

The Si_5O_{16} Pentamer in Zunyite Refined and Empirical Relations for Individual Silicon–Oxygen Bonds

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(Received 27 April 1981; accepted 1 July 1981)

Abstract

Single-crystal X-ray diffraction data for two zunyites [$\text{Si}_{4.95}\text{Al}_{13.05}\text{O}_{19.95}(\text{OH})_{13.96}\text{F}_{4.09}\text{Cl}$ and $\text{Si}_{4.68}\text{Al}_{13.32}\text{O}_{19.68}(\text{OH})_{14.71}\text{F}_{3.61}\text{Cl}$] have been refined to $R = 0.016$ and 0.020 for 904 and 813 F_o respectively. The minerals crystallize in space group $F\bar{4}3m$ with $a = 13.8654$ (1) and 13.8796 (3) Å respectively. The cell constants vary with the degree to which Si is replaced by Al in the Si(1) site. A Keggin-molecule-type group $\text{Al}^{(4)}\text{Al}^{(6)}\text{O}_{16}(\text{OH})_{24}$ is a dimensionally constant unit of the $\text{Al}_{13}\text{O}_{16}(\text{OH})_{18}$ framework in zunyite. There is no indication for a statistical disorder of O(2) forming a straight bridging Si–O–Si bond. The bond lengths in the pentamer Si_5O_{16} are: $4 \times \text{Si}(1)\text{--O}(2)$ 1.623 (1), $4 \times \text{Si}(2)\text{--O}(2)$ 1.636 (1) and $12 \times \text{Si}(2)\text{--O}(5)$ 1.633 (1) Å. The bond lengths involving O(2) are longer than estimated from the Si–O versus $-\sec(\text{Si--O--Si})$ relationship. Regression analyses with individual bond lengths $(\text{Si--O})_{\text{ind}}$ as the dependent variable and $-\sec(\text{Si--O--Si})$ as the independent variable for data from zunyite, and for other charge-balanced O atoms from silicates and silica polymorphs result in a negative slope statistically identical to zero. Other regressions on small samples result in slopes ranging from negative (low quartz) to 0.07 Å (coesite). However, large samples from silicates and silica polymorphs subjected to multiple linear regression in which all known significant empirical influences are properly taken into consideration show a dependence, in order of importance, on (1) bond-strength deviation, (2) coordination number and (3) negative secant of the angle Si–O–Si. For such samples the value of the slope of $(\text{Si--O})_{\text{mean}}$ over $-\sec(\text{Si--O--Si})$ is 0.032 Å.

Introduction

Pauling (1933) determined the crystal structure of zunyite, $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$, and established the existence of Si_5O_{16} groups there. In this pentameric arrangement four silicate tetrahedra are connected *via*

bridging O atoms to a central silicate group. As an isolated group the Si_5O_{16} pentamer is unique, both in its symmetry ($\bar{4}3m$) and in its chemical composition. Topologically similar to it is the $\text{AlSi}_4(\text{O},\text{OH})_{16}$ pentamer in harkerite, $\text{Ca}_{24}\text{Mg}_8[\text{AlSi}_4(\text{O},\text{OH})_{16}]_2(\text{BO}_3)_8(\text{CO}_3)_8(\text{H}_2\text{O},\text{Cl})$ (Giuseppetti, Mazzi & Tadini, 1977). The symmetry of that group is $3m$. The three bridging O atoms in harkerite, which are not located on the threefold axis, have nevertheless bridging bonds close to straight (176°). Because there is a positional disorder in harkerite involving the pentamer and four BO_3 groups, the bond lengths are not sufficiently precise to be compared directly with those of zunyite. Likewise of $3m$ symmetry is an analogous $\text{PCr}_4\text{O}_{16}$ group (with P in the central position) in $(\text{NH}_4)_3\text{PCr}_4\text{O}_{16}$ recently described by Averbuch-Pouchot & Durif (1980). The structure of zunyite was refined by Kamb (1960) who proposed that the actual chemical formula should be $\text{Al}_{13}\text{Si}_5\text{O}_{20}\text{F}_2(\text{OH},\text{F})_{16}\text{Cl}$, because the presence of at least two F atoms per formula unit would allow the construction of a likely hydrogen-bonding scheme. Bartl (1970) confirmed a part of Kamb's hydrogen-bonding assignment by a neutron diffraction study of zunyite [$\text{O}(3)\text{--H}(2)\cdots\text{Cl}$ and $\text{O}(4)\text{--H}(1)\cdots\text{O}(4)$, with H(1) statistically occupying one half of a 48-fold set of equivalent positions]. Zagalskaya & Belov (1964) argued that some of the Al and Si atoms in zunyite were wrongly assigned and that the Si_5O_{16} tetrahedral group actually should have an $\text{AlSi}_4\text{O}_{16}$ composition with the central tetrahedron occupied by an Al atom. This proposal was rejected by Louisnathan & Gibbs (1972) on the basis of a new refinement of zunyite, which yielded a distance of 1.628 (10) Å for $\text{Si}(1)\text{--O}(2)$. This value is clearly not compatible with occupation by aluminium (the distance would have to be in the 1.73 to 1.80 Å range). However, it is also not quite compatible with an occupation by Si alone. In plots of 314 observed mean Si–O distances against predicted Si–O distances (Baur, 1978) the value of $\text{Si}(1)\text{--O}(2)$ in zunyite is an outlier [the estimated expected value of $\text{Si}(1)\text{--O}(2)$ is about 1.60 Å]. Is the $\text{Si}(1)$ atomic site partly occupied by aluminum in a statistical fashion? Liebau (1961) suspected that the O(2) site in zunyite is disordered around the threefold

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axis in such a way as to allow an angle Si(1)–O(2)–Si(2) of less than 180°. If this were the case the actual distance Si(1)–O(2) would be even larger. The work by Louisnathan & Gibbs (1972) does not shed any light on this latter problem since isotropic temperature factors were used in the refinement. In order to obtain experimental answers to these questions, another refinement of two different zunyite crystals was undertaken.

Experimental

Four samples of zunyite were used for the investigation: (1) two from the type locality, the Zuni Mine, Silverton, Colorado (samples M9003 and 14163 from the Field Museum of Natural History, Chicago); (2) one from Ait Azegrou, New Mexico (M19079 from the Field Museum); (3) one from Quartzsite, Yuma County, Arizona (collection S. Guggenheim).

In all cases the crystals occur as colorless to grey tetrahedra with edge lengths up to 3 mm. The grey hue stems from inclusions which are less frequent in the Quartzsite sample than in the other samples. There are three kinds of inclusions: TiO₂ (most likely rutile), FeS₂ (probably pyrite) and a third which was not identified (it contains Al, Cl, K and Na). The samples were analyzed by electron microprobe analysis using apatite, magnetite, enstatite, fluorite and albite of known composition as standards. Eight to ten analyses were performed on 4 to 5 grains each (Table 1). No evidence for the presence of Mg, P, K, Ca or Ti was found. The variations in the Si to Al ratio in our samples are similar to those reported by Pauling (1933), Konta & Mráz (1961) and Turco (1962). The cell constants of the samples (Table 1) were determined from powder data (Debye–Scherrer camera with diameter 114.6 mm, asymmetric film mounting) by least-squares refinement (Appleman & Evans, 1973). There appears to be a strong correlation ($r^2 = 0.94$) between the cell constants and the Si content of the four samples (Fig. 1). The data reported by Louisnathan & Gibbs (1972), namely a cell constant a of 13.860 (3) Å and an Si to Al ratio of 5.01 to 12.98, fit the trend found here. However, consideration of the probable errors in the chemical analyses and the error in the cell constant given by Louisnathan & Gibbs indicates that the cell constants and the Si content of their Zuni sample and our Quartzsite sample are statistically identical. On the other hand their sample and our sample M9003 from the Zuni Mine are significantly different. It will be assumed that our Quartzsite sample is a zunyite with an Si₅O₁₆ group without any replacement of Si by Al. The chemical analysis certainly agrees with this assumption within the limits of its precision. Furthermore the Si(1)–Si(2) distances (see below) in our Quartzsite specimen [3.2589 (5) Å] and Louisnathan's

& Gibbs's (1972) Zuni Mine specimen [3.258 (2) Å] are identical within one half an estimated standard deviation of their determination. This is significant since their chemical analysis actually shows an Si proportion larger than 5. The Si–Si distance is used for comparison because its precision is higher than the precision of the Si–O bond length.

The Quartzsite sample and one of the Zuni samples (M9003) were studied by single-crystal methods (Table 2). The crystals were ground into spheres and the cell constants were determined at room temperature by the setting of 17 reflexions on a computer-controlled four-circle X-ray diffractometer. The diffractometer control program was devised by Lenhart (1975). The resulting values for the cell constant were within one or two standard deviations of the values obtained by the

Table 1. Cell constants (Å) based on powder work [2θ range 11 to 162°; $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å; $\lambda(\text{Cu } K\alpha_2) = 1.54433$ Å] and chemical analyses by electron microprobe calculated on the basis of 18(Si, Al) for four zunyite samples

Standard deviations are given here and in the following tables in parentheses. They correspond to the least significant digits of the values.

	Quartzsite Arizona	Zuni Mine Colorado (No. 14163)	Zuni Mine Colorado (No. M9003)	Ait Azegrou New Mexico (No. M19079)
a	13.8654 (5)	13.8784 (6)	13.8796 (3)	13.8882 (3)
Number of reflexions used	49	54	42	41
Si	4.95 (6)	4.69 (15)	4.68 (7)	4.61 (17)
Al	13.05 (8)	13.31 (20)	13.32 (9)	13.39 (16)
Fe	0.005 (3)	—	—	—
Na	0.04 (1)	0.03 (3)	0.05 (3)	0.16 (7)
Cl	0.92 (2)	0.86 (7)	0.90 (2)	0.94 (3)
F	4.1 (1)	4.1 (2)	3.6 (3)	4.3 (3)

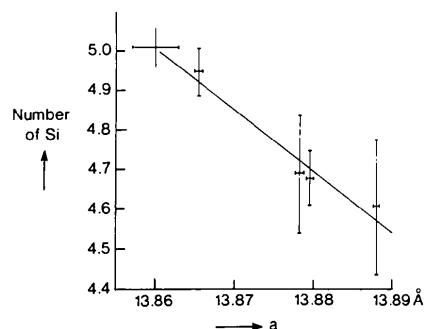


Fig. 1. Plot of Si-atom proportion versus cell constant, a , for the four zunyite specimens studied here and the sample of Louisnathan & Gibbs (1972). The bars indicate the estimated standard deviations of the values. The error in the chemical analysis of Louisnathan & Gibbs is not known. The line is the regression line through our four points. Considering the probable errors the good fit is likely to be fortuitous.

powder method (Table 1). Three-dimensional X-ray diffraction intensities were collected in two octants (hkl and $\bar{h}\bar{k}\bar{l}$) using graphite-crystal-monochromatized Mo $K\alpha$ radiation. Lorentz-polarization and absorption corrections were applied to the intensity data. For a list of most of the computer programs used in the course of this work and for details of data-measuring procedures, see Baur & Khan (1970). Reflexions were only observed with h , k and l either all odd or all even. This is consistent with space group $F\bar{4}3m$ as proposed by Pauling (1933) and confirmed by later workers.

The atomic scattering curves from *International Tables for X-ray Crystallography* (1974) were employed for the structure factor calculations. The anomalous-scattering corrections were not applied in the final calculations because earlier tests on our data sets showed that refinements with and without them yielded essentially identical results. The scattering curve for atom Si(1) from the Zuni Mine sample was taken as $(3 \times \text{Si} + \text{Al})/4$. This was based on the chemical analysis, the Si(1)–O(2) distance and the difference synthesis (the different estimates ranged from 20% to 32% Al content). The scattering curve for O(h4) was assumed to be $(2 \times \text{O} + \text{F})/3$, thus reflecting the chemical analyses.

A density of $0.3 \text{ e } \text{\AA}^{-3}$ was found in our difference Fourier maps at the site labelled H(1) by Bartl (1970), and a density of $0.5 \text{ e } \text{\AA}^{-3}$ was present at the H(2) site but, except for the positional parameter of H(2) of the crystal from the Quartzsite sample, they did not remain stable in the least-squares refinement. An additional H-atom site (density $0.3 \text{ e } \text{\AA}^{-3}$) in the vicinity of atom O(h4) was found and labelled H(1b) by us. Its

Table 2. *Crystal data, details of data collection and R values for the zunyite crystals*

	Quartzsite Arizona	Zuni Mine Colorado (No. M9003)
Chemical formula*	Si _{4.95} Al _{13.05} O _{19.95} (OH) _{13.96} F _{4.09} Cl	Si _{4.68} Al _{13.32} O _{19.68} (OH) _{14.71} F _{3.61} Cl
Space group	$F\bar{4}3m$	$F\bar{4}3m$
V (\AA^3)	2665.6	2673.8
Z	4	4
D_x (Mg m^{-3})	2.894	2.883
FW	1160.94	1159.95
λ (Mo $K\alpha$) (\AA)	0.71069	0.71069
μ (Mo $K\alpha$) (mm^{-1})	0.9590	0.9516
R , radius (mm)	0.138 (4)	0.115 (5)
μR	0.13	0.11
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	1.186	1.190
Time for background count (s)	20	10
Scan range ($^\circ$)	± 0.7	± 0.55 to ± 0.85
Scan rate ($^\circ \text{ min}^{-1}$)	1.0	1.0
Number of I_{hkl} measured	9239	8483
Number of unique I_{hkl}	995	1008
Number of unobserved reflexions	91	195
$[I < 3\sigma(I)]$		
$R_1 = \sum F_o - F_c / \sum F_o $	0.016	0.020
$R_2 = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$	0.030	0.034

* Calculated on the basis of 18(Si, Al) and 39(O, OH, F, Cl).

Table 3. *Fractional coordinates ($\times 10^5$ for Si, Al, and O, except for the fractions; $\times 10^3$ for H) and equivalent isotropic thermal parameters in \AA^2 ($\times 10^2$) for two zunyite specimens*

Equi-point	Point symmetry	x	y	z	B_{eq}
(1) Zunyite from Quartzsite, Arizona					
Si(1)	4(c)	$\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	31 (1)
Si(2)	16(e)	$3m$	11430 (2)	11430 (2)	26 (1)
Al(1)	4(d)	$\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	25 (1)
Al(2)	48(h)	m	8556 (2)	8556 (2)	76670 (3)
O(1)	16(e)	$3m$	82478 (6)	82478 (6)	82478 (6)
O(2)	16(e)	$3m$	18243 (7)	18243 (7)	18243 (7)
O(h3)	24(f)	mm	27949 (8)	0	0
O(h4)*	48(h)	m	17870 (4)	17870 (4)	54601 (6)
O(5)	48(h)	m	13834 (4)	13834 (4)	152 (6)
Cl	4(b)	$\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
H(1a)†‡§	48(h)	m	228	228	530
H(1b)†§	48(h)	m	190	190	480
H(2)‡§	24(f)	mm	336 (3)	0	0
(2) Zunyite from Zuni Mine, Colorado					
Si, Al(1)‡	4(c)	$\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	37 (2)
Si(2)	16(e)	$3m$	11399 (3)	11399 (3)	11399 (3)
Al(1)	4(d)	$\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	30 (2)
Al(2)	48(h)	m	8565 (2)	8565 (2)	76675 (3)
O(1)	16(e)	$3m$	82472 (8)	82472 (8)	82472 (8)
O(2)	16(e)	$3m$	18128 (10)	18128 (10)	18128 (10)
O(h3)	24(f)	mm	27927 (11)	0	0
O(h4)*	48(h)	m	17866 (6)	17866 (6)	54558 (8)
O(5)	48(h)	m	13802 (5)	13802 (5)	119 (9)
Cl	4(b)	$\bar{4}3m$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
H(1a)†‡§	48(h)	m	228	228	530
H(1b)†§	48(h)	m	190	190	480
H(2)‡§	24(f)	mm	352	0	0

* The scattering factor for this site was taken to be $(2 \times \text{O} + \text{F})/3$.

† The occupancy factor for this site was assumed to be $\frac{1}{4}$.

‡ The positional parameters for this site were taken from Bartl (1970) and kept constant in the refinement.

§ The thermal parameter for this site was taken from Bartl (1970) and kept constant in the refinement.

|| The positional parameters for this site were taken from a difference synthesis and kept constant in the refinement.

‡ The scattering factor for this site was taken to be $(3 \times \text{Si} + \text{Al})/4$.

positional parameters likewise could not be refined in the least-squares procedure. The final positional coordinates are given in Table 3.*

Description and discussion of the structures

Geometric units

The crystal structure of zunyite was solved (Pauling, 1933) by searching for a pattern in which trimeric groups of three Al coordination octahedra with one common corner and three shared edges, $\text{Al}_3(\text{O}, \text{OH})_{13}$, could be combined into a framework which had the correct symmetry and unit-cell size. The structure can be described clearly by following Chieh's (1980) approach. While Chieh prefers to use polyhedra

* Lists of observed and calculated structure factors, anisotropic thermal parameters and orientation angles of the thermal ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36317 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Geometric units of zunyite

Composition	Description
Al(2) ₃ O(5) ₃ O(h3) ₃ O(1)O(h4) ₆	Trimeric unit of three octahedra sharing corner O(1) and edges O(1)—O(5).
Al(2) ₁₂ O(5) ₁₂ O(h3) ₆ O(1) ₄ O(h4) ₂₄	Cluster around <i>A</i> formed by four trimeric units sharing corners O(h3).
Al(2) ₁₂ O(5) ₁₂ O(h3) ₆ O(1) ₄ O(h4) ₁₂	Octahedral framework formed by clusters <i>A</i> sharing corners O(h4).
Si(1)O(2) ₂ Si(2) ₂ O(5) ₁₂	Pentameric unit <i>C</i> of five SiO ₄ tetrahedra surrounded tetrahedrally by <i>A</i> clusters, with which it shares corners O(5).
ClH(2) ₆ O(h3) ₆	Octahedral <i>B</i> unit of hydrogen-bonded Cl surrounded octahedrally by six <i>A</i> units with which it shares corners O(h3).
Al(1)O(1) ₄	Tetrahedral <i>D</i> unit AlO ₄ surrounded tetrahedrally by four <i>A</i> units with which it shares corners O(1).
Al(1)O(1) ₄ O(h4) ₁₂ Al(2) ₁₂ O(5) ₁₂ O(h3) ₁₂	Cuboctahedral cluster around <i>D</i> including central tetrahedron and four trimeric units sharing corners O(h4) with each other.
Al(1)O(1) ₄ O(5) ₁₂ Al(2) ₁₂ O(h4) ₁₂ O(h3) ₆	Framework formed by the cuboctahedral clusters sharing corners O(h3).

outlined by the atoms closest to the fourfold sets of equivalent sites of symmetry $\bar{4}3m$, we shall emphasize the chemically relevant geometric units. In space group $F\bar{4}3m$ there are four such sets *A*, *C*, *B*, *D*, named after the Wyckoff notation and listed in ascending order along the body diagonal of the cube: *A* in 000; *C* in $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; *B* in $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and *D* in $\frac{3}{4}\frac{3}{4}\frac{3}{4}$. Set *A* itself is not occupied in zunyite. It is surrounded in tetrahedral fashion by four Al₃O₄(OH)₉ groups which all share two of their OH corners with each of the neighboring trimers to form the Al₁₂O₁₆(OH)₃₀ clusters centered on *A*. These clusters in turn share OH vertices to form an octahedral framework of composition Al₁₂O₁₆(OH)₁₈ (Table 4). Since set *A* by itself is arranged in the face-centered cubic pattern, each Al₁₂O₁₆(OH)₁₈ cluster is connected to twelve such neighboring clusters and it shares two corners with each of them. The pentameric Si₅O₁₆ unit is centered on set *C*. It shares O atoms with the octahedral framework. The relative arrangement of *A* and *C* clusters is identical to the array of Zn and S in the zinc-blende type. This zinc-blende-type framework has the composition Si₅Al₁₂O₂₀(OH)₁₈ and is further interconnected by tetrahedral AlO₄ units in set *D*, which likewise share O atoms with the octahedral framework. The resulting complex octahedral-tetrahedral framework Si₅⁴⁺Al₁₂⁴⁺Al₁₂⁶⁺O₂₀(OH)₁₈ is charge balanced by Cl⁻ ions located in set *B*, each of which receives six hydrogen bonds from hydroxyl groups O(h3)H(2) belonging to the octahedral framework. The overall empirical chemical formula is therefore Si₅Al₁₃O₂₀(OH)₁₈Cl, as established by Pauling (1933) (see Tables 4 and 5).

Hydrogen bonding

The hydrogen bonds from O(h4) are not as clearly defined as the O(h3)—H(2)···Cl bonds. On the basis of a neutron diffraction study, Bartl (1970) placed one

Table 5. Interatomic distances (Å) and angles (°) for two zunyites

The numbers after the bond designation refer to multiplicities per polyhedron.

	Quartzsite	Zuni
(a) Si(1) tetrahedron		
Si(1)—O(2) (4×)	1.623 (1)	1.652 (1)
O(2)—O(2) (6×)	2.650 (1)	2.698 (2)
O(2)—Si(1)—O(2) (6×)	109.47	109.47
(b) Si(2) tetrahedron		
Si(2)—O(2) (1×)	1.636 (1)	1.618 (1)
Si(2)—O(5) (3×)	1.633 (1)	1.635 (1)
Si(2)—O, mean	1.634	1.631
O(2)—O(5) (3×)	2.653 (1)	2.640 (2)
O(5)—O(5) (3×)	2.683 (1)	2.686 (1)
O(2)—Si(2)—O(5) (3×)	108.49 (4)	108.50 (6)
O(5)—Si(2)—O(5) (3×)	110.44 (4)	110.43 (5)
Si(1)—Si(2)	3.259 (1)	3.270 (1)
Si(1)—O(2)—Si(2)	180.0 (1)	180.0 (2)
Si(2)—Al(2)	3.250 (1)	3.252 (1)
Si(2)—O(5)—Al(2)	131.35 (4)	131.34 (5)
(c) Al(1) tetrahedron		
Al(1)—O(1) (4×)	1.796 (1)	1.796 (1)
O(1)—O(1) (6×)	2.933 (1)	2.933 (2)
O(1)—Al(1)—O(1) (6×)	109.47	109.47
Al(1)—Al(2)	3.233 (1)	3.234 (1)
Al(1)—O(1)—Al(2)	120.13 (5)	120.16 (6)
(d) Al(2) octahedron		
Al(2)—O(h3)	1.796 (3)	1.798 (1)
Al(2)—O(h4) (2×)	1.859 (1)	1.863 (1)
Al(2)—O(5) (2×)	1.931 (1)	1.931 (1)
Al(2)—O(1)	1.935 (1)	1.935 (1)
Al(2)—O, mean	1.885	1.887
O—O, edges in Al(2) octahedron	2.555 (1)	2.556 (2)
O—Al(2)—O	-2.742 (1)	-2.741 (2)
	82.78 (3)	82.80 (4)
	-94.62 (3)	-94.55 (4)
Al(2)—Al(2)	2.897 (1)	2.897 (1)
Al(2)—O(1)—Al(2)	97.02 (4)	96.97 (5)
Al(2)—O(5)—Al(2)	97.23 (4)	97.22 (6)
Al(2)—Al(2)	3.355 (1)	3.362 (1)
Al(2)—O(h3)—Al(2)	138.21 (7)	138.39 (9)
Al(2)—Al(2)	3.552 (1)	3.555 (1)
Al(2)—O(h4)—Al(2)	145.54 (5)	145.13 (7)
(e) Cl environment		
Cl—H(2) (6×)	2.27 (4)	2.05
Cl—O(h3) (6×)	3.057 (1)	3.064 (2)
O(h3)—H(2) (6×)	0.78 (4)	1.01
(f) O(h4) environment		
O(h4)···O(h4)	2.796 (1)	2.801 (1)
O(h4)—H(1a)	0.99	0.99
O(h4)···H(1a)	1.84	1.85
O(h4)—H(1)···O(h4)	160.2	160.7
H(1a)—H(1a)	0.86	0.86
H(1a)—H(1b)	1.02	1.02
H(1a)—H(1b)	1.75	1.75
O(h4)—H(1b)	0.94	0.94
O(h4)···H(1b)	2.73	2.73
O(h4)—H(1b)···O(h4)	84.0	84.3
H(1b)—H(1b)	2.35	2.36

half of a hydrogen atom H(1) at a distance of 0.99 Å from O(*h4*). The arrangement is $\text{O}(h4) - \frac{1}{2}\text{H}(1) \cdots \frac{1}{2}\text{H}(1) - \text{O}(h4)$, with a distance H(1)—H(1) of 0.86 Å, which means that locally only one of the two H(1) sites can be occupied (they are related by a mirror plane). Obviously, Bartl's study has identified only one half of the H atoms which potentially can be associated with O(*h4*). If it is taken literally the chemical formula of zunyite would be $\text{Si}_5\text{Al}_{13}\text{O}_{26}(\text{OH})_{12}\text{Cl}$, which is not charge-balanced. Of course one could assume the chemical composition to be $\text{Si}_5\text{Al}_{13}\text{O}_{20}(\text{OH})_{12}\text{F}_6\text{Cl}$, but this is clearly at variance with all chemical analyses of zunyite including those reported here, except for those of a variety of zunyite called dillnite which has seven F for five Si (Konta & Mráz, 1961). A search of the difference maps in the vicinity of O(*h4*) revealed two peaks which are possible H-atom positions: H(1*a*), which corresponds to the site labelled H(1) by Bartl (1970), and H(1*b*), with approximately the same electron density as H(1*a*) and at a distance of 0.94 Å from O(*h4*). The two angles Al(2)—O(*h4*)—H(1*b*) are 107°, the angle Al(2)—O(*h4*)—Al(2) measures 146°. The arrangement is coplanar, since the sum of the angles is 360°. This means that H(1*b*) is in the position of least electrostatic energy (Baur, 1965), thus making it a very likely site for a H atom. Kamb (1960) had proposed that the H atoms attached to O(*h4*) and not engaged in the O(*h4*)...O(*h4*) hydrogen bond are 'sticking out towards the chlorine atom'. This is unlikely, because H atoms located on the line O(*h4*)—Cl would approach each other closely at the threefold axis (two neighbors at 1.87 Å each) as well as having close contacts to H(2) (two distances of 1.86 Å each). In addition, the distance to Al(2) would be only 2.13 Å and the angle Al(2)—O(*h4*)—H would measure a mere 91.5°. Electrostatically this is a poor choice. Thus, the H(1*b*) position is not only supported by the difference electron density map, but also by steric arguments. It seems to be the only location within 1.0 Å of O(*h4*) which is not too close to other electropositive surrounding atoms.

According to the chemical analyses of our samples about four F are present per five Si. Assuming that all the fluorine is occupying the O(*h4*) site each of the electron densities at H(1*a*) and H(1*b*) must correspond to only one third of an H atom. Therefore it is not surprising that these two positions could not be refined by least squares. For H(1*a*) we are reporting the position due to Bartl (1970), for H(1*b*) we are giving in Table 3 the parameters read from the difference synthesis. The interpretation of the results is that a hydrogen bond is formed between two O(*h4*) sites *via* H(1*a*) when the site corresponding to the hydrogen-bond acceptor is occupied by an F atom and the other by an OH group. If the occupants of both neighboring O(*h4*) sites are OH groups, both H atoms must be located in H(1*b*) because only then is their distance

(2.35 Å) longer than twice the van der Waals radius of hydrogen (1.0 Å, Baur, 1972). If one H atom were in H(1*a*) forming a hydrogen bond to an OH group whose H atom were located in H(1*b*) the distance H(1*a*)—H(1*b*) would be only 1.75 Å (see Table 5) and therefore this local arrangement is impossible. The relatively short distance O(*h4*)...O(*h4*) of 2.80 Å is not so much due to the hydrogen bond between the two atoms, as to the fact that O(*h4*) is part of the trimeric unit $\text{Al}_3\text{O}_4(\text{OH})_6$. O(1) is located on a threefold axis and has six equidistant O(*h4*) neighbors arranged in an approximately hexagonal arrangement. The O(*h4*)—O(*h4*) distances on the perimeter of this hexagon (actual symmetry is $3m$) are 2.60 and 2.80 Å. The 2.60 Å distance is the shortest unshared edge in the coordination octahedron around Al(2). If the hydrogen bond really contributed to a shortening of the O(*h4*)...O(*h4*) hydrogen-bond distance then the O(*h4*)—O(*h4*) edge should be longer than observed.

This interpretation of the hydrogen bonding around O(*h4*) does not require a minimum F substitution as proposed by Kamb (1960), nor does it place any limit on the amount of fluorine substituting for OH in the O(*h4*) site. The composition of zunyite could vary from $\text{Si}_5\text{Al}_{13}\text{O}_{20}(\text{OH})_6\text{F}_{12}\text{Cl}$ to $\text{Si}_5\text{Al}_{13}\text{O}_{20}(\text{OH})_{18}\text{Cl}$. The dillnite from Banska Bela (Konta & Mráz, 1961) has the highest known fluorine content of the zunyite series: $\text{Si}_5\text{Al}_{13}\text{O}_{20}(\text{OH})_{11}\text{F}_7\text{Cl}$, which is still far less than the 12 F atoms necessary to replace all OH in the O(*h4*) site. The fact that Bartl (1970) did not find the H(1*b*) position in his neutron diffraction study might mean that in *his* sample about 50% of the O(*h4*) site was occupied by F atoms, so that all H atoms were engaged in O(*h4*)—H...F bonds. Inasmuch as Bartl does not report a chemical analysis of his material, this is only a hypothesis.

Bond lengths

The estimated standard deviations of the bond lengths determined in the present work are one order of magnitude smaller than in the most precise of the previous refinements. Therefore, the bond-length differences found here can be considered to be more significant than in the earlier work. The single biggest difference in individual bond lengths between the two specimens is in the distances Si(1)—O(2) which are larger by 0.029 (2) Å in the more Al-rich Zuni Mine zunyite. Since we assume that in the Quartzsite sample Si(1) is occupied only by Si then (taking 1.746 Å as a typical Al^{IV}—O distance, where all O atoms are shared with other Al or Si tetrahedra) the Zuni Mine sample with its Si(1)—O(2) distance of 1.652 Å corresponds to a 24% occupation of Si(1) by aluminum. This estimate assumes linearity between Al content and bond distance and agrees approximately with the chemical analysis of our sample.

The second largest difference is in the Si(2)—O(2) distance which is 0.018 (2) Å shorter in the Al-rich Zuni zunyite when compared with the Quartzsite specimen. This is apparently due to the fact that O(2) is underbonded in the Al-rich specimen because statistically in one out of four locations the Si(1) site is occupied by Al instead of Si, thus contributing only 0.75 valence units (v.u.) instead of 1.0 v.u. to O(2). The predicted values for the given amount of underbonding are 1.626 Å for Si(2)—O(2) and 1.633 Å for Si(2)—O(5) (Baur, 1981). This is less than the observed shortening (Table 5), but the deviation is in the right direction. Interestingly, in the Quartzsite specimen Si(2)—O(2) is longer by 0.003 Å than Si(2)—O(5), thus reinforcing the assumption that the Si(1) site here is occupied only by Si.

The trimeric $\text{Al}_3\text{O}_4(\text{OH})_9$ group and the AlO_4 tetrahedron are virtually identical in both samples. The $\text{Cl}(\text{OH})_6$ octahedron and the cluster around A, $\text{Al}_{12}\text{O}_{16}(\text{OH})_{30}$, are slightly enlarged (0.007 Å) in the Zuni sample relative to the Quartzsite specimen. The difference in the size of the cluster can be read from the larger distance Al(2)—Al(2) [where the Al atoms share the corner O(h3)]: 3.362 vs 3.355 Å.

Si, Al content and cell constants

Fig. 1 shows the strong negative correlation between Si content and cell constants of the zunyites. What is the geometry on which this correlation is based? The distance Si(1)—Si(2) in the Si-rich Quartzsite sample is 3.259 Å; in the Al-rich Zuni sample it is 3.270 Å. If this larger size of the pentameric (Si, Al) Si_4O_{16} group were fully reflected in the cell constant, it would be 0.0254 Å [= 4(3.270 - 3.259)/ $\sqrt{3}$] larger for the Zuni sample than for the Quartzsite sample. Actually the difference is only 0.0142 Å (or 56% of the potential difference). Apparently almost one half of the size difference of the pentamer is absorbed by adjustments in the structure. There is an indication for a deformation due to compression in the (Si, Al) Si_4O_{16} group of the Zuni specimen. The O(2)—O(5) edge of the Si(2) O_4 tetrahedron is much shorter, while the O(5)—O(5) edge is longer than in the Si_3O_{16} group of the Quartzsite specimen (Table 5). Through this distortion the pentamer in the Zuni sample accommodates some of the expansion due to its larger Si(1) site. The remaining expansion of the pentamer is absorbed by shifts in the $\text{Al}_{13}\text{O}_{16}(\text{OH})_{18}$ framework.

A zunyite with complete replacement of one Si atom by aluminum, that is with a proportion $\text{Si}_4\text{Al}_{14}$, should have a cell constant $a = 13.93$ Å (by extrapolation from Fig. 1). This is exactly the value given by Turco (1962) for zunyite from Beni-Embarek. However, the chemical analysis of this material shows 4.69 Si. It is likely that either of these values reported by Turco is in error. A cell constant of 14.034 (3) Å has been

reported for zunyite from Postmasburg (Vermaas, 1952). This zunyite is so Cl-rich that chlorine must replace some of the hydroxyl groups in site O(h4). The large cell constant is compatible with such substitution and should not be connected directly with the Al content.

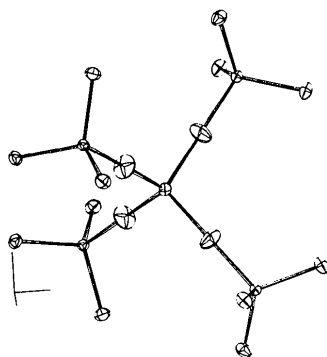
The part of the octahedral framework which is *least* affected by the different size of the pentamer is the cluster of four trimeric units around set *D* centered on the AlO_4 tetrahedron (Table 4). Within this $\text{Al}^{41}\text{Al}^{61}\text{O}_{16}(\text{OH})_{24}$ cluster the various Al—Al distances do not differ by more than 0.003 Å in the two zunyites. It has the same arrangement as has Keggin's (1934) molecule, $\text{PW}_{12}\text{O}_{40}^{3-}$, with Al^{41} taking the position of P, and the remaining Al atoms the positions of W (Brown, Noe-Spirlet, Busing & Levy, 1977). This analogy has been pointed out by Zagalskaya & Belov (1964), except that these authors wrongly assumed Si to be at the center of this cluster. Apparently, this is a stable configuration because it occurs also in numerous heteropolyacids containing B, Al, Si, P, V, Co, Mo or W [and other elements as well; see Evans (1971), Wells (1975) and Björnberg & Hedman (1980)]. Furthermore, in zunyite, it is a geometrically constant unit, which is not much affected by size changes in the rest of the structure. Conceivably, the cluster $\text{Al}_{13}\text{O}_{16}(\text{OH})_{24}$ is present in the solution out of which zunyite is crystallizing. However, it must be emphasized that this cluster is geometrically not identical to the group $\text{Al}_3\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}$ crystallizing out of basic solutions and described by Johansson (1960, 1962) in $\text{Na}[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SeO}_4)_4 \cdot X\text{H}_2\text{O}$ and a similar basic aluminum sulfate. While these groups have the same symmetry, the same number of O atoms, both have a central Al coordination tetrahedron and are composed of four $\text{Al}_3(\text{O}, \text{OH}, \text{H}_2\text{O})_{13}$ groups each, they nevertheless are joined in a geometrically different pattern: the trimeric octahedral groups in Johansson's molecules share edges with each other, not corners as in Keggin's molecule.

Straight Si—O—Si bonds

Recently data were collected from the literature to show that straight Si—O—Si bonds do exist in silicates and in SiO_2 polymorphs (Baur, 1980). They occur not only in cases where the O atoms are located on symmetry elements (as in zunyite) but also when the straight configuration is not required by symmetry. The examples used in that literature survey were, with the exception of coesite (*C2/c*) (Gibbs, Prewitt & Baldwin, 1977), from structures which were less precisely determined than the present zunyite refinement and the recently published refinement of petalite, $\text{LiAlSi}_4\text{O}_{10}$ (Effenberger, 1980). Inasmuch as Liebau (1961) cited coesite, petalite and zunyite, among others, as possible

Table 6. *Root-mean-square thermal displacements ($\times 10^3$) along principal axes (\AA) for two zunyites*

Axis	1	2	3
(a) Zunyite from Quartzsite, Arizona			
Si(1)	63 (1)	63 (1)	63 (1)
Si(2)	56 (1)	56 (1)	61 (1)
Al(1)	56 (1)	56 (1)	56 (1)
Al(2)	61 (1)	68 (1)	71 (1)
O(1)	59 (1)	70 (1)	70 (1)
O(2)	66 (1)	121 (1)	121 (1)
O(<i>h</i> 3)	69 (2)	73 (2)	123 (2)
O(<i>h</i> 4)	67 (1)	94 (1)	104 (1)
O(5)	61 (1)	70 (1)	91 (1)
Cl	97 (1)	97 (1)	97 (1)
(b) Zunyite from Zuni Mine, Colorado			
Si, Al(1)	68 (1)	68 (1)	68 (1)
Si(2)	60 (1)	60 (1)	66 (1)
Al(1)	61 (1)	61 (1)	61 (1)
Al(2)	64 (1)	71 (1)	75 (1)
O(1)	62 (2)	72 (2)	72 (2)
O(2)	84 (1)	130 (1)	130 (1)
O(<i>h</i> 3)	71 (3)	74 (3)	122 (2)
O(<i>h</i> 4)	70 (2)	96 (2)	108 (2)
O(5)	64 (2)	73 (2)	96 (2)
Cl	106 (1)	106 (1)	106 (1)

Fig. 2. Thermal ellipsoids scaled to 50% probability for the Si₅O₁₆ group in Quartzsite zunyite as drawn by *ORTEP* (Johnson, 1976). The origin of the unit cell is indicated in the lower left corner.

examples of structures where a straight Si—O—Si angle is only apparent, because of fractional statistical occupations of multiple sites off the symmetry element, it is necessary to look closely at the thermal parameters of the O atoms in question. The root-mean-square (r.m.s.) displacement of the O(2) of the zunyite from Quartzsite along its principal axes (Table 6) is the largest for any of the O atoms in zunyite participating in tetrahedral coordination; however, it is smaller than observed for the O atoms in petalite, including those which are not involved in straight bonds. For comparison, the principal r.m.s. displacements of the O atom ($\angle\text{Si—O—Si} = 143.5^\circ$) in low quartz (Burnham, 1965) are 0.063, 0.098 and 0.122 \AA , which means that the extreme values are larger and smaller than for O(2)

in Quartzsite zunyite. The ratio of largest to smallest r.m.s. displacement for O(2) in zunyite is 1.8, the mean for all O atoms in petalite and quartz is 1.9. This demonstrates that the thermal ellipsoids of O atoms involved in straight Si—O—Si bonds are similar to those in bent bonds. Fig. 2 shows a representation of the thermal ellipsoids of the Si₅O₁₆ pentamer in zunyite. Neither the size nor the shape of the thermal ellipsoids of O(2) makes it necessary to assume that it is statistically disordered around the threefold axis. The results of the refinements of zunyite, coesite and petalite demonstrate that straight Si—O—Si bonds do occur.

Mean Si—O distances

The regression equation (Baur, 1978)

$$(\text{Si—O})_{\text{mean}} = 1.560 (3) + 0.032 (2) \text{NSEC}_{\text{mean}} + 0.0031 (8) \text{CN}_{\text{mean}} \quad (1)$$

can be applied postdictively to see how a particular observed mean Si—O bond length fits observations made in other crystal structures. In equation (1) $\text{NSEC}_{\text{mean}}$ is the mean negative secant of the angle Si—O—Si of all O atoms in the tetrahedron, where O atoms which do not form a bridging bond to another tetrahedral cation are arbitrarily assigned an NSEC value of 2.0, while CN_{mean} is the mean coordination number of the O atoms in the SiO₄ tetrahedron. The estimated values from equation (1) for $[\text{Si}(1)\text{—O}]_{\text{mean}}$ and $[\text{Si}(2)\text{—O}]_{\text{mean}}$ are 1.598 (7) and 1.625 (7) \AA , while the observed values are 1.623 and 1.634 \AA , respectively (for the Quartzsite specimen). The agreement is good for Si(2), since the estimated value is within 1.3 standard deviations of the regression line; however, it is poor for Si(1), because the deviation amounts to 3.6 standard deviations of the estimated value. The observed mean value for the Si(1)—O(2) distance continues to be an outlier in plots of Si—O *versus* the negative secant of Si—O—Si. Louisnathan & Gibbs (1972) reported the value of Si(1)—O(2) as 1.628 (10) \AA ; the new measurement is 1.623 (1) \AA . While this value is smaller and therefore closer to the estimate, it is also more precise than the previous determination, thus making the deviation even more pronounced. Even a correction based on an assumption of a 5% Al replacement in the Si(1) site (according to the 4.95 Si from the microprobe analysis) does not change the significance of this result. Such correction would reduce the 1.623 (1) \AA value to 1.617 (1) \AA , which is still much longer than the estimated value of 1.598 \AA .

Factors influencing individual Si—O distances

$\Delta p(0)$ and Si—O—Si

Over the years many empirical and theoretical factors have been identified which are thought to

influence mean and individual cation-anion distances in ionic or partly ionic compounds (for a listing of the empirical factors, see Baur, 1981). The empirical influences connected with the variation of *mean* Si-O bond lengths in silicon-oxygen tetrahedra were studied recently (Baur, 1978) and are not considered here. Among the influences on *individual* Si-O distances two have received much attention in the past twenty years. Cruickshank (1961) proposed on the basis of a review of structures containing the tetrahedral (*T*) groups SiO₄, PO₄, SO₄, and ClO₄ that the *T*-O bond became shorter as the bridging *T*-O-*T* angle became larger. He interpreted this observation on the basis of the *d*-*p* π -bonding theory (increasing bond overlap as the *T*-O-*T* angle opens up). On the other hand it has been shown that individual bond-length variations in many compounds, including the silicates, can be correlated successfully with the Pauling bond strengths [*p*(0)] received by the anions (Baur, 1970). The latter method orders correctly not only the bridging bonds in coordination tetrahedra, but the nonbridging bonds as well and applies also to coordinations other than tetrahedral. The development of this subject with regard to the Si-O bond has been reviewed recently by Dent Glasser (1978), where numerous relevant references can be found. This review demonstrates that the dependence of individual Si-O distances on the bridging angle Si-O-Si is sufficiently ambiguous to lead to widely different correlation coefficients and to different numerical values for the slopes of the regression lines, depending on the sample chosen and on the details of the method used for evaluation. Meanwhile Hill & Gibbs (1979) collected 332 data from four silica polymorphs (terrestrial low tridymite, low quartz, low cristobalite and coesite) and 174 data from 56 silicates and found a statistically significant correlation between the individual Si-O distances and the negative secant of the bridging angle Si-O-Si (percent variation explained 55% and 53%, respectively). Furthermore, they find that the slopes of the dependence for the silica polymorphs and for the silicates are essentially identical (0.068 and 0.080, respectively).

Regression analysis

Levien, Prewitt & Weidner (1980) refined precisely the crystal structure of low quartz, SiO₂, at seven pressures from 0.1 to 6.14 GPa. As quartz is subjected to increasing pressure the angle Si-O-Si decreases from 143.7(1) to 134.2(1)°. According to the relationship between $-\sec(\text{Si-O-Si})$ and the bond length Si-O, the distance Si-O in quartz should increase with increasing pressure. Actually, Levien *et al.* (1980) found that it *decreases* significantly from 1.609 to 1.605 Å. In this particular instance the slope of Si-O on $-\sec(\text{Si-O-Si})$ is *negative* (-0.015 Å, but

not significantly different from zero). Since we have at our disposal as well the crystal structure determination of a new polymorph of coesite, it is appropriate to restudy the relationship between Si-O and Si-O-Si. The following SiO₂ polymorphs were included in the sample (Fig. 3): low quartz (Levien, Prewitt & Weidner, 1980); low cristobalite (Dollase, 1965); synthetic low tridymite (Baur, 1977); *C2/c* coesite (Gibbs, Prewitt & Baldwin, 1977); and *P2₁/a* coesite (Kirfel, Will & Arndt, 1979). The mean estimated standard deviation of all the individual Si-O bond lengths in the sample is 0.005 Å. Not included in it are the data from terrestrial tridymite (Konnert & Appleman, 1978) because this structure as published is a hybrid between an experimentally determined and a simulated structure. It is unknown what the experimental values for terrestrial tridymite would be if the refinement had not been geometrically restrained. Secondly the relationship was tested including 16 additional values for O atoms which are charge balanced [$\Delta p(0) = 0.0$ (Baur, 1970)] and in which all O atoms are bridging either to Si or to Al atoms (NC = 4). However, only the Si-O-Si bridges were entered into the sample. The additional data came from the present refinement of zunyite from Quartzsite, from petalite (Effenberger, 1980), leifite (Coda, Ungaretti & Giusta, 1974), and yugawaralite (Kerr & Williams, 1969). The third regression calculation involved an additional 35 values for which $\Delta p = 0.0$ (Fig. 4), but the number of bridging bonds per tetrahedron is less than four (NC = 1, 2 or 3). With the exception of data from pyrophyllite (Lee & Guggenheim, 1981) these are from the same data base which had been used previously in different contexts (Baur, 1977, 1978, 1980). However, whenever new precise refinements became available their results were substituted for the old values (as was done for zunyite). Fourthly, all

Table 7. *Results of linear regression analysis*

The dependent variable is in all cases the individual Si-O distance; all values are weighted by the inverse square of the estimated standard deviation of the bond length. The sample size is *N*, the percent variation explained is *r*², the negative secant of the angle Si-O-Si is *-sec*, the deviation of the O atom from the Pauling bond strength is $\Delta p(0)$, the intercept *a*, the slopes for the independent variables are *b*, and the significance probability (the probability that the slope equals zero) is *s.p.*, where 0.0001 means that it is 0.0001 or less. For the description of the sample population see text.

Sample	<i>N</i>	<i>r</i> ²	<i>a</i>	Independent variable	<i>b</i>	<i>s.p.</i>
SiO ₂ polymorphs	100	9%	1.575 (11) Å	-sec	0.026 (8) Å	0.003
$\Delta p(0) = 0.0$:	116	0	1.615 (8)	-sec	-0.004 (7)	0.55
NC = 4						
$\Delta p(0) = 0.0$	151	0	1.613 (8)	-sec	0.001 (6)	0.83
Silicates	496	64	1.585 (5)	{ -sec	0.028 (4)	0.0001
				{ $\Delta p(0)$	0.108 (5)	0.0001
Silicates and SiO ₂	596	65	1.591 (4)	{ sec	0.019 (4)	0.0001
				{ $\Delta p(0)$	0.131 (5)	0.0001

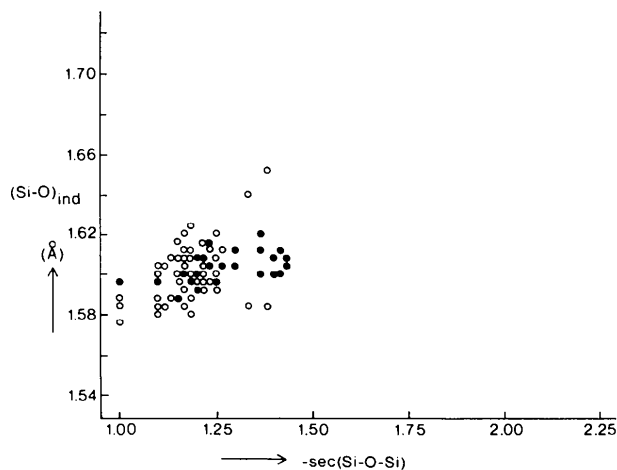


Fig. 3. Scatter plot of observed individual $(\text{Si-O})_{\text{ind}}$ distances against negative secant of bridging angle Si-O-Si for five SiO_2 polymorphs ($N = 100$). Open circles: single points; solid circles: multiple points.

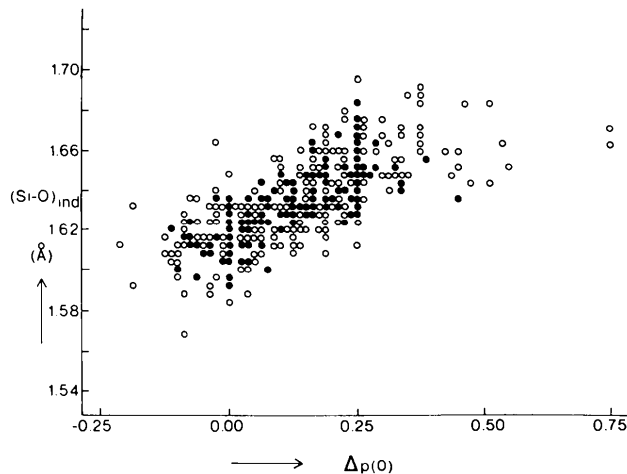


Fig. 6. $(\text{Si-O})_{\text{ind}}$ against the bond-strength deviation, $\Delta p(\text{O})$, of the O atoms for 496 silicates excluding the SiO_2 polymorphs.

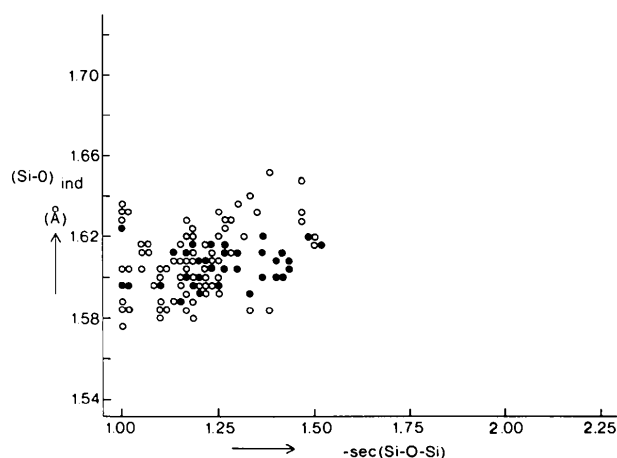


Fig. 4. $(\text{Si-O})_{\text{ind}}$ against $-\sec(\text{Si-O-Si})$ for 100 data points from SiO_2 polymorphs and an additional 51 silicate points for which $\Delta p(\text{O}) = 0.0$.

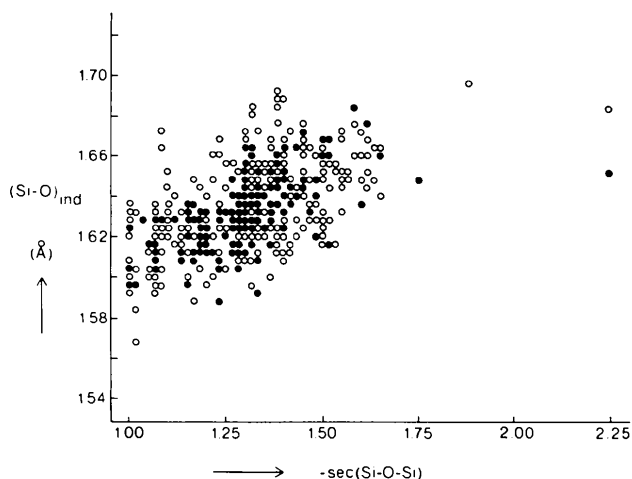


Fig. 5. $(\text{Si-O})_{\text{ind}}$ against $-\sec(\text{Si-O-Si})$ for 496 silicates excluding the SiO_2 polymorphs.

silicates from the data base were used. The mean standard deviation of these Si-O bonds is 0.004 \AA . All the Si-O bonds involved in Si-O-Si bridging bonds were regressed against $-\sec(\text{Si-O-Si})$ and $\Delta p(\text{O})$ (Figs. 5 and 6) separately as well as jointly in multiple linear regression. Finally, the same procedure was applied to the silicates and the silica polymorphs together. This total sample consisted of 596 data points, which were counted on the basis of SiO_4 tetrahedra, as detailed in Baur (1980). All statistical calculations were performed using the SAS system (*SAS User's Guide*, 1979). The numerical results are given in Table 7.

The correlation between individual Si-O bond lengths $(\text{Si-O})_{\text{ind}}$ and $-\sec(\text{Si-O-Si})$ observed for the SiO_2 polymorphs is significant, even though the percent variation explained is only 9%. The numerical value of the slope is, within one standard deviation, identical to the slope found for the dependence of $(\text{Si-O})_{\text{mean}}$ on $-\sec(\text{Si-O-Si})$, which is $0.032 (2) \text{ \AA}$ (Baur, 1978). The addition of other data involving charge-balanced O atoms (rows 2 and 3 of Table 7) destroys the correlation between $(\text{Si-O})_{\text{ind}}$ and $-\sec(\text{Si-O-Si})$ and thus reinforces Louisnathan's & Gibbs's (1972) suggestion that the Si-O vs Si-O-Si relationship is not a ubiquitous one. The slopes in these regressions are slightly negative [as they are for the low-quartz data alone (Levien, Prewitt & Weidner, 1980)], but these negative slopes are clearly not significantly different from zero slope. Higher correlation coefficients and larger slopes for the bond lengths versus bridging angle relationship can be obtained from the regression calculations using the silicate sample (either alone or jointly with the SiO_2 polymorphs): r^2 is 33 and 22%, the slopes are 0.069 and 0.063 \AA [these are similar to the values reported by Hill & Gibbs (1979)]. A least-squares model, however, in which an important

independent variable has been omitted, is meaningless because part of the variation due to the omitted variable is falsely attributed to the included independent variable. Therefore, these simple regression models are unacceptable. A better approach is a multiple linear regression model as listed in the bottom rows of Table 7. Both the secant and the bond-strength terms are highly significant and their slopes are of the proper magnitude expected in *each other's presence*. The relative contributions of the independent variables can be estimated by comparing the incremental sums of squares due to each variable when it is entered last into the model. Of the 64.6% variation explained, 2.3% is due to the secant term, while 62.3% is due to the bond-strength term. This is a typical result for such calculations. The reason why the silicate sample yields a more significant secant relationship than the SiO₂ sample is to be sought in the wider range of values covered by the former (compare Figs. 3 and 5). The range of (Si-O)_{ind} is 70% larger, while the spread in -sec(Si-O-Si) values (even when we ignore the two points with secant values of 1.75 and higher) is 50% larger in the silicate sample as compared with the silica polymorph sample. If we include the points to the very right in Fig. 5, the spread in secant values is even three times higher. The wider range in values and the fact that the term which explains most of the variation [$\Delta p(0)$] is allowed for makes this regression analysis more reliable.

In an even larger sample of 1256 distances which included not only (Si-O)_{ind} involved in bridging bonds to other Si atoms, but also bridging bonds to aluminum and other tetrahedral cations, as well as non-bridging Si-O distances, the relative contributions of the two terms are similar to those discussed above (Baur, 1981). This regression equation explains 78.1% of the variance in (Si-O)_{ind} and the mean deviation of the estimated from the observed value is only 0.010 Å:

$$\begin{aligned} (\text{Si-O})_{\text{ind}} = & 1.560 (2) + 0.131 (3) \Delta p(0)_n \\ & + 0.014 (1) \text{CN}_{\text{mean}} - 0.0108 (9) \text{CN} \\ & + 0.019 (2) \text{NSEC} \\ & + 0.013 (3) \text{NSEC}_{\text{mean}}. \end{aligned} \quad (2)$$

Here $\Delta p(0)_n$ is the bond-strength deviation of the O atom involved in the (Si-O)_{ind} bond (Baur, 1970) normalized by multiplying each bond strength from a cation *A* by [(A-O)_{mean}/(A-O)_{ind}]² (Felsche, 1973). The sum of squares due to $\Delta p(0)_n$ explains 65.7% of the variation in (Si-O)_{ind}; CN_{mean} is the mean coordination number of all O atoms in one silicate tetrahedron, as established to influence mean bond lengths by Shannon & Prewitt (1969) (4.6% of the sum of squares is due to this term); CN is the coordination number of the oxygen atom in (Si-O)_{ind} itself (4.4% is due to it); NSEC and NSEC_{mean} are the individual and the mean secant term as defined above for equation (1)

(the sums of squares due to them amount to 2.7 and 0.7%). The relative importance of the various terms decreases dramatically from $\Delta p(0)_n$ to NSEC_m, but even the least important term is statistically significant. Nevertheless, bond lengths can be predicted from bond-strength deviations alone (if such are present) because the contribution from this term is so large. However, for all SiO₂ polymorphs $\Delta p(0) = 0.0$ and CN = 2 and the secant term is for them the only useful empirical factor. Therefore, it is unfortunate that their (Si-O)_{ind} versus -sec(Si-O-Si) relationship is as equivocal as indicated by the regression results of Table 7.

The same difficulty in reconciling observations with theories is encountered in the series of bridging O atoms in neutral X₃Si-O-SiX₃ species, where X is H, C, F or Cl, as shown by Glidewell & Liles (1978) on the occasion of the structure determination of oxobis[triphenylsilicon(IV)]. In this case the bond Si-O-Si is straight and the Si-O bond length measures 1.616 Å. That means it is too long to fit into a (Si-O)_{ind} versus -sec(Si-O-Si) relationship with a steep slope.

Equation (1) can be obtained from equation (2) by omitting the $\Delta p(0)$ term (mean bond lengths are not a function of bond strengths) and by collapsing the pairs of CN and NSEC terms. In doing so we recognize how mean bond lengths depend on the individual bond lengths and that mean bond lengths do not maintain constant values as was suggested a number of years ago (Cruickshank, 1961) when the empirical data base was not as large and precise as it is now.

(Si-O)_{ind} in zunyite

According to equation (2) the estimated individual Si-O bond lengths for zunyite are Si(1)-O(2) 1.598 (10), Si(2)-O(2) 1.623 (10) and Si(2)-O(5) 1.625 (10) Å (compared with 1.623, 1.636 and 1.633 Å, respectively, for the observed values). This agreement is much worse than it is on average for the 1256 values used for the regression analysis. Thus the zunyite data continue, even after the new refinement, not to fit very well into the empirical scheme. This is mainly due to the bond length Si(1)-O(2) which does not obey the bond length versus bridging angle correlation. For this very reason zunyite does not fit either into more theoretical treatments such as semi-empirical CNDO/2 molecular-orbital calculations. In addition such calculations predict that in H₂Si₅O₁₆ clusters bent Si-O-Si angles are more stable than straight ones (Meagher, Tossell & Gibbs, 1979), which is at variance with the observations in zunyite. Clearly, nature does not read our empirical and theoretical papers, or else the zunyite structure would look differently. Let us heed Chargaff's (1978) warning and avoid a kind of science 'in which reality only serves to

corroborate predictions; and if it fails to do so, it is replaced by another reality'. Or, to turn this statement into a positive one: zunyite is a good crystal structure for the testing of theories.

Conclusions

(1) Zunyite occurs in nature with variable Si to Al ratios: compositions between Si_{4.61}Al_{13.39} and Si_{5.01}Al_{12.98} have been observed. The excess Al replaces Si mostly in the Si(1) site.

(2) There is a clear correlation between Si/Al ratio and cell constant.

(3) Hydrogen bonding takes place between OH and Cl and OH and F. Bonds O—H...O—H are not likely to occur.

(4) The dimensionally most constant unit in the structure is an Al₁₃O₁₆(OH)₂₄ cluster of the Keggin-molecule type with a central aluminum atom in tetrahedral coordination.

(5) There is no indication that the oxygen atom O(2) involved in the straight Si—O—Si bond is statistically disordered around its centroid.

(6) The bond length Si(1)—O(2) is an outlier in a regression analysis of mean Si—O bond lengths. The individual bond lengths involving oxygen atom O(2) [Si(1)—O(2) 1.623 and Si(2)—O(2) 1.636 Å] likewise do not fit into empirical bond-length schemes.

(7) Neither these bond lengths nor the straight bridging bond Si—O—Si can be rationalized on the basis of present theoretical semi-empirical treatments.

(8) Regression analyses involving (Si—O)_{ind} as the dependent variable and —sec(Si—O—Si) as the independent variable for data from zunyite and for other charge-balanced O atoms from silicates and silica polymorphs show no statistical correlation.

(9) Analogous regression analyses for small data sets can have negative slopes (low quartz at various pressures) or values up to +0.07 Å (C2/c coesite).

(10) Analogous calculations for larger samples give slopes of 0.026 Å for all the presently experimentally determined silica polymorphs and up to 0.032 Å for various large silicate samples in which other independent variables (bond-strength deviation and coordination numbers) have been properly taken into consideration. The value of 0.032 Å obtained for the slope of (Si—O)_{mean} over —sec(Si—O—Si) appears to have the widest applicability.

(11) The most important contributor to the sums of squares explaining the variance in individual Si—O bond lengths in silicates is the bond-strength variation; it is followed by the dependence on the coordination numbers, and finally by the secant term.

(12) Half a century after the structure of zunyite was determined by Pauling it continues to be a fascinating subject of study.

We thank the Computer Center of the University of Illinois, Chicago, for computer time, S. Guggenheim for the Quartzsite specimen, E. Olsen and the Field Museum of Natural History for the other three specimens of zunyite, I. Steele for the electron microprobe analyses and Carolyn Cline for the typing of the manuscript.

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Hydrogen Bonds in $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$: Neutron Diffraction, X-ray Diffraction and Vibrational Spectroscopic Studies

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(Received 11 February 1981; accepted 12 August 1981)

Abstract

The structure of $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$ has been refined from neutron data to $R = 0.052$ for 2144 reflections and from X-ray data to $R = 0.022$ for 3310 reflections. It crystallizes in space group $P2_1/c$, with $a = 8.683$ (2), $b = 12.979$ (2), $c = 13.702$ (2) Å, $\beta = 103.40$ (1)° and $Z = 4$. The structure consists of $\text{Na}(\text{D}_2\text{O}, \text{S})_6$ octahedra and AsS_4 tetrahedra which are linked to form corrugated layers parallel to (010), with the composition $\text{Na}_3\text{AsS}_4 \cdot 8\text{D}_2\text{O}$. Fifteen different D atoms of the structure form one O–D···O bond ($\text{D} \cdots \text{O} = 1.906$ Å), thirteen approximately linear O–D···S bonds ($\text{D} \cdots \text{S} = 2.248$ – 2.551 Å) and one bifurcated O–D···S,S bond ($\text{D} \cdots \text{S} = 2.732$ and 2.768 Å). The sixteenth D atom, D(32), is surrounded by one O and two S atoms at distances $\text{D} \cdots \text{O} = 2.798$, $\text{D} \cdots \text{S} = 3.213$ and 3.195 Å that are far outside the range

usually thought to indicate hydrogen bonding. Single-crystal Raman spectra were measured in the range $T = 295$ – 75 K on the D_2O , H_2O and isotopically dilute HDO variants of the title compound. With one exception the uncoupled O–D(H) stretching frequencies were in the range $\tilde{\nu} = 2430$ – 2580 (3270 – 3490) cm^{-1} . Reasonable assignments of these frequencies to the 15 different hydrogen-bonded O–D(H) groups are presented. An additional O–D(H) stretching frequency observed at $\tilde{\nu} = 2664$ (3618) cm^{-1} is due to O–D(H) (32) and shows that this group has very weak, but not negligibly small, interactions with the surrounding atoms.

Introduction

This study was stimulated by our interest in hydrogen bonds between water molecules and sulfur in crystalline