_{0.85}Al_{0.15})^{IV}$ about O1. The long (K,Na,Ca)-O2 bond length (3.102[6] Å), however, indicates a relatively weak bond; accordingly, the effective coordination about O2 is probably closer to 2 than 3. If
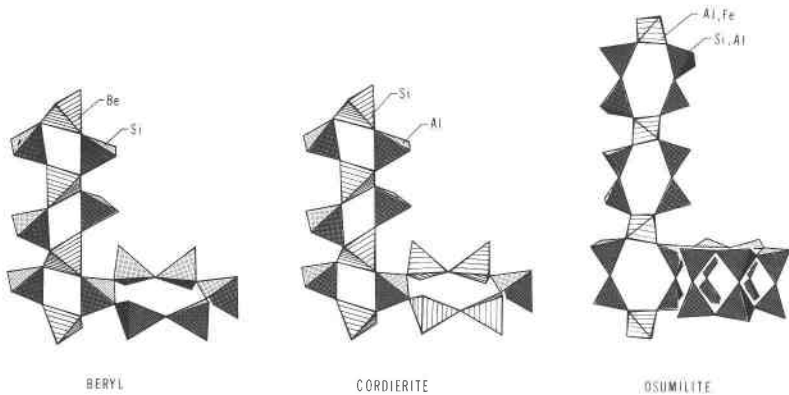
FIG. 3. Comparison of the vertical chains of four-membered rings in beryl and low cordierite and the six-membered rings in osumilite.
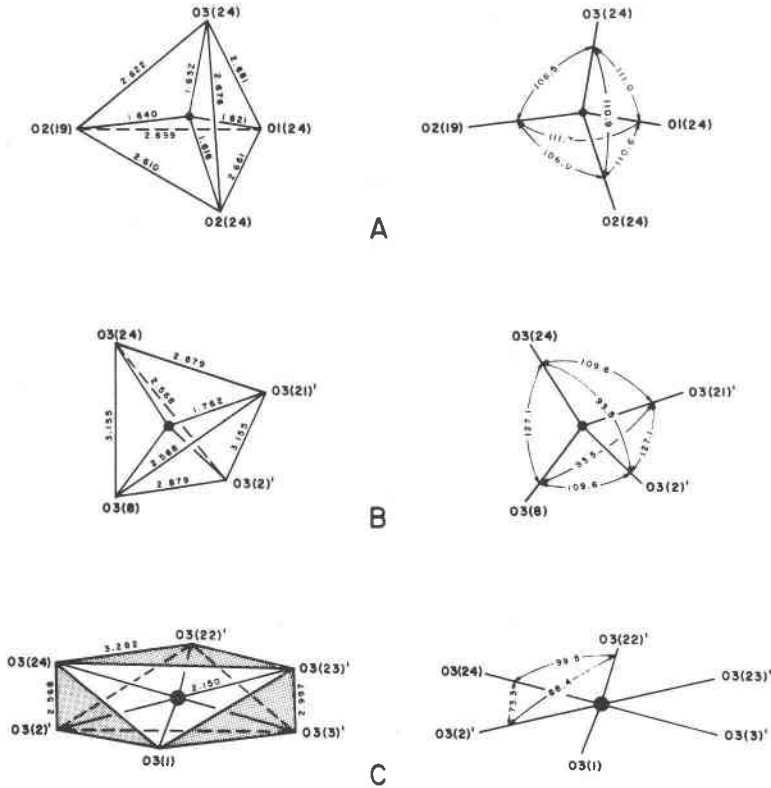
Fig. 4. The T1 tetrahedron (A), T2 tetrahedron (B) and M octahedron (C) in osumilite.

O2 is considered to be coordinated by the three cations mentioned, electrostatic charge balance is maintained; an assignment of two ligands, however, reduces the charge on the coordinating cations to 1.92, on the average, and results in a deficiency on O2 of −0.08. Charge balance also fails on O1 which appears to be coordinated by two $(Si_{0.85}Al_{0.15})^{IV}$ resulting in −0.08. This imbalance might be satisfied if either $(Mg,Fe^{2+},Mn)^{VI}$ or $(K,Na,Ca)^{XII}$ or both partly coordinate and thus contribute some charge to O1. This seems unlikely, however, because the long M-O1(4.329[7] Å) and C(1)-O1(5.107[7] Å) distances suggest a relatively weak bond between O1 and these two cations. Therefore, the effective coordination of O1 is apparently closer to 2 than 3.

A study of the variation in mean Si-O bond length with average oxygen coordination (Gibbs and Brown, 1968) indicates that Si-O
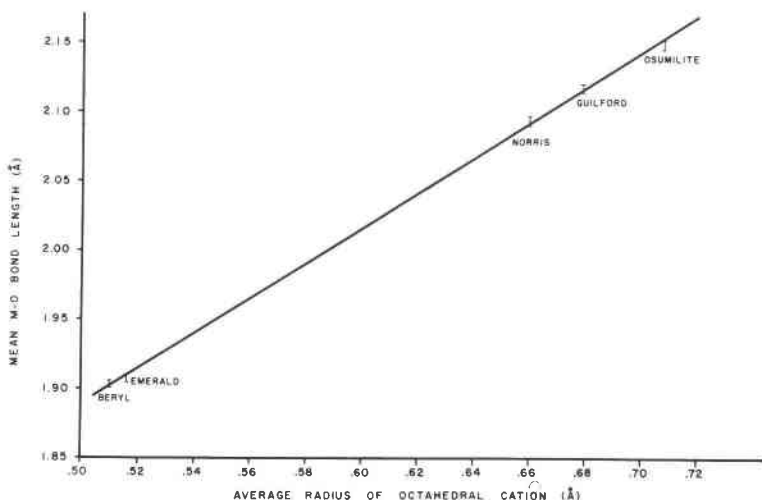
Fig. 5. Variation of the mean M-O bond length with average radius of the octahedral cations for beryl, emerald, the Norris and Guilford cordierites and osumilite using Ahren's radii.

bonds to two-coordinated oxygens are, on the average, shorter than those to three-coordinated oxygens. However, the T1-O bond (1.632[5] Å) to the three-coordinated oxygens in osumilite is not significantly longer than the mean T1-O bond length (1.626[3] Å) for the other oxygens. This disagreement may be due in part to the incorrect assignment of primary coordination spheres about O1 and/or O2 or to the effect of tetrahedrally coordinated Al^{3+}. In structures such as osumilite, the assignment of primary coordination spheres is especially difficult because of the variation in cation-oxygen bond lengths and the role that molecular water plays as a ligand.

The apparent isotropic thermal parameters, B, of the three non-equivalent oxygens ($B_{01} = 2.5[2]$ Å^2, $B_{02} = 2.4[1]$ Å^2, $B_{03} = 1.8[1]$ Å^2) support the assigned coordination numbers of the oxygens in light of Burnham's (1964) findings that two-coordinated oxygens have larger rms amplitudes of vibration than do three-coordinated oxygens in ordered silicate structures. The apparent rms amplitudes of vibration are 0.18 Å and 0.17 Å for O1 and O2 respectively, but 0.15 Å for O3. The magnitudes of these vibration amplitudes are larger than those cited by Burnham for ordered silicates and agree with his observation that site disorder tends to result in increased rms amplitudes of vibration of oxygen atoms.

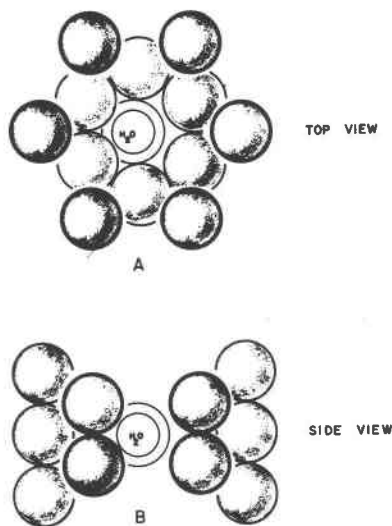The open channels paralleling c in osumilite are formed by a stacking

Fig. 6. Schematic drawings of the cavity formed by the double hexagonal rings as viewed down the *c*-axis (A) and normal thereto (B). Only oxygen atoms are pictured, some of which have been omitted, in order to show the water molecule (double circle) in one of six symmetry-equivalent positions.

of the double hexagonal rings which are linked laterally and vertically by T2 tetrahedra. Two different sites lie in the channels. One within the hexagonal antiprism between the double hexagonal rings, houses Na, K, Ca at $(0,0,\frac{1}{4})$. This position is designated C(1) in the bond-length tables. The second site, within the cavity formed by the double hexagonal rings, contains the water molecule (Figure 6) which is randomly distributed in one of six topologically and energetically equivalent positions. The oxygen-water bond lengths (2.6[1] Å) and the oxygen-water-oxygen angle (91.7[3]°) indicate the water molecule is hydrogen-bonded to the channel-wall oxygens. The refined water-oxygen position is displaced 0.29 Å along x and 0.97 Å along y from the position $(0,0,0)$ at the center of the cavity. This conforms with Smith and Schreyer's (1962) findings in their study of water in cordierite and supports their suggestion that a water molecule cannot be stably accommodated at the center of large cavities such as those found in cordierite, beryl and osumilite. The large *esd* of the x and y coordinates and relatively large temperature factor ($B = 9[3]$ Å²) of the water molecule suggests that the hydrogen bonds between the water molecule and the oxygen atoms of the cavity walls are relatively weak. However, on the basis of the water-oxygen bond length (2.89[4] Å) reported by

McDonald and Cruickshank (1967b) for the framework silicate, hemimorphite, and its assessment as indicating a weak hydrogen bond, the shorter distance in osumilite would indicate a moderately strong hydrogen bond, if bond shortening can be considered an indicator of increased bond strength. The short water-oxygen contact in osumilite is not surprising because of the Al content of the tetrahedra forming the double hexagonal rings. The replacement of Al^{3+} for Si^{4+} leads to a local charge imbalance on the cavity wall oxygens, O2, electrostatically enhancing the bond to the oxygen of the water molecule.

In milarite molecular water was assigned to the three-fold axis near the faces of the distorted Ca octahedra (Bakakin and Soloveva, 1966). An attempt was made to locate water in the same position in osumilite; however, a least-squares refinement with water in this position raised the R factor to 10%.

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