American Mineralogist
Vol. 57, pp. 1089–1108 (1972)

ALUMINUM-SILICON DISTRIBUTION IN ZUNYITE

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Abstract

A least squares refinement of the structure of zunyite from the type locality was undertaken to clarify its tetrahedral Al/Si distribution and to locate the hydrogen atoms. The oxygen atoms in zunyite form a continuous tetrahedral framework of cubododecahedra linked through double 4–membered and single 6–membered rings. The composition of the framework is $[XY_5\square_4O_{20}]$, where according to Pauling (1933) and Kamb (1960) X = Al, Y = Si such that the AlO_4 tetrahedra are separated from the Si_5O_{16} groups by vacant $\square O_4$ tetrahedra. The T–O bond lengths within the Y_5O_{16} group are statistically identical and average 1.63 Å, whereas those in the XO_4 tetrahedra are 1.798 Å indicating an ordered Al/Si distribution, in agreement with the Pauling–Kamb model. Accordingly, Zagal'skaya and Belov's (1964) proposal that Y_5O_{16} group has the composition $Al[SiO_4]_4$ should be discarded. The proposal by Kamb that O(3) is an hydroxyl ion is confirmed by the location of H atom at distance of 0.73 Å from the oxygen.

In the Si_5O_{16} group all O–Si–O angles are close to the ideal tetrahedral angle and the Si(1)–O(2)–Si(2) linkages are linear. The approximate equality of Si–O(br) and Si–O(nbr) bonds may be a result of all O–Si–O angles being close to 109.5° as evinced by extended Hückel molecular orbital calculations.

Introduction

The crystal structure of zunyite was solved by Pauling in 1933. More than ten years ago, a careful refinement of the structure permitted Kamb (1960) (i) to confirm Pauling's original model of insular Si_5O_{16} tetrahedral ions separated from "isolated" AlO_4 tetrahedral ions, and (ii) to make predictions about the location of the hydrogen atoms. On the basis of the proposed hydrogen and fluorine arrangement, Kamb also modified the chemical formula of the mineral to $Al_{13}Si_5O_{20}F_2(OH,F)_{16}Cl$ from its original form $Al_{13}Si_5O_{20}F_3(OH)_{15}Cl$, and indicated that at least two fluorine atoms per formula unit are essential for the stabilization of the structure. Turco (1962) has since investigated the thermal stability of zunyite and concluded that the presence of fluorine is essential for its synthesis. Even though Kamb's refinement is precise, the reliability of the chemical composition of the zunyite was unfortunately unknown. Analyses of natural zunyites quoted by Pauling (1933), Turco's (1961, 1962) analyses of Algerian zunyites, and our microprobe scans show that the ideal Al:Si ratio of 13:5 may vary due to the presence of other ions (Ti, Fe, Na, K, Ca, Mg, P and Cr). Zagal'skaya and Belov (1964) consider Kamb's refinement to be incomplete because it employed only 133 structural amplitudes of the type *hk*0 and 340 of the type *hhl*. By comparing the zunyite structure with heteropoly-acid complexes where the contents of the central polyhedron contrasts sharply with that of peripheral polyhedra, they suggest that the T_5O_{16} group should contain a central Al–tetrahedron such that its composition is $Al[SiO_4]_4$, which interchanges the positions of one Al^{IV} and one Si^{IV} in the Pauling–Kamb model. The Al/Si distribution proposed by Zagal'skaya and Belov is also inconsistent with the predictions of Brown and Gibbs (1970) for Al/Si ordering in aluminosilicates. The present investigation was undertaken to clarify the tetrahedral Al/Si distribution and to locate the positions of hydrogen atoms (Louisnathan and Gibbs, 1971).

EXPERIMENTAL

Crystal Data

A number of zunyite specimens from four different localities were examined with the electron microprobe. The specimen chosen for the structure analysis is from Zuni Mines, Colorado (HU-80964, kindly supplied by Dr. Joel Arem of the U. S. National Museum at Washington, D. C.). Quantitative X–ray emission microanalysis using topaz of known composition and synthetic chlorapatite as standards, gave the following composition, (calculated on the basis of 39(O, OH, F)):

$$Al_{12.98}Si_{5.01}P_{0.03}F_{3.86}(OH)_{14.20}O_{20}Cl_{1.07}\,.$$

A colorless tetrahedron of zunyite (0.12 mm edge length) was mounted on a [110] axis and the space group conditions were checked from precession photographs. The Laue symmetry and the systematic presences are consistent with space group $F\bar{4}3m$ originally determined by Pauling (1933) and confirmed by Kamb (1960). The cell edge *a*, calculated from 4θ values of 040, 060, 080, and 0,14,0 measured on the single crystal with the Picker diffractometer, is 13.860(3)Å. The density 2.903 $g \cdot cm^{-1}$ calculated from *a* (obs) and the composition given above, compares well with the measured density range of 2.873–2.904 $g \cdot cm^{-1}$ quoted by Pauling (1933).

Intensity Data

Intensity data were collected on a four circle single–crystal–diffractometer, using Nb–filtered Mo radiation. The absorption was statistically constant for the complete rotation of the crystal; the linear absorption coefficient ($\mu_{MoK\alpha} = 9.7\ cm^{-1}$) and the crystal volume ($\sim 3 \times 10^{-4}\ cm^3$) being small, no absorption correction was applied to the data. Lorentz–polarization corrections were made and all data whose observed amplitudes were less than one e.s.d., ($\hat{\sigma}[|F(hkl)|]$), obtained from counting statistics were rejected yielding 971 independent intensities for the refinement.

Refinement

The structural parameters were refined using the ORFLS least–squares program (Busing, Martin, and Levy, 1962). The first cycle of refinement, using the atomic coordinates of Kamb (1960), unit weights and individual isotopic thermal parameters, $B = 1.0$ for anions, and $B = 0.5$ for cations, gave an $R = 0.17$ with negative temperature factors being calculated for several atoms. Two additional cycles converted all B's to positive values and lowered R to 0.16. Deleting 80 data whose observed amplitudes were less than $2\hat{\sigma}$, two more iterations of refinement gave an $R = 0.127$, with large residuals associated with weak reflections. Removing of all data whose structural amplitudes were less than $4\hat{\sigma}$, one additional cycle with 566 data resulted in an $R = 0.082$. The calculated least squares estimates of the parameters were statistically identical with those obtained before removing these data, but the e.s.d's of the estimates were significantly reduced thus justifying the removal of data. The next cycle of refinement included the least square adjustment of the site-occupancies of tetrahedral silicon (4c site, central Si of Si_5O_{16} group and aluminum (4d) sites), and the site occupancies of oxygen atoms O(3) and O(4). According to Kamb (1960) O(3) is an OH ion, and O(4) disordered (OH, F). This refinement which gave an $R = 0.084$ showed that the only significant shift was that of O(4) site-occupancy factor which was +0.07(2). This shift is in the right direction to change the scattering function of O(4) site from pure oxygen to (5/6 O + 1/6 F) as required by the chemical composition. Further refinements used the (OH, F) composite scattering function for O(4) site. A calculation of T–O distances showed that $T(4c)$–O(2) = 1.63 and $T(4d)$–O(1) = 1.79Å. Thus the T–O distances, together with the results of site-occupancy test indicate that the tetrahedron centered at 4c contains only Si whereas that centered at 4d contains only Al. At this stage a weighting scheme with

$$w = \frac{1}{\mathrm{var}(|F(hkl)|)} = \{1 + [(F_0 - PA\cdot FT)/FT\cdot XX]^2\}^{-1}$$

was introduced, where PA, FT, and XX are variables which are adjusted until $\langle w\Delta^2\rangle$ is constant over ten equally populated groups of increasing $|F_o|$, indicating that $\langle w\Delta^2\rangle$ is independent of $|F_o|$ and that the weights are valid. The final adjusted values of PA, FT, and XX are 4.62, 13.0, and 1.4, respectively. Two further cycles of refinement with site-occupancies fixed at ideal values gave an $R = 0.072$ and weighted $R' = 0.063$. Next, a hydrogen atom was placed at 1.0Å from O(3) such that O(3)—H ··· Cl link is linear, as proposed by Kamb (1960). One cycle of refinement, which included adjustment of positional and isotropic thermal parameters of the H atom, gave $R = 0.070$ and $R' = 0.061$. Attempts to locate the other H atom in the vicinity of O(4), the (OH, F) disordered site, resulted in large positive B for this H atom. Refinement with anisotropic βs for Si, Al, O, and Cl atoms was not successful. In order to eliminate polar dispersion errors in bond lengths, anomalous- scattering correction terms for Si, Al, and Cl (values of f' and f'' (from Cromer, 1965)) were applied using the RFINE (L. W. Finger, personal communication) program. In three cycles, the refinement converged giving final $R = 0.066$ and $R' = 0.056$ for one absolute configuration, and $R = 0.072$ and $R' = 0.063$ for the other. Site-refinement calculations (Finger, personal communication) for Si(1) and Al(t) site resulted in strong correlations between site-occupancies and temperature factors and did not yield meaningful results. However, two cycles of refinement with the Al/Si distribution of the Zagal'skaya-Belov model resulted in negative $B(-0.17)$ for the Al in the central tetrahedron of the T_5O_{16} group suggesting that Al does not occupy this site.

Results

The final least squares estimates of the positional and thermal parameters of atoms in zunyite together with Wycoff site notations are given in Table 1. A

Table 1. Positional and thermal parameters of atoms in zunyite.

atom	site (Wycoff)	fractional coordinates			isotropic β
		x	y	z	
Si(1)	4*c*	0.25	0.25	0.25	0.14(7)
Al(*t*)	4*d*	0.75	0.75	0.75	0.26(9)
Si(2)	16*e*	0.1143(1)			0.13(3)
Al(*O*)	48*h*	0.0854(1)		0.7669(1)	0.31(2)
O(1)	16*e*	0.8250(3)			0.46(10)
O(2)	16*e*	0.1822(4)			0.80(11)
O(3)	24*f*	0.2800(5)	0	0	0.79(9)
H	24*f*	0.32(1)	0	0	4.6*
O(4)	48*h*	0.1783(2)		0.5454(3)	0.25(5)
O(5)	48*h*	0.1377(2)		0.0013(3)	0.41(5)
Cl	4*b*	0.50	0.50	0.50	0.63(7)

*not varied after the first few cycles.

table comparing the calculated and observed structure amplitudes has been deposited with ASIS-NAPS.[1]

Interatomic distances and bond angles and their associated e.s.d.'s were calculated using the ORFFE (Busing *et al.*, 1966) program. The bond distances and angles obtained in our study (Table 2) are compared with those obtained by Pauling (1933) and Kamb (1960). Almost all the discrepancies between the results of Pauling and Kamb can be attributable to the precision of modern techniques that were available to Kamb. Our results are statistically identical to those obtained by Kamb; the largest difference is in the O(5)–O(5′) tetrahedral edge length where our calculations indicate a slightly shorter (by 0.047 Å) distance.

Extended Hückel Molecular Orbital (EHMO) Calculations

In zunyite, despite the linearity of the Si–O–Si angles, all the Si–O distances (1.63 Å) are statistically identical in the $(Si_5O_{16})^{12-}$ ion contrary to a more generally observed trend that suggests that Si–O(br) bonds are shorter than Si–O(nbr) bonds (*cf.*, Brown and Gibbs, 1969). Our study (Louisnathan and Gibbs, 1972a) of hypothetically distorted (SiO_4) suggest that O–Si–O angles play an important role in determining the Si–O bond lengths. In order to understand this effect in polymerized (SiO_4) tetrahedral groups, EHMO calculations were under-

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[1] To obtain a copy of this material, order NAPS Document Number 01806. The present address is National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, New York 10022, and price $2.00 for microfiche or $5.00 for photocopies, payable in advance to CCMIC-NAPS. Check a recent issue of the journal for current address and price.

Table 2. Interatomic distances and bond angles in zunyite

Bond	Pauling (1933)	Kamb (1960)	This study
The Si_5O_{16} group:			
4 Si(1)-O(2)	1.59	1.64	1.628(10)Å
6 O(2)-O(2')	2.60	2.67	2.658(16)
6 O(2)-Si(1)-O(2')			109.471(2)°
1 Si(2)-O(2)	1.59	1.625	1.629(10)Å
3 Si(2)-O(5)	1.59	1.65	1.632(5)
3 O(2)-O(5)	2.60	2.66	2.654(9)
3 O(5)-O(5')	2.60	2.72	2.673(8)
3 O(2)-Si(2)-O(5)			109.0(2)°
3 O(5)-Si(2)-O(5')			110.0(2)
4 Si(1)-O(2)-Si(2)			180.0
Isolated Al-tetrahedron:			
4 Al(t)-O(1)	1.74	1.80	1.798(9)Å
6 O(1)-O(1')	2.84	2.94	2.937(14)
Al_3O_{13} octahedral cluster:			
2 Al(0)-O(4)[a]	1.89	1.86	1.863(2)Å
1 Al(0)-O(3)[b]	1.85	1.78	1.794(3)
1 Al(0)-O(1)	1.86	1.93	1.934(5)
2 Al(0)-O(5)	1.93	1.92	1.905(3)
2 O(3)-O(4)	2.67	2.64	2.616(3)
2 O(3)-O(5)	2.67	2.73	2.742(5)
2 O(4)-O(1)	2.68	2.69	2.712(4)
2 O(4)-O(5)	2.64	2.67	2.683(5)
2 O(5)-O(1)[c]	2.64	2.53	2.517(9)
1 O(4)-O(4')	2.67	2.60	2.600(7)
1 O(5)-O(5')	2.84	2.72	2.673(8)
2 O(3)-Al-O(4)			91.3(2)°
2 O(3)-Al-O(5)			95.6(2)
2 O(4)-Al-O(1)			91.1(2)
2 O(4)-Al-O(5)			90.8(2)
2 O(5)-Al-O(1)			81.9(2)
1 O(4)-Al-O(4')			88.5(3)
1 O(5)-Al-O(5')			89.0(3)
Non-bonded contacts in Al(t) containing $Al^{IV}\{Al_3^{VI}O_{13}\}_4$ group:			
O(4). . . O(4")	2.71	2.77	2.813(8)Å
Al(0). . . Al'(0)			
(i) across shared edge	2.72	2.90	2.896(3)
(ii) across O(4) shared corner	3.58	3.56	3.558(3)
Al(0). . . Al(t)	3.17	3.24	3.236(2)
Al(0). . . O(4). . . Al'(0)	142	146.6	145.5(2)°
Al(0). . . O(1). . . Al(t)			120.2(2)
Non-bonded contacts in the O(3) linked $(Al_3^{VI}O_{13})_4$ group:			
Al(0). . . Al'(0) across O(3) shared corner	3.49	3.34	3.347(4)Å
Al(0). . .O(3). . .Al'(0)	142	139.2	137.7(4)°
Al(0). . . Cl	4.16	4.06	4.060(2)Å
Hydrogen bonds:			
O(3)-H. . . Cl	3.14	3.08	3.052(7)Å
O(3)-H[d]			0.73
H. . . Cl[e]			2.383
O(4)-H. . . . Cl	3.59	3.58	3.551(4)

[a] O(4) = disordered (OH,F)

[b] O(3) = OH

[c] shared edge

[d,e] listed value corrected for H atom riding on O(3) or Cl (d) uncorrected 0.68(19), (e) uncorrected 2.37(19)Å.

taken for (1) the $(Si_2O_7)^{6-}$ ion (all Si–O = 1.63 Å, D_{3h} point-group *i.e.*, the seven oxygen atoms in an approximate hcp configuration, and Si–O–Si at 180°) where only the O–Si–O angles were varied within the constraints of D_{3h} symmetry, and (2) for the $(Si_5O_{16})^{12-}$ ion with the dimensions as observed in zunyite. The details of EHMO calculations are described elsewhere (Louisnathan and Gibbs, 1972). The VOIP values used are from the work of Basch, Viste, and Gray (1965), Slater exponents from the work of Clementi and Raimondi (1963), except for Si 3*d*, for which we have used $H_{3d3d} = -5.5$ eV and $\xi_{3d} = 1.0$ (Gibbs *et al.*, 1972).

DISCUSSION

Description of the Structure

The key structural units in zunyite are (1) the (Si_5O_{16}) tetrahedral silicate pentamers (Fig. 1), (2) the $[Al_3(O, OH, F)_{13}]$ close-packed octahedral groups (Fig. 2), (3) the vacant $(\square O_4)$–tetrahedra in the centers of the foregoing octahedral groups, and (4) the isolated (AlO_4) tetrahedra. The oxygen atoms of the AlO_4 tetrahedra bridge four vacant tetrahedra to form $(Al\square_4O_{16})$–groups in geometrically the same con-

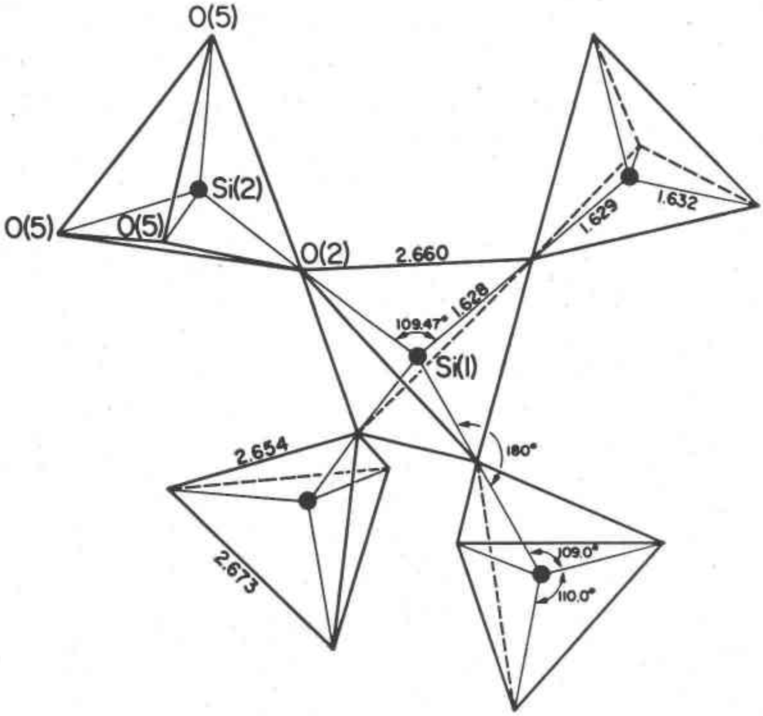

FIG. 1. The dimensions of the Si_5O_{16} group.

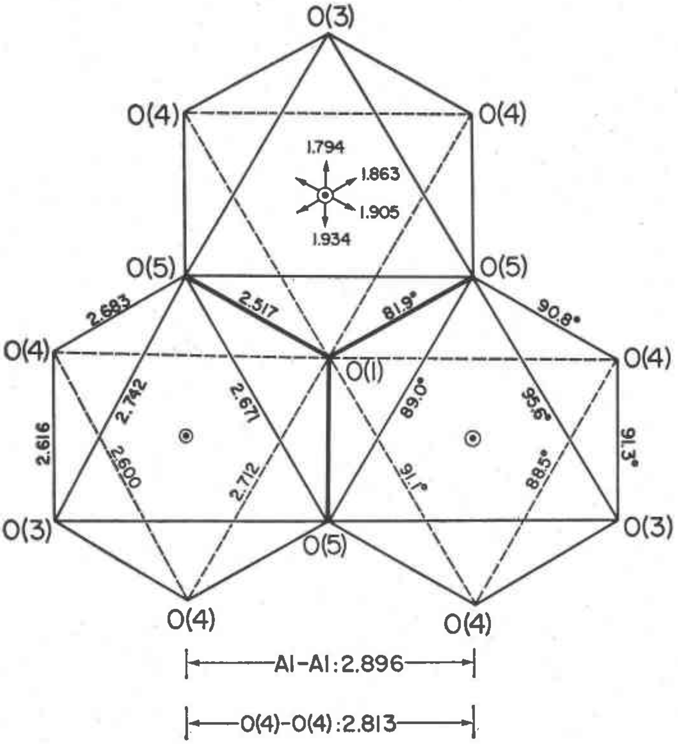

FIG. 2. The dimensions of $[Al_3(O,OH,F)_{13}]$ group shown in an idealized projection along the 3-fold axis.

figuration as the Si_5O_{16} pentamer. The terminal oxygen atoms of the vacant tetrahedra bridge the outer Si containing tetrahedra of the (Si_5O_{16}) group. Thus the (Si_5O_{16}) groups and $(Al\square_4O_{16})$ groups link to form a continuous framework of tetrahedra. The structural units of this framework are the undistorted cubododecahedra and cubes depicted in Figure 3. Both the cube and the cubododecahedron have T_d symmetry due to ordering of tetrahedral atoms. The adjacent cages link through single six-membered (-Si-Si-Si-□-Al-□-) and double four-membered (-Si-□-Si-□-) rings as shown in Figure 4. The manner in which the octahedral groups connect with the tetrahedral framework can be understood with the aid of Figure 5; four groups of $[Al_3(O, OH, F)_{13}]$ octahedra polymerize via bridging O(3) atoms to form a larger cluster of $4[Al_3(O, OH, F)_{13}]$ octahedral groups (Figures 13–14 of Pauling, 1960). There are four cubic cages surrounding the Al containing tetrahedron (Fig. 4c) implying that this tetrahedron should be surrounded by four $[Al_3(O, OH, F)_{13}]$ groups. These four octahedral groups form yet another kind of [$Al_{12}(O, OH, F)_{40}$] cluster (Fig. 6) where octahedral polymerization is effected by bridging pairs of O(4) atoms. The [$Al_3(O, OH, F)_{13}$] groups line the walls of the cubododecahedral cage, and the chlorine atom is located at its center. Other aspects of the crystal structure of zunyite have been discussed exceedingly well by Pauling (1933), Kamb (1960) and Zagal'skaya and Belov (1964) and will not be repeated here.

Al/Si Distribution in Zunyite

The composition of the Si–Al–□–framework (Fig. 4a) can be represented as [$XY_5\square_4O_{20}$], where according to Pauling (1933) and Kamb (1960) X = Al, Y = Si such that AlO_4 tetrahedra are separated from the Si_5O_{16} groups by □–tetrahedra. The chemical analyses quoted by Pauling (1933) show a slight excess in aluminum with respect to the ideal stoichiometry of $Al_{13}Si_5O_{20}(OH)_{16}F_2Cl$. Kamb (1960) obtained 1.64(1) Å for all the Si–O distances in the Si_5O_{16} group, a distance that is 0.02 Å larger than the mean Si–O (1.62 Å; Smith, 1954) distance. This led to the suggestion that the excess Al randomly replaces Si in the 4*c* and 16*e* sites of the Y_5O_{16} group, *apart* from one full Al–occupancy at the 4*d* site. The excess Al may also be considered to occupy the □–tetrahedra but this is unlikely as it requires face sharing between Al–containing tetrahedra and octahedra.

Zagal'skaya and Belov (1964) *compared* the structure of zunyite with heteropolyacid complexes where the central polyhedron contrasts sharply from the terminal polyhedra, (such as the $Al\square_4O_{16}$ unit in the zunyite structure) and suggested interchanging the position of Al to 4*c* and an Si to 4*d*. This would extend the symmetry–antisymmetry character, that is well obeyed for the octahedral oxygen clusters of zunyite (Zagal'skaya and Belov, 1964), to the tetrahedral polymers also. Thus the Si_5O_{16} group in their opinion would become ($AlSi_4O_{16}$) and the ($Al\square_4O_{16}$) group would become ($Si\square_4O_{16}$) group. The X–ray emission microanalysis of the HU–80964 zunyite on which our structure refinement was undertaken does not show excess aluminum. All the T–O distances in the Y_5O_{16} group are statistically identical at 1.63(1) Å and the T–O distance for the tetrahedron centered at 4*d* is 1.798(9) Å. These distances confirm the Pauling–Kamb model of the Si_5O_{16} groups in zunyite. Accordingly, the proposal by Zagal'skaya and Belov that the groups have composition ($AlSi_4O_{16}$) should be discarded. Based on the T–O d–p π–bonding model (T = Si, Al, B, Be, or Mg) Brown and Gibbs (1970) have proposed that in framework silicates, Si should prefer those tetrahedral sites involved in widest average T–O–T angles and Al, B, Be, or Mg those involved in narrowest T–O–T angles. They

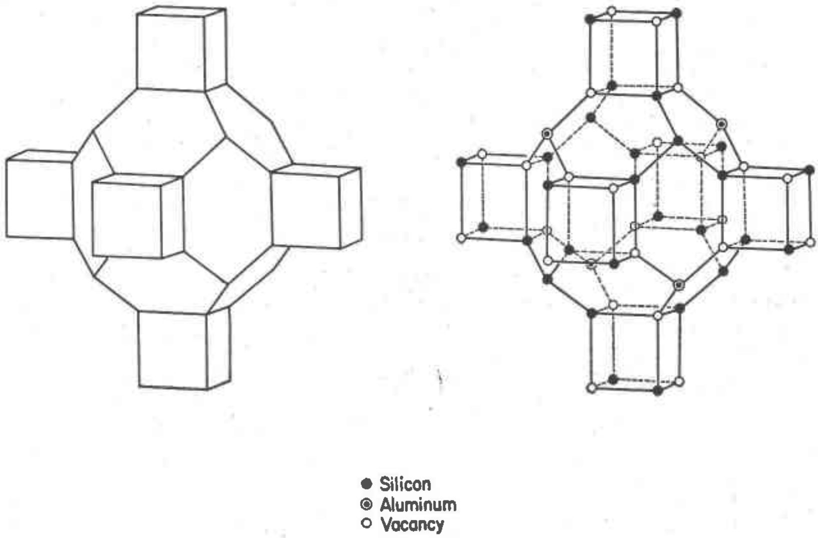

FIG. 3. The cubodecahedral and cubic cages in zunyite. The corners of the polyhedra represent the centers of tetrahedral sites as shown in the right side.

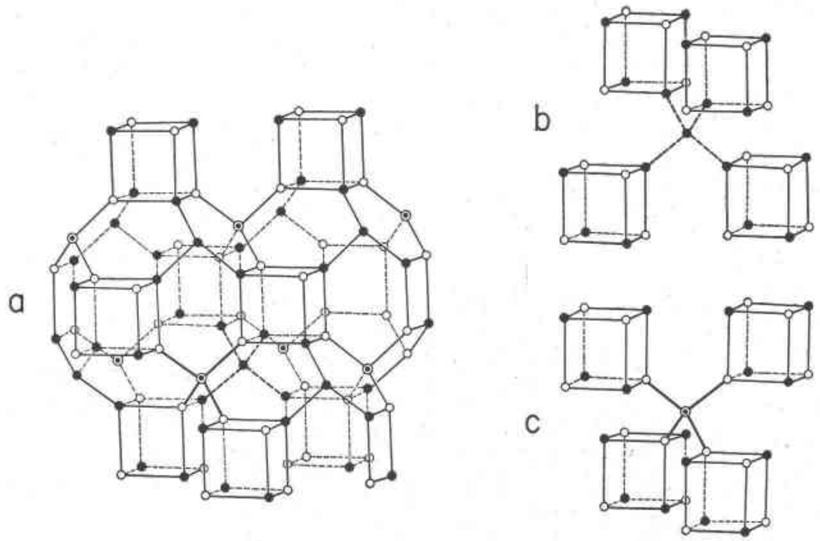

FIG. 4. (a) The $[\mathrm{Al^{IV}Si_5\square_4O_{20}}]$ framework in zunyite, (b) and (c) show respectively the environments of the $(\mathrm{Si_5O_{16}})$ and $(\mathrm{Al_4O_{16}})$ insular groups.

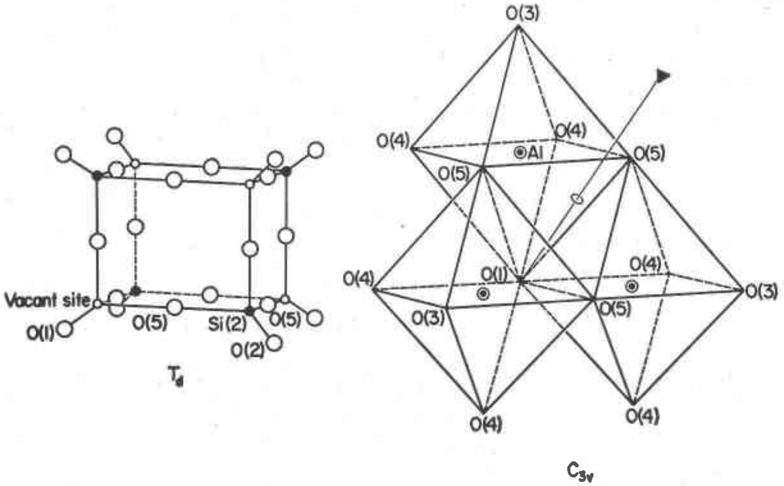

FIG. 5. The anion–cation composition of the cubic cage (left). The [Al_3(O,OH, F)$_{13}$] groups (right) occupy the alternate corner of the cubic cage.

also noted that Zagal'skaya–Belov Al/Si distribution for zunyite results in severe charge imbalances. Our results are consistent with the proposal by Brown and Gibbs.

Chemical Bonding in Zunyite

The Si_5O_{16} Group. The dimensions of the Si_5O_{16} group are given in Table 2 and Figure 1. The tetrahedron centered about 4*c* contains Si(1) and has a local T_d point–symmetry. To our knowledge, zunyite is

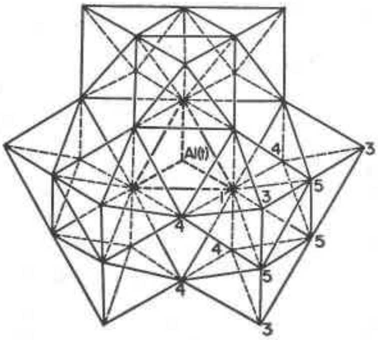

FIG. 6. The O(4) bridging [Al_{12}(O, OH, F)$_{40}$] group, shown projected along the 3–fold axis, houses the (AlO_4) tetrahedron.

the only mineral to contain an "ideal" (SiO_4) tetrahedron. The Si(1)–O(2) distance of 1.63 Å exactly equals Pauling's (1952) predicted distance based on a single σ– and a partial d–p π–bond. The Si(2)–O(2, br) and Si(2)–O(5, nbr) distances of the terminal tetrahedra, 1.629(10) and 1.632(10) Å respectively, are not statistically different from Si(1)–O(2, br). However, the EHMO bond overlap populations, calculated with a valence Si(sp) basis set, for the $(Si_5O_{16})^{12-}$ ion show a variation that correlates fairly well with the observed variation (Table 3). Since the distances are not significantly different, little significance should be attached to the correlation but the overlap populations do suggest that the Si–O(nbr) should be slightly longer than the Si–O(br) bonds, a prediction consistent with both Kamb's and our results (⟨Si–0(br)⟩ = 1.627; ⟨Si–O(nbr)⟩ = 1.637 Å). The overlap populations

TABLE 3

T-O distances and bond overlap populations for the T_5O_{16} groups in zunyite and anorthite, calculated in the Si($\underline{sp}$) basis using observed dimensions.

Zunyite				Anorthite		
	T-O(Å)*	$\underline{n}$(T-O)			T-O(Å)**	$\underline{n}$(T-O)***
		T(1) = Si T(2) = Si	T(1) = Al T(2) = Si			T ($\underline{m}$000) = Al all other T = Si
T(1)-O(2)[4x]	1.628	0.514	0.396	$T_1(\underline{m}000) - O_A(1000)$	1.776	0.326
				$- O_B(\underline{m}000)$	1.705	0.383
				$- O_C(\underline{m}000)$	1.739	0.349
				$- O_D(\underline{m}000)$	1.778	0.331
T(2)-O(2)[1x]	1.629	0.504	0.510	$T_1(0000) - O_A(1000)$	1.644	0.479
T(2)-O(5)[3x]	1.632	0.499	0.500	$- O_B(0000)$	1.619	0.501
				$- O_C(0000)$	1.581	0.542
				$- O_D(0000)$	1.616	0.502
				$T_2(\underline{m}000) - O_B(\underline{m}000)$	1.580	0.546
				$- O_A(2000)$	1.644	0.483
				$- O_C(0\underline{zi}0)$	1.607	0.510
				$- O_D(0\underline{z}00)$	1.628	0.496
				$T_20\underline{zi}0 - O_C(\underline{m}000)$	1.613	0.509
				$- O_A(2\underline{zi}0)$	1.617	0.495
				$- O_B(0\underline{zi}0)$	1.627	0.497
				$- O_D(\underline{m}0\underline{i}0)$	1.573	0.538
				$T_2(0\underline{z}00 - O_D(\underline{m}000)$	1.603	0.531
				$- O_A(2\underline{z}00)$	1.634	0.479
				$- O_B(0\underline{z}00)$	1.621	0.505
				$- O_C(\underline{m}0\underline{i}0)$	1.607	0.509

*Our refinement
**Calculated from the positional parameters given by Wainwright and Starkey (1971)
***Values quoted from Louisnathan et al. (1972).

computed with an extended Si(*spd*) basis set also show the same trend, n[Si(1)–O(2)] = 0.797, n[Si(2)–O(2)] = 0.779 and n[Si(2)–O(5)] = 0.921. We also computed the bond overlap populations for the T–O bonds of a T_5O_{16} group of the same geometry as the insular Si_5O_{16} group but with Al in the central T(1) site (the Zagal'skaya–Belov model). In this calculation T(1)–O(2) populations are considerably reduced (Table 3, col. 4) and compare more closely with the Al–O populations of an $(AlSi_4O_{16})^{13-}$ unit in anorthite (Table 3, col. 7). The anorthite data (Table 3) show a single linear correlation ($r = -0.91$) between $n(T–O)$ and T–O bond lengths, T = Si or Al. In the light of this empirical fact the calculated $n[T(1)–O(2)]$ value of 0.396 for the zunyite–type T_5O_{16} group would correspond to a length of approximately 1.71 Å which is very long compared to Kamb's (1960) and our experimental distance of 1.63(1) Å. Thus, even though the interchanging of Si and Al between the 4*c* and 4*d* sites would extend the symmetry–antisymmetry character to the tetrahedral linkages (Zagal'skaya and Belov, 1964), nature's architectural rules appear to be violated for such an interchange in the structure of zunyite.

Within the last decade there has been considerable discussion about the relationship between the length of the Si–O(br) bond and the size of the Si–O–Si angle (Cruickshank, 1961; Lazarev, 1964; McDonald and Cruickshank, 1967; Cannillo, Rossi, and Ungaretti, 1968; Bokii and Struchkov, 1968; Brown, Gibbs, and Ribbe, 1969; Brown and Gibbs, 1970; Louisnathan and Smith, 1971; and Mitchell, Bloss, and Gibbs, 1971). These investigators have argued that shorter Si–O(br) bonds tend to be involved in wider Si–O–Si angles. More recently Gibbs *et al.* (1972) have shown that the relationship between Si–O(br) length and Si–O–Si angle in a large number of silicates is a non–linear one as predicted by the EHMO results. On the other hand, work of Smolin and Shepelev (1970) on some rare–earth pyrosilicates and our own structural refinement of zunyite suggest that the relationship is not an ubiquitous one.

Using the concept of atomic orbital hybridization one may define the quantity

$$P_{O(br)} = \lambda^2 = -1.0/\cos(\text{Si–O–Si}) \qquad (1)^1$$

as a partial measure of strength of the Si–O(br) bond (where λ is the $2p$ mixing coefficient in an $s + \lambda p$ hybrid on a two-coordinated bridging oxygen atom). According to equation (1) the number of lone–pair $2p$

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[1] Derived from the orthogonality condition, $1.0 + \lambda_i\lambda_j \cos\theta_{ij} = 0$, *cf.* Coulson (1961).

π–orbitals on O(br) not utilized in σ–bonding increases with increasing $P_{\mathrm{O(br)}}$, *i.e.*, with widening Si–O–Si angle. Thus, for an Si–O–Si angle of 109.47° there are zero $2p$ π–orbitals, one at 120°, and two at 180° to form either $3p$–$2p$ or $3d$–$2p$ π–bonds with the adjacent Si atoms. Despite the fact that equation (1) takes into account only the hybridization characteristics on O(br) and completely neglects such properties on Si, Gibbs *et al.* (1972) have shown that a linear trend between Si–O(br) and $P_{\mathrm{O(br)}}$ (*i.e.*, 1/—cos (Si–O–Si)) is fairly well-developed in a large number of silicates. Although the p–character in the $2p$ π–orbitals increases with widening Si–O–Si angle, the availability of the $3p$ π– or $3d$ π–orbitals on silicon is a function of O–Si–O angles (Louisnathan and Gibbs, 1972).

In order to gain some insight into the effect of O–Si–O angles on Si–O(br) and Si–O(nbr) bonds, Mulliken (1955) bond overlap populations, n(Si–O), were calculated in the EHMO approximation for a series of $(\mathrm{Si_2O_7})^{6-}$ groups where the O(nbr)–Si–O(br) angles were varied within the constraints of D_{3h} symmetry. The resulting n(Si–O) are plotted as a function of the O(nbr)–Si–O(br) angle in Figures 7 and 8. In the valence Si(sp) basis set calculation, the curves of n[Si–O(br)] and n[Si–O(nbr)] cross in the vicinity of 108.3° (Fig. 7), predicting shorter Si–O(br) bonds only when O(nbr)–Si–O(br) angles are larger than O(nbr)–Si–O(nbr) angles. No quantitative significance should be attached to the point of intersection (108.3°) of the two n(Si–O) curves in Figure 7, because of the inherent approximations in the EHMO calculation and because the $(\mathrm{Si_2O_7})^{6-}$ ion is considered as an isolated group necessitating that the calculated n(Si–O) for the Si–O(br) bonds belong to a different trend than those for the Si–O(nbr) bonds (Gibbs *et al.*, 1972). Our observation in zunyite that all O–Si–O angles are ideal tetrahedral angles in the central Si(1) tetrahedron and all Si–O distances equal (1.63 Å) appears to suggest that the point of intersection should be in the vicinity of 109.47°. We therefore *assumed* that the equilibrium bond populations, n_e[Si–O(br)] and n_e[Si–O(nbr)], are those obtained when all the O–Si–O angles are equal to 109.47°, and all Si–O = 1.63 Å. With these assumptions we calculated the approximate Δr(Si–O) values, Figures 7 and 8, from the equation

$$-\frac{\Delta n}{n_e} = \frac{\Delta r}{r_e} \qquad (2)^1$$

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[1] Δr obtained from (2) when added to the ⟨Si–O⟩ gives a very crude estimate of the Si–O bond length, Si–O(est.) = ⟨Si–O⟩ — $(r_e/n_e)\Delta n$, an equation which bears a resemblance with the one proposed by Baur (1971), *viz.* Si–O = ⟨Si–O⟩ + $b\Delta\zeta(\mathrm{O})$.

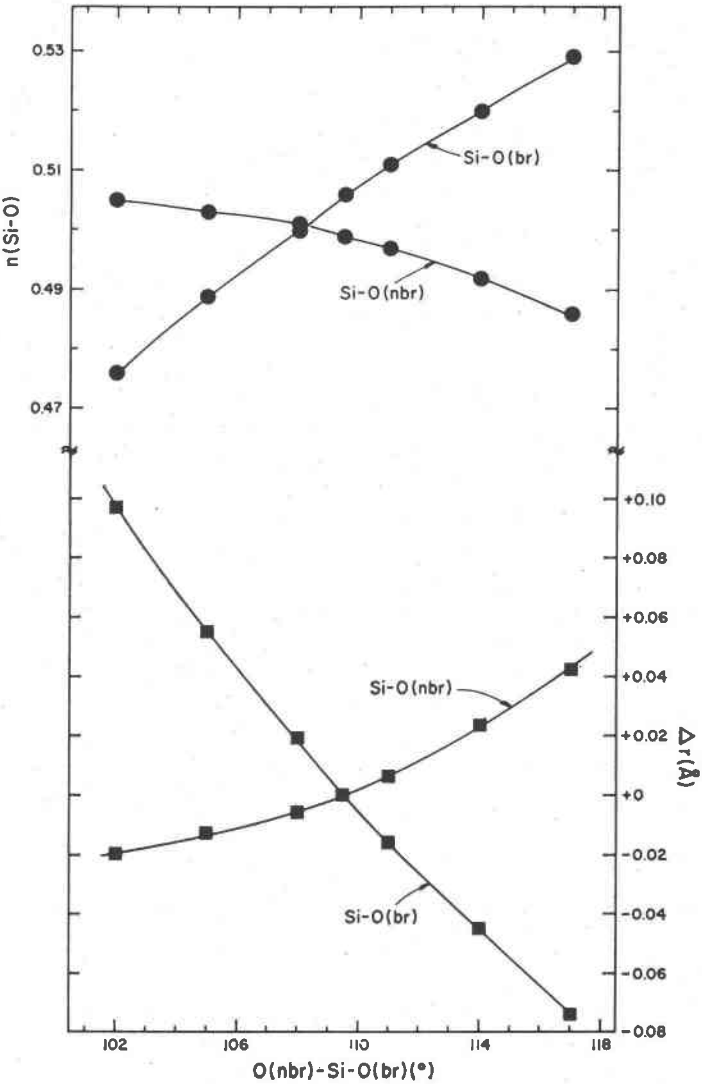


FIG. 7. Variation of n[Si–O(br)] and n[Si–O(nbr)] as a function of O(nbr)–Si–O(br) angle in the $(Si_2O_7)^{6-}$ group of D_{3h} point symmetry calculated in the Si(sp) basis. The lower set of curves predict Δr(Si–O) as a function of the same tetrahedral angle.

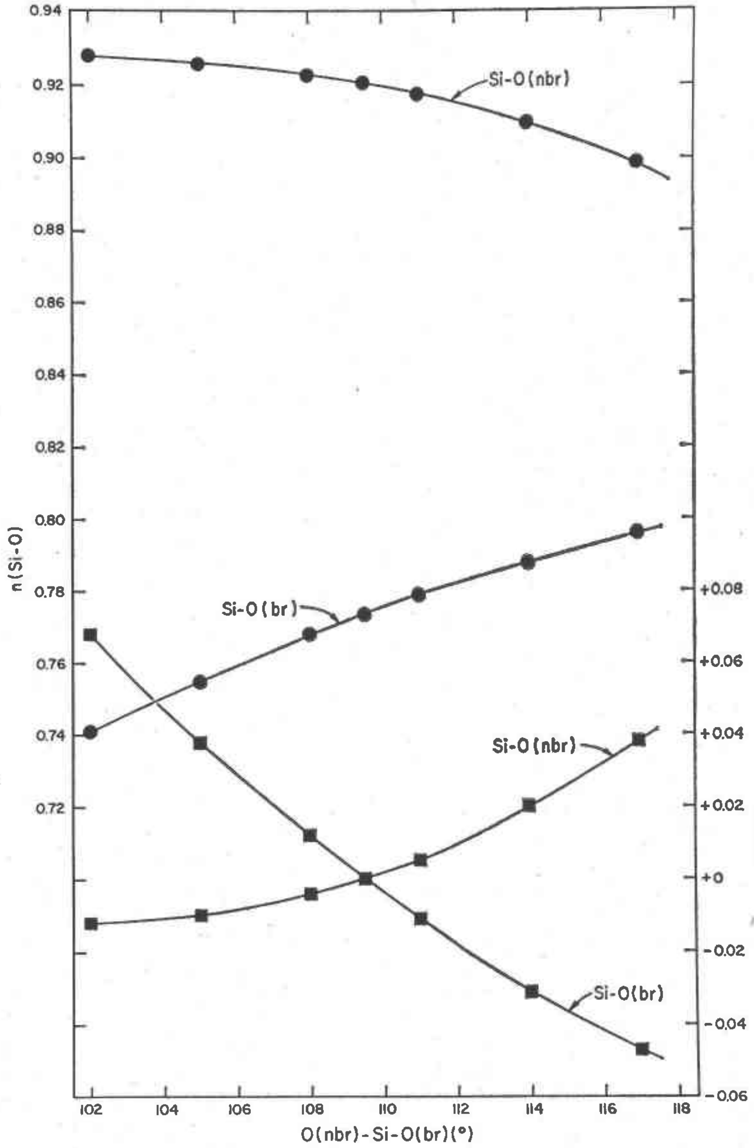
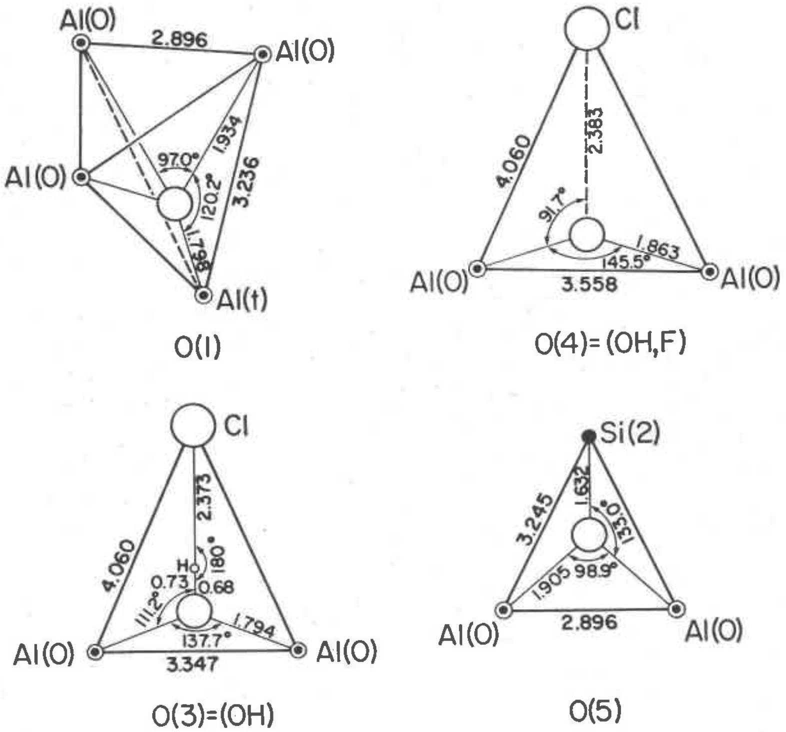


FIG. 8. Same as Figure 7 but calculated in the Si(*spd*) basis. The *n*[Si–O(br)] and *n*[Si–O(nbr)] curves do not intersect in the region of 108–109° because of (a) differences in the bond-types between Si–O(br) and Si–O(nbr), (b) omission of non-tetrahedral cations that are bonded to the O(nbr)s, and (c) the neglect of electrostatic interactions in the EHMO approximation (cf. Gibbs *et al.,* 1972).

which, we have elsewhere suggested, gives a crude estimate of bond length changes (Louisnathan and Gibbs, 1972a). The Δr curves reiterate the EHMO predictions that in the $(Si_2O_7)^{6-}$ group (D_{3h} symmetry) the Si–O(br) bonds will be shorter than Si–O(nbr) only when O(nbr)–Si–O(br) angles are wider than O(nbr)–Si–O(nbr), and vice versa. The Si_2O_7 group in the $Ba_3Nb_6Si_4O_{20}$ compound (Shannon and Katz, 1970) exhibits D_{3h} symmetry with O(nbr)–Si–O(br) angles of 113.0(3)°. For such an angle the Δr curves (Figs. 7 and 8) predict Si–O(1, br) = 1.60, Si–O(4, nbr) = 1.64 Å that compare reasonably with the observed distances of 1.599(6) and 1.629(7) Å respectively, suggesting that the assumptions made in calculating the Δr curves are fairly reasonable.

An $(Si_2O_7)^{6-}$ group exhibiting D_{3h} symmetry and with O(nbr)–Si–O(nbr) angles larger than O(nbr)–Si–O(br) has not yet been discovered to our knowledge. However, the $(Si_2O_7)^{6-}$ groups observed in some of the rare earth pyrosilicates (Smolin and Shepelev, 1970) appear to fit with the predictions of the lower angle portion of the curves (Figs. 7 and 8). A detailed discussion of these and other pyrosilicate ions will be given at a later date.

The $Al_3(O,OH,F)_{13}$ *Group.* The dimensions of the $Al_3(O,OH,F)_{13}$ group are shown in Figure 2. O(1) is four-coordinated and involved in a longer (1.934 Å) Al^{VI}–O distance than the three-coordinated oxygen atoms, O(3), O(4), and O(5). The O(1) oxygen-centered (OAl_4) tetrahedron (Fig. 9) has C_{3v} point symmetry with Al^{VI}–O(1)–Al^{VI} angles much narrower (97°) than the Al^{VI}–O(1)–Al^{IV} angles (120.2) suggesting that both the σ- and π-bonding potentials of O(1) will be concentrated toward tetrahedral Al making the octahedral Al–O bonds highly polar (*cf.* Louisnathan and Gibbs, 1972). The three Al-octahedra in the approximately close packed $[Al_3(O,OH,F)_{13}]$ group share a common corner at O(1) (Fig. 2) suggesting that the $Al^{VI} \cdots Al^{VI}$ repulsive forces may also play a role in lengthening the Al^{VI}–O(1) distance (Pauling, 1970; Kamb, 1960). In discussing the variation of Si–O tetrahedral distances as a function of O–Si–O angles, we pointed out (Louisnathan and Gibbs, 1972a) (1) that angular distortions (O–T–O, T–O–T, O–M–O, M–O–M) are dictated to a polyhedron by the crystal chemistry of the entire crystal structure, (2) that the small energy increase accompanying the distortion is compensated by the removal of certain degeneracies in the symmetric configuration whereby some bonds shorten and others lengthen, and (3) that such bond length changes are accomplished by non-equivalent hybridizations (both in σ and π) on the central atom. The Al-octahedron in zunyite appears to be another example of this mechanism, because the mean of the four octahedral angles



O(1) O(4)=(OH,F)

O(3)=(OH) O(5)

FIG. 9. Nearest neighbor cations of oxygen atoms O(1), O(3), O(4), and O(5) in zunyite.

associated with a bond, ⟨O–Al–O⟩₄, shows a correlation with the length of the bond under consideration:

⟨O–Al–O⟩₄	Al^{VI}–O	
93.3°	Al–O(3)	1.794 Å
90.4	Al–O(4)	1.863
89.2	Al–O(5)	1.905
86.3	Al–O(1)	1.934

As expected the short Al^{VI}–O distances are associated with hydroxyl oxygen O(3) and the disordered hydroxyl–fluor oxygen O(4). The short Al^{VI}–O(3) distance is similar in dimension to Al–O tetrahedral distance, perhaps resulting from a relative strengthening of the $3p$–$2p$ and $3d$–$2p$ σ– and π–bonds as required by the angular distortions. The variation of Al–O bond lengths with the electrostatic bond strengths, $\zeta(O)$, has been discussed by Pauling (1960) and will not therefore be repeated here. Suffice it to say that the semi-quantitative bonding discussions given above do *not* violate the arguments based on $\zeta(O)$.

Hydrogen Bonding. The linear hydrogen bonded O(3)–H ... Cl distance of 3.052 Å in zunyite compares well with the O–H ... Cl distance (bent) of 3.09 Å in methylglyoxal bisguanylhydrazone, (I), (Hamilton and LaPlaca, 1968) and with the O–H ... Cl distance (linear) of 3.18 Å in $CuCl_2 \cdot 2H_2O$, (II), (Peterson and Levy, 1957). In zunyite the O(3)–H distance of 0.68 Å (or 0.73 Å if corrected for H riding on O) is relatively very short when compared to the O–H distances in compounds (I) = 1.02 Å and (II) = 0.95 Å. The latter values were obtained by neutron diffraction techniques. The short O(3)–H distance in zunyite may be attributed to the inaccuracy of H atom positional parameters as obtained by X-ray diffraction methods (Hamilton and Ibers, 1968).

ACKNOWLEDGMENTS

We wish to thank our good friends Dr. Joel Arem of the National Museum at Washington, D. C. for the loan of several zunyite specimens and Professor Jen Ho Fang at the Department of Geology, Southern Illinois University, Carbondale, Illinois and Mr. Dana Griffen of the Geological Sciences Department at V.P.I. & S.U. for reading the manuscript and offering a number of helpful criticisms. This study was supported by NSF grants GA-12702, GA-30864X and GU-1392.

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Manuscript received, December 30, 1971; accepted for publication, February 22, 1972.