

REFINEMENT AND COMPARISON OF THE STRUCTURES OF ZOISITE AND CLINOZOISITE

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ABSTRACT

The crystal structures of the orthorhombic and monoclinic forms of $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}\text{OH}$ have been refined to conventional R -factors of 4 and 3 percent, respectively. Although the general topologies conform to those suggested in earlier studies, the Ito-proposed relationship between the structures does not hold exactly, *i.e.*, the zoisite positional parameters differ by as much as 0.33 Å from those obtained by "twinning" clinozoisite on (100) by an n -glide operation. These differences result, for example, in different calcium atom surroundings and Si-O-Si angles in the two polymorphs.

The structures display a wide range of bond lengths and angles (although smaller than that proposed in some of the earlier studies) and most of the variation is shown to be related to the rather large, formal local charge imbalance and the mode of polyhedral linkage. Tentative hydrogen atom locations are suggested on the basis of difference Fourier maps.

INTRODUCTION AND PREVIOUS STRUCTURAL STUDIES

The epidote group comprises a widespread and chemically complex family of rock forming silicates whose composition can be represented as $\text{A}_2\text{M}_3\text{Si}_3\text{O}_{12}\text{OH}$. Excluding the lanthanide-bearing allanite minerals, A is predominantly Ca and M is principally Al, Fe^{3+} or Mn^{2+} . The ideal Al end member is dimorphous with a monoclinic form, clinozoisite, and an orthorhombic form, zoisite.

The crystal structure of an epidote with composition near (Al_2Fe_1) was proposed by Ito (1950). His results were confirmed and refined by Belov and Rumanova (1953, 1954) and Ito *et al.* (1954). Gottardi (1954) compared the X-ray reflection intensities of an epidote of about this composition with those of a clinozoisite and concluded they were isostructural. On the basis of the relationship of the space group and cell dimension of zoisite to that of epidote, Ito (1950) proposed a structure for zoisite composed of unit cell sized blocks of epidote; the blocks being related by an n glide operation parallel to (100) of the monoclinic cell. A later restudy by Fesenko, Rumanova, and Belov (1955, 1956) confirmed that this relationship held, at least approximately.

All of these studies, as well as those of allanite (Ueda, 1955; Rumanova and Nikolaeva, 1959) agree on the fundamental topology of these structures but differ widely in the detailed geometry. Some of this variation is no doubt due to chemical differences, however the uniformly high R factors (all > 20%), heavy reliance on two-dimensional data and occasional anomalous bond length (*e.g.*, Si—O = 1.39 Å in zoisite, quoted

by Fesenko *et al.*) make the details and differences between the structures suspect.

More recently, the ordering of the *M* cations in the three available sites has been considered by Strens (1964), Burns and Strens (1967), and Bancroft *et al.* (1967), who propose ordering schemes for the iron and manganese epidotes from refractive index, optical absorption spectra and Mössbauer effect measurements, respectively.

Partly because of some anomalous bond lengths reported by the earlier studies and partly because of the small number of compositions of this group studied, this investigation was begun. This paper reports and compares the structures of the aluminous end members zoisite and clinozoisite.

MATERIAL

Zoisite from the Conway formation (Segerstrom, 1956), collected near Shelburne Falls, Massachusetts, was obtained from the UCLA collections (No. Ms-3290). An X-ray spectrographic analysis for the principal impurities gave 1.4 weight percent Fe_2O_3 and less than 0.1 weight percent Mn_2O_3 . Emission spectrograph and electron microprobe analysis of Shelburne Falls zoisite, quoted in Newton (1966), yield 1.9 weight percent $\text{FeO} + \text{Fe}_2\text{O}_3$. In terms of the usual thirteen oxygen-atom formula there are thus about 0.08 to 0.11 Fe atom per formula unit.

Optical examination showed this zoisite to have its optic plane parallel to (100), the dominant cleavage, and dispersion $r < v$, strong. The composition, optics, and cell dimensions (given below) fit very well with the data for five zoisites given by Myer (1966).

The clinozoisite was selected from a specimen from Willsboro, New York, kindly provided by Dr. Ronald DeRudder. The occurrence, composition and optics of this material have been described (DeRudder and Beck, 1964). The reported composition (no details of analysis) corresponds to about 0.03 Fe atom per formula unit.

SYMMETRY AND CELL DIMENSIONS

Zoisite shows diffraction symmetry $mmmPn-a$ which limits the possible space groups to $Pnma$ if centric or $Pn2_1a$ if acentric. Clinozoisite shows diffraction symmetry $2/mP2_1/-$ and is therefore $P2_1/m$ if centric or $P2_1$ if acentric. On the basis of the good agreement between observed structure amplitudes and those calculated for centric models, space group $Pnma$ was adopted for zoisite and $P2_1/m$ for clinozoisite.

The cell parameters of zoisite are $a = 16.212 \pm 0.008 \text{ \AA}$, $b = 5.559 \pm 0.006$, and $c = 10.036 \pm 0.004$. These values are the average of those

obtained by direct measurement of precession films and by extrapolation of Weissenberg film measurements to $\theta = 90^\circ$. The differences in the cell dimensions obtained by the two methods were all less than their corresponding standard errors, the latter computed from the dispersion of the individual measurements. The values given by Newton (1966) for Shelburne Falls zoisite are similar except for the a axis which is 0.2 percent shorter than that reported here.

The clinozoisite cell dimensions are $a = 8.879 \pm 0.005 \text{ \AA}$, $b = 5.583 \pm 0.005$, $c = 10.155 \pm 0.006 \text{ \AA}$, $\beta = 115.50 \pm 0.05^\circ$, obtained from precession films by measurements using only those high-angle reflections showing $\text{MoK}\alpha_1$ — $\text{K}\alpha_2$ splitting. The values obtained by Myer (1966) from powder diffraction studies of the Willsboro clinozoisite are all 0.1 to 0.2 percent smaller but within three standard deviations. For both zoisite and clinozoisite the cell dimensions reported here were obtained from the actual crystals later used in the intensity data collection.

DATA COLLECTION

The intensity data were measured on a single-crystal counter diffractometer employing equi-inclination geometry. For zoisite, in order to reduce reflection overlap caused by the long a axis dimension, Mn filtered $\text{FeK}\alpha$ radiation was used with a proportional counter detector. The zoisite crystal measured about $0.06 \times 0.16 \times 0.09$ mm. For clinozoisite Zr filtered $\text{MoK}\alpha$ radiation was employed with a scintillation counter as detector. The clinozoisite intensity crystal measured about $0.08 \times 0.15 \times 0.16$ mm.

The total count accumulated while the crystal was rotated through the reflecting position with the counter fixed, was subsequently corrected for background, Lorentz, and polarization factors. Within the uncertainties of 100 second background counts, the background level appeared to a function only of theta, consequently individual background counting rates were obtained by interpolation of an experimentally determined "theta versus background" curve. For zoisite the linear absorption coefficient of 335 cm^{-1} necessitated an absorption correction which was made following Wuensch and Prewitt (1965) using a program written by C. T. Prewitt. For clinozoisite no absorption correction was made as the difference in transmission factors, over the range of data collected, differed by less than one percent.

A total of 333 independent reflections were measured for zoisite which constitutes 67 percent of the data accessible with these experimental conditions. The measured data include all of the strongest reflections up to $\sin \theta/\lambda = 0.5 \text{ \AA}^{-1}$. The weak or near-zero reflections (as judged from

Weissenberg films) were not measured. For clinozoisite a total of 750 independent reflections were measured which represents essentially all but the very weakest reflections up to $\sin \theta/\lambda = 0.6 \text{ \AA}^{-1}$.

REFINEMENT

Refinement was by full-matrix, least-squares methods using the unpublished program of Prewitt. Scattering curves for unionized atoms were taken from the tabulation of Ibers (1962) except for hydrogen for which the values given by Steward, Davidson and Simpson (1965) were used. Starting parameters for zoisite were those given by Fesenko *et al.* (1956), and for clinozoisite those obtained from a previous refinement of piemontite (Dollase, submitted for publication). For each structure only one scale factor was used and all measured reflections were included throughout the computations. Initial refinement with equal weights isotropic temperature factors, and no hydrogen atoms led to conventional *R*-factors of 6 and 4 percent for zoisite and clinozoisite, respectively.

At this point, to determine if the weighting scheme was appropriate, rms ($|F_o| - |F_c|$) was computed for small ranges of $|F|$ values and again for small ranges of theta values. It was found that the agreement of observed and calculated structure factors was statistically independent of either of these quantities and consequently unit weighting was retained. Electron density and difference maps were also computed at this point. The largest anomalies in both cases were peaks near where the single hydrogen atom was expected on crystal chemical grounds. Indications of anisotropic thermal motion could also be seen about some of the atom locations.

Attempted refinement including these trial hydrogen positions resulted in the temperature factors of the hydrogen atom becoming negative in both cases, although not by more than three standard deviations. This coupled with the high standard errors of the hydrogen positional parameters suggests that these data are not really sufficient to locate accurately the hydrogen atoms and the suggested location given below must be considered as tentative. For purposes of refinement the hydrogen temperature factors were fixed at 0.5 \AA^{-2} .

The last stages of refinement incorporated correction of anomalous dispersion using the values computed by Cromer (1965) and occupancy refinement of the octahedral sites in an attempt to locate the small amount of iron present. In addition, for clinozoisite, anisotropic temperature factors were included for the two heavy calcium atoms and for O(9) which is the oxygen atom showing the highest isotropic tem-

perature factor. Limitation of anisotropic refinement to only those cases which would have the greatest effect on the model was done to maintain a high ratio of observations to variables. Due to the smaller amount of zoisite data, all of its atoms were refined as isotropic.

With these conditions refinement was continued until all parameter changes were much less than their standard errors. The final *R*-factors are 4.4 percent for zoisite and 3.1 percent for clinozoisite. The refined parameters are listed in Tables 1 and 2. The quoted standard errors are those obtained from the inverse normal equation matrix. They do not

TABLE 1. ZOISITE POSITIONAL AND THERMAL PARAMETERS

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)
Ca(1)	0.3667(2)	0.25	0.4376(4)	0.72(9)
Ca(2)	.4518(2)	.25	.1150(4)	.85(9)
Si(1)	.0816(3)	.25	.1064(5)	.3(1)
Si(2)	.4104(3)	.75	.2821(5)	.4(1)
Si(3)	.1601(3)	.25	.4356(5)	.6(1)
Al(1, 2)	.2496(2)	.9971(9)	.1899(3)	.53(8)
Al(3)	.1054(3)	.75	.3006(5)	.3(1)
O(1)	.1317(4)	.000(2)	.1451(8)	.4(2)
O(2)	.1012(5)	.015(2)	.4300(7)	.5(2)
O(3)	.3584(5)	.990(2)	.2452(8)	.4(2)
O(4)	.2178(7)	.75	.301(1)	.4(2)
O(5)	.2273(7)	.25	.312(1)	.2(2)
O(6)	.2713(7)	.75	.060(1)	.3(2)
O(7)	.9905(7)	.25	.164(1)	.4(2)
O(8)	.9954(8)	.75	.295(1)	.6(2)
O(9)	.4209(7)	.75	.443(1)	.7(3)
O(10)	.2680(8)	.25	.074(1)	.7(2)
H	.26(1)	.25	.95(2)	.5 ^b

^a Standard errors, given in parentheses, refer to last digit.

^b See text.

contain the effects of nonrandom errors, the most important of which is probably due to the absorption correction in the case of zoisite. Trial computations showed that with the linear absorption coefficient of 335 cm⁻¹ small differences in the estimation of the shape of the crystal resulted in significant differences in the refined temperature factors but appeared to have little effect on the positional parameters.

Location of the minor amount of iron was only partially successful. For clinozoisite site occupancy refinement gave 0.04 ± 0.01 Fe atom per formula unit in the Al(3) site and no substitution in either Al(1) or Al(2). This total agrees almost exactly with the chemical analysis. For the case of zoisite the corresponding standard error of the site occu-

TABLE 2. CLINOZOISITE POSITIONAL AND THERMAL PARAMETERS

Atom	x/a	y/b	z/c	$B(\text{\AA}^2)$
Ca(1)	0.7617(2)	0.75	0.1555(1)	^b
Ca(2)	.6063(2)	.75	.4234(1)	^b
Si(1)	.3382(2)	.75	.0478(2)	.39(3)
Si(2)	.6776(2)	.25	.2753(2)	.42(3)
Si(3)	.1822(2)	.75	.3158(2)	.39(3)
Al(1)	0	0	0	.43(3)
Al(2)	0	0	.5	.41(3)
Al(3)	.2873(2)	.25	.2238(2)	.45(6)
O(1)	.2346(3)	.9972(6)	.0452(3)	.58(5)
O(2)	.3004(3)	.9867(6)	.3509(3)	.58(5)
O(3)	.7874(3)	.0128(6)	.3471(3)	.63(5)
O(4)	.0551(5)	.25	.1322(4)	.44(7)
O(5)	.0395(5)	.75	.1433(4)	.42(7)
O(6)	.0596(5)	.75	.4010(4)	.45(7)
O(7)	.5166(5)	.75	.1779(5)	.63(7)
O(8)	.5090(5)	.25	.2950(5)	.92(8)
O(9)	.6420(6)	.25	.1042(5)	^b
O(10)	.0751(5)	.25	.4241(4)	.51(7)
H	.046(8)	.25	.341(8)	.5 ^c

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	.0031(2)	.0053(4)	.0027(1)	0	.0019(1)	0
Ca(2)	.0027(2)	.0076(5)	.0023(1)	0	.0011(1)	0
O(9)	.0058(7)	.013(2)	.0034(6)	0	.0025(5)	0

^a Standard errors, in parentheses, refer to last digit.

^b Anisotropic temperature factors

^c See text.

pancy refinement was 0.03 Fe atom making the location of 0.08 Fe atom indeterminate with these data.

Comparison of the zoisite model proposed by Fesenko *et al.* (1956) with Table 1 shows axial shifts of up to 0.27 Å. The variable y positional parameters of the four atoms not on mirror planes, Al(1,2), O(1), O(2), and O(3), were set to zero in the previous study on the basis of the very high intensity of the 040 reflection. This refinement, however, shows that all but O(1) are shifted significantly from zero. In the b axis projection, which was the dominant source of their data, the pair of atoms O(4), O(5) and the pair O(6), O(10) coalesce and consequently were given identical x and z values by Fesenko *et al.* This three dimensional refinement indicates that each of the atoms do in fact have different x and z values.

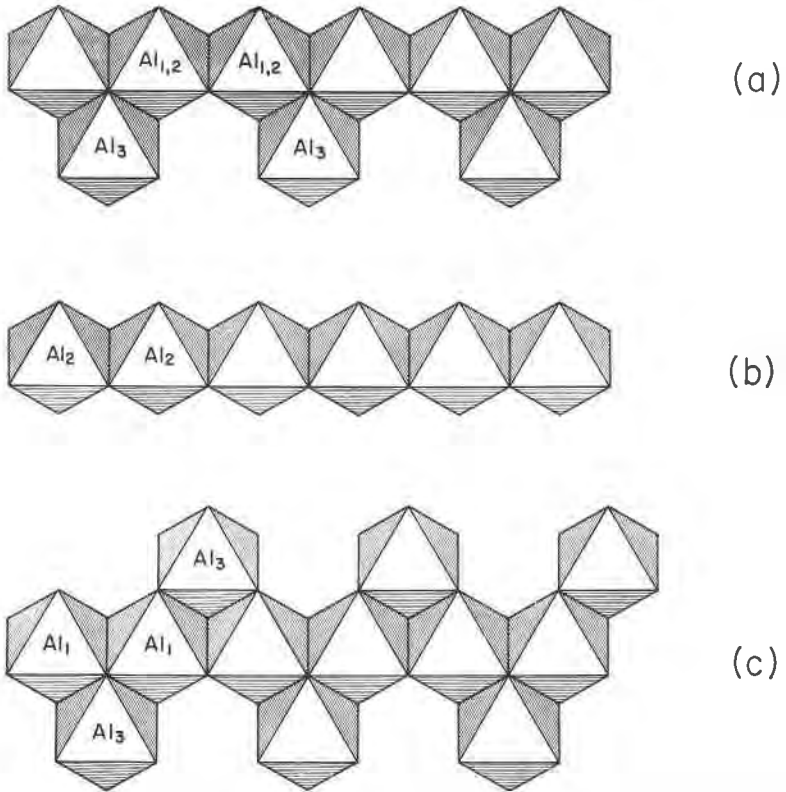


Fig. 1. Idealized octahedral chains in zoisite (a) and clinozoisite, (b) and (c).

The refined clinozoisite values also differ significantly from those previously determined for more iron-rich epidotes. Comparison of the monoclinic members with each other, however, will be done elsewhere.

DESCRIPTION OF THE STRUCTURES

The refinements confirm the general polyhedral linkages proposed by the earlier studies. Briefly, both structures contain aluminum octahedra which share edges forming endless chains which parallel the short, b , axis. Zoisite has one type of chain (see Fig. 1a) composed of two nonequivalent octahedra. In clinozoisite there are two different types of chains, one of which has a single type of octahedron (Fig. 1b), while the other is composed of two nonequivalent octahedra (Fig. 1c). The number of shared edges per octahedron are 4 for $Al(1)$ in clinozoisite, 3 for $Al(1,2)$ in zoisite, and 2 for $Al(2)$ and $Al(3)$ in clinozoisite and $Al(3)$ in zoisite.

The cross-linking of the chains by the remaining cations is best seen

in the perspective views shown in Figures 2 and 3. The most notable features of this arrangement are the occurrence of both Si_2O_7 groups and isolated SiO_4 groups. No edges are shared between tetrahedra and octahedra, however each tetrahedron bridges between unshared corners of edge-sharing octahedra, thereby forming Si-Al-Al rings.

The calcium atoms occupy irregular shaped cavities between the chains and as such pose a problem as to the maximum Ca-O distance that should be considered a significant bond. In this study a bond length cutoff value of 2.85 Å has been used which seems consistent with the known crystal chemistry of calcium. Use of a smaller value would give one of the Ca atoms a rather one-sided, five-fold coordination. Including,

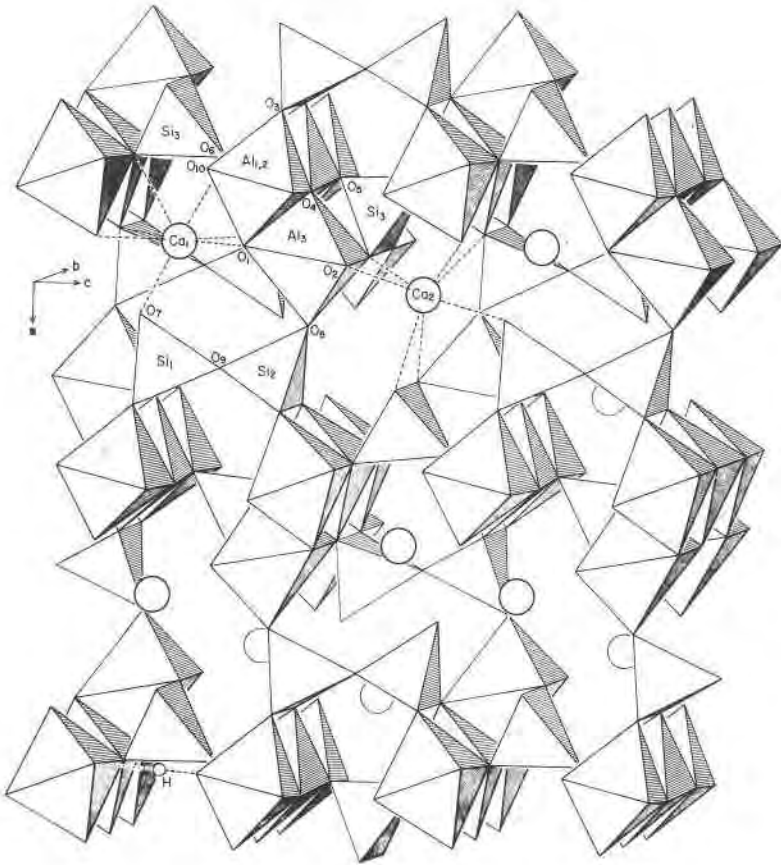


FIG. 2. Polyhedral linkage in zoisite as seen viewed nearly along the b axis. To simplify the illustration the bonds to calcium atoms and the tentative hydrogen atom location are shown only once.

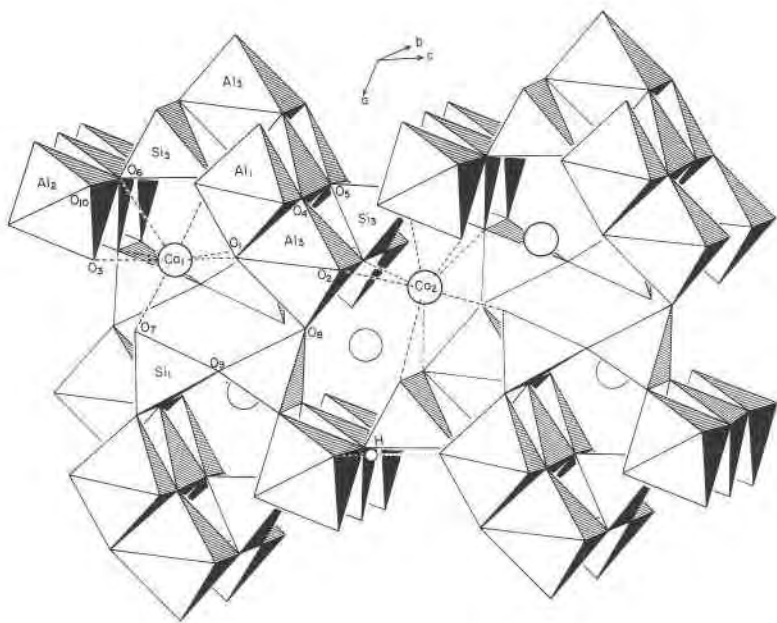


FIG. 3. Polyhedral linkage in clinozoisite viewed nearly along the *b* axis.
Same conventions as Figure 2.

all neighbors up to 2.85 Å, both of the independent calcium atoms of zoisite and Ca(1) of clinozoisite are seven-coordinated. These polyhedra are perhaps best described as trigonal prisms with a seventh, and closer oxygen ligand lying outside one of the equatorial prism faces. The Ca(2) atom of clinozoisite is eight-fold coordinated, with a similar shape except that there is an additional oxygen ligand outside of one of the other equatorial prism faces.

The only tetrahedral edges shared are two opposite edges of the Si(3) tetrahedron which join with calcium polyhedra. As seen from the figures, there are a number of edges shared between Ca and Al polyhedra.

The individual bond lengths are given in Table 3. The standard errors quoted take into account correlation between parameters. Selected interatomic angles are given in Table 4. The wide range of bond lengths observed and the (partially dependent) distortions of the polyhedra can mainly be related to (1) the formal local charge imbalance and (2) the mode of polyhedral linkage.

Assignment of formal Pauling bond strengths to each bond leads to the total bond strengths to each oxygen shown in Table 5. Note that they fall into three well separated groups. Also listed in Table 5 are the lengths of bonds from cations to these oxygen atoms. There is a general

TABLE 3. ZOISITE AND CLINOZOISITE BOND LENGTHS^a

Bond	Frequency	Zoisite	Clinozoisite
Ca(1) —O(1)	2×	2.505 Å	2.490 Å
—O(3)	2×	2.415	2.369
—O(5)		2.587	2.522
—O(6)		2.553	2.745
—O(7)		2.249	2.284
Ca(2) —O(2)	2×	2.521	2.543
—O(2)′	2×	2.789	2.819
—O(3)	2×	2.468	2.531
—O(7)		2.307	2.267
—O(10)		3.008 ^b	2.575
Si(1) —O(1)	2×	1.655	1.652
—O(7)		1.585	1.566
—O(9)		1.645	1.628
Si(2) —O(3)	2×	1.621	1.620
—O(8)		1.582	1.593
—O(9)		1.620	1.627
Si(3) —O(2)	2×	1.620	1.629
—O(5)		1.648	1.661
—O(6)		1.670	1.657
Al(1) —O(1)	2×		1.930 Å
—O(4)	2×		1.850
—O(5)	2×		1.937
Al(2) —O(3)	2×		1.859
—O(6)	2×		1.923
—O(10)	2×		1.852
Al(1,2) —O(1)		1.963 Å	
—O(3)		1.849	
—O(4)		1.839	
—O(5)		1.901	
—O(6)		1.927	
—O(10)		1.849	
Al(3) —O(1)	2×	2.133	2.184
—O(2)	2×	1.964	1.927
—O(4)		1.821	1.862
—O(8)		1.784	1.781
H —O(10)		1.2 (±0.2)	0.8 (±0.1)
O(10) —H···O(4)		2.76 (±0.02)	2.89 (±0.01)

^a Unless otherwise indicated bond length standard errors are 0.006 Å in clinozoisite and 0.01 Å in zoisite.

^b Not considered as bonded in text.

correlation of these properties, as shown by the group means listed in the lower part of the table.

Apparently redistribution of valence electrons, in the direction of reducing the charge imbalance, leads to a change in bond order and there-

TABLE 4. SELECTED INTERATOMIC ANGLES IN ZOISITE AND CLINOZOISITE^a

Angle	Frequency	Zoisite	Clinozoisite
O-Si-O angles which deviate more than 5° from ideal tetrahedral value			
O(5)-Si(3)-O(6)		97.0°	100.2°
O-Al-O angles which deviate more than 5° from ideal octahedral value			
O(1)-Al(1, 2)-O(4)		82.7	
O(4)-Al(1, 2)-O(5)		96.3	
O(5)-Al(1, 2)-O(10)		82.8	
O(4)-Al(1, 2)-O(10)		173.0	
O(1)-Al(3)-O(1)'		81.4	80.5
O(1)-Al(3)-O(4)	2×	78.5	77.9
O(1)-Al(3)-O(8)	2×	100.8	98.1
O(2)-Al(3)-O(2)'		97.1	99.5
O(1)-Al(3)-O(2)'	2×	168.3	168.3
2-coordinated oxygen			
Si(2)-O(8)-Al(3)		152.4(±0.8)	152.0(±0.5)
Si(1)-O(9)-Si(2)		172.6(±0.8)	164.3(±0.5)
3-coordinated oxygen			
M-O-M'		97 to 132°	98 to 133°
4-coordinated oxygen			
M-O-M'		90 to 130°	91 to 132°

^a Unless otherwise indicated standard errors of bond angles are 0.3° for clinozoisite and 0.6° for zoisite.

fore bond length. This "valence balancing" has been discussed by Zachariassen (1963) and shown to account for much of the observed bond length variations in borates and demonstrated to be similarly applicable in a number of silicate refinements (Pant and Cruickshank, 1967, 1968). This approach seems adequate to account for the major bond length variations observed in zoisite and clinozoisite although other factors, as discussed below, are no doubt also involved.

The polyhedra show the usual effects of sharing edges; in zoisite and clinozoisite taken together, the mean octahedral edge length is 2.71 Å but the mean length of edges shared between octahedra is 2.53 Å and the mean edge length parallel to Al-Al vectors is 2.84 Å. Similarly the

TABLE 5. COMPARISON OF FORMAL PAULING STRENGTH TO ANIONS AND THE LENGTH OF BONDS TO THESE ANIONS

Atom	Bond strength	Bond lengths (Å)		
		Si-O	Al-O	Ca-O
O(8) ZO	1.50	1.58	1.78	
O(8) CZ	1.50	1.59	1.78	
O(4) ZO	1.50		2(1.82), 1.84	
O(4) CZ	1.50		2(1.85), 1.86	
O(7) CZ	1.54	1.57		2.27, 2.28
O(7) ZO	1.57	1.59		2.25, 2.31
O(9) CZ	2.00	1.63, 1.63		
O(9) ZO	2.00	1.62, 1.65		
O(10) CZ	2.00 ^a		2(1.85)	
O(3) CZ	2.04	1.62	1.86	2.37, 2.53
O(2) CZ	2.04	1.63	1.93	2.54, 2.82
O(3) ZO	2.07	1.62	1.85	2.42, 2.47
O(2) ZO	2.07	1.62	1.96	2.52, 2.79
O(10) CZ	2.25 ^a		2(1.85)	2.58
O(5) ZO	2.29	1.65	2(1.90)	2.59
O(6) CZ	2.29	1.66	2(1.92)	2.75
O(6) ZO	2.29	1.67	2(1.93)	2.55
O(5) CZ	2.29	1.66	2(1.94)	2.52
O(1) ZO	2.29	1.66	1.97, 2.13	2.50
O(1) CZ	2.29	1.65	1.93, 2.18	2.49
Group means				
	1.52	1.58	1.82	2.28
	2.03	1.63	1.89	2.56
	2.28	1.66	1.97	2.57

^a Including hydrogen.

only highly distorted tetrahedral edge length (and O-Si-O angle) is that shared between Si(3) and Ca(1). (In the case of the only other shared tetrahedral edge the Si and Ca atoms are so widely separated by the 2.8 Å Ca-O bonds that there appears to be little interaction.)

In addition to this type of departure from regularity, the bridging of tetrahedra between edge-sharing octahedra necessitates some sort of distortion since the mean tetrahedral edge length of 2.66 Å is considerably shorter than the distance to be bridged, which would in general be equal to the octahedral edge length which parallels the Al-Al vector, *i.e.* ~2.84 Å. Such bridging by the Si(1) and Si(2) tetrahedra is simply

accomplished by a combined slight undulation of the octahedral chains and a slight increase in the O-Si-O angles involved. However, the simultaneous bridging by Si(3) from Al(3) to Al(1) or Al(1, 2) and between successive Al(3) octahedra is accomplished principally by the further distortion of the Al(3) octahedron already distorted by its asymmetric edge sharing with other octahedra. The extent of the combined distortions can be seen from the range of O-Al(3)-O angles given in Table 4. Bond lengths of course are not independent of such polyhedral distortions but here it seems likely that these distortions augment the range of bond lengths, partly accounting for the extreme distances found in this octahedron.

TABLE 6. THERMAL VIBRATION ELLIPSOIDS FOR CLINOZOISITE

Atom	Ellipsoid axis	rms amplitude	ϕ_1^a	ϕ_J	ϕ_K
Ca(1)	1	0.082 ± 0.003	$24 \pm 4^\circ$	$90^\circ -$	$140 \pm 4^\circ$
	2	$.091 \pm .004$	$90 -$	$0 -$	0
	3	$.113 \pm .002$	66 ± 4	$90 -$	50 ± 4
Ca(2)	1	$.092 \pm .003$	2 ± 15	$90 -$	118 ± 15
	2	$.109 \pm .003$	$90 -$	$0 -$	$90 -$
	3	$.099 \pm .003$	88 ± 15	$90 -$	28 ± 15
O(9)	1	$.139 \pm .008$	36 ± 12	$90 -$	79 ± 12
	2	$.141 \pm .010$	$90 -$	$0 -$	$90 -$
	3	$.110 \pm .011$	126 ± 12	$90 -$	11 ± 12

^a The ϕ 's are the angles between the axes of the ellipsoid and the crystallographic axes.

Although very inaccurately located, the hydrogen atom does fall near the O(10) atom in both structures and reference to Table 5 shows that crystal chemically this is the most reasonable "hydroxyl" oxygen. The resulting O-H bond lengths do not differ by more than a few standard errors from their expected values of $\sim 1 \text{ \AA}$. From the approximate position of the hydrogen atom and the length of the O(10)-O(4) separation and the fact that O(4) is "underbonded," it appears likely that there is an O(10)-H . . . O(4) hydrogen bond in these structures. (See Figs. 2 and 3 for its location.)

ANISOTROPIC THERMAL MOTION

The thermal vibration ellipsoids for those atoms refined as anisotropic in clinozoisite are given in Table 6. Surprisingly O(9), the two-coordinated central oxygen atom of the Si_2O_7 group is only marginally anisotropic. Its orientation however is the expected one with the shortest

axis of the ellipsoid making a small angle ($17 \pm 12^\circ$) with the Si-Si axis of the Si_2O_7 group. The strongest Ca-O bonds are undoubtedly the short bonds to O(7). The Ca(1) thermal ellipsoid is accordingly oriented with its shortest axis making an angle of $3 \pm 4^\circ$ with the Ca(1)-O(7) bond. The Ca(2) ellipsoid has its two shortest (and essentially equal) axes lying in the mirror plane with the Ca(2)-O(7) bond and therefore its direction of greatest vibration is normal to this bond.

COMPARISON OF ZOISITE and CLINOZOISITE

The space-group-twinning hypothesis of Ito (1950) is illustrated in Figure 4. In the upper part of the diagram the monoclinic clinozoisite unit cell—outlined in light lines—is shown repeated in its normal fashion. The blocks represent the single and multiple octahedral chains seen end-on in this b axis view. In the lower half of the diagram this same clinozoisite cell is repeated by an n -glide "twin" operation oriented parallel to (100). This operation, repeated every unit cell, produces a higher symmetry, and larger, repeating unit: the orthorhombic zoisite cell shown in heavy lines.

The different ways of connecting the clinozoisite cells lead to several obvious, second neighbor, differences between the polymorphs, *viz.*, (1) the different types of chains (see Fig. 1), and (2) the different arrangement of coordinating (OH) groups, such that Al(1,2) is coordinated by one (OH) group in zoisite and Al(2) is coordinated by two (OH) groups in clinozoisite. All other aluminum atoms have no hydrogen second neighbors.

In the ideal Ito arrangement the parameters of an asymmetric unit of the zoisite cell are derived from an asymmetric unit of the clinozoisite cell (arbitrarily chosen with $x \geq 1/2$) by

$$(x - 1/2, y, z)_{\text{ortho}} = x + 1/2, y, z + 1/2)_{\text{mono}} \begin{pmatrix} 1/2 & 0 & a_m \cos \beta_m / c_m \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Using this equation the parameters of the ideal Ito zoisite were generated from the refined clinozoisite model and compared to those of refined zoisite. Of the 38 positional variables (excluding H), 22 were statistically different in the two models with positional differences up to 0.33 Å. Qualitatively then it can be seen that the space group twinning concept is useful, especially for descriptive purposes, but quantitatively does not strictly hold.

In hypothetical zoisite the Al(1,2) octahedron is formed by joining half the Al(1) octahedron, of clinozoisite, with half of the Al(2) octa-

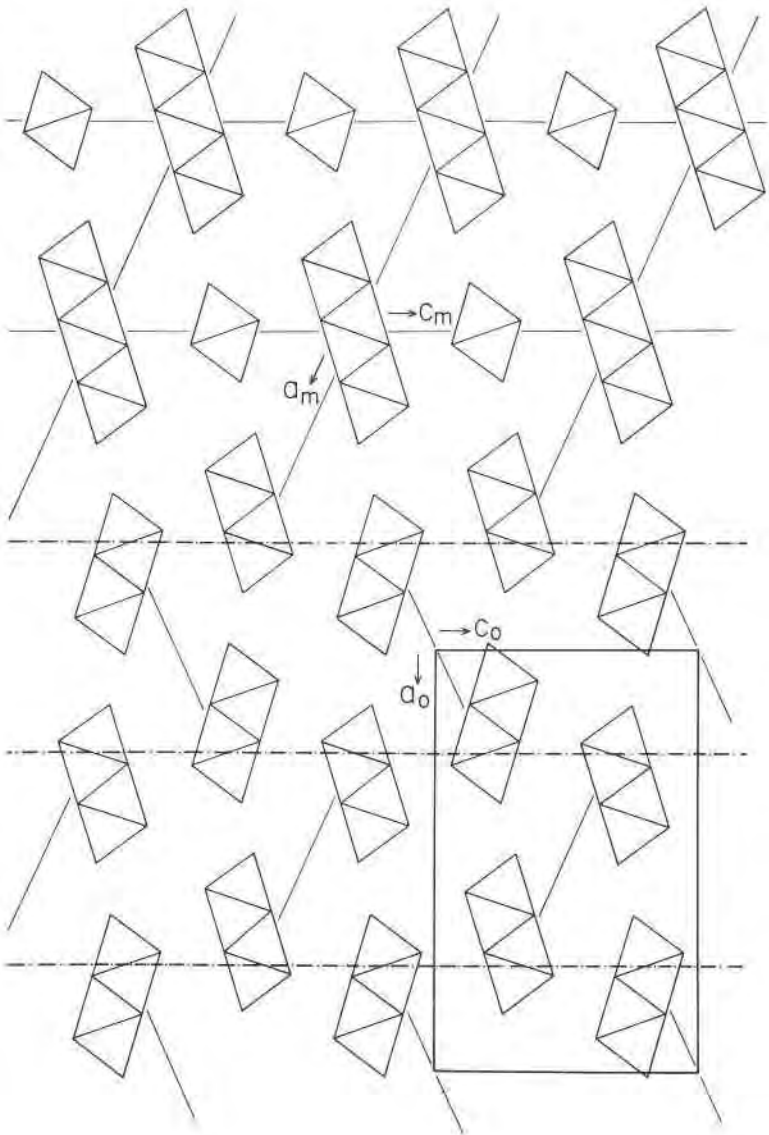


FIG. 4. Relation of zoisite and clinozoisite unit cells after Ito (1950).

hedron through the twinning operation. If the Al(1) and Al(2) octahedra are unequally inclined to the twin plane the resulting Al(1,2) octahedron will be distorted. In clinozoisite the difference in orientation of these octahedra, relative to (100), amounts to 7.9° (plane Al(1),

O(4), O(5), O(4)', O(5)' \wedge (100) = 17.3°; plane Al(2), O(6), O(10), O(6)', O(10)' \wedge (100) = 25.2°.) In the refined zoisite structure, however, the Al(1,2) octahedron is nearly regular, and in fact, this difference in regularity is the principal difference between zoisite models. The increase in regularity of the Al(1,2) octahedron of refined zoisite is accomplished through the different locations taken up by the O(3), O(6), and O(10) atoms which form one half of this polyhedron. These different positions taken together can be viewed as a "rotation" of half the Al(1,2) octahedron. In addition to the change produced in the octahedron, this "rotation" produces the principal bond length and angle differences between the zoisite models and therefore between the refined zoisite and clinozoisite structures. Specifically, the O(10) atom is shifted directly away from the Ca(2) atom lowering the calcium coordination number from 8 in clinozoisite to 7 in zoisite and (2) the O(3) shift rotates the Si(2) tetrahedron, increasing the Si-O-Si bond angle from 164° in clinozoisite to 173° in zoisite.

Some idea of the effect, on the polymorphic relationships, of substitution of larger atoms for aluminum can be gained from the structure of piemontite (Dollase, submitted for publication). Substitution of (Fe-Mn) occurs mainly in the Al(3) site expanding this octahedron. The expansion rotates the connecting Si(2) and Al(2) polyhedra. The sense of rotation of the latter is such that the angle made with (100) (as defined above) is increased to 29.3°. Interpolating then it appears that a hypothetical "space group twinned" form would become increasingly distorted with increasing (Fe,Mn) substitution. This is at least consistent with the observation that the orthorhombic form has a much more restricted substitution range than the monoclinic epidote series.

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