

The crystal structure of epistilbite

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Summary. The crystal structure of epistilbite ($(\text{Ca}_{2.59}\text{Na}_{1.06}\text{K}_{0.10})(\text{Al}_{6.29}\text{Si}_{17.71}\text{O}_{48}) \cdot 15.74\text{H}_2\text{O}$; $C2/m$; $a = 9.08$, $b = 17.74$, $c = 10.25 \pm 0.01$ Å; $\beta = 124.54 \pm 0.05^\circ$) was determined by 3-D least-squares methods. The aluminosilicate framework is composed of 4-, 5-, and 8-membered rings of tetrahedra. There are two sets of intersecting channels each defined by 8-membered rings. The (Ca, Na) atoms in the channels are in contact with seven water molecules and two oxygen atoms giving a coordination of nine at a cut-off distance of 2.77 Å. The average tetrahedral distance is lower than for anhydrous framework aluminosilicates but consistent with some other zeolite structures. Partial Al-Si ordering exists with one tetrahedron occupied preferentially by aluminum. This tetrahedron contains the two oxygen atoms that are coordinated with the (Ca, Na) atom.

THE determination of the crystal structure of epistilbite is part of an effort to classify zeolite minerals by their aluminosilicate frameworks. A second objective is to determine the positions of the exchangeable cations and water molecules that reside in the structural cavities. Epistilbite has been placed in the heulandite group by Deer, Howie, and Zussman (1963). The comprehensive review by Smith (1963) extended by Fischer and Meier (1965) gives a structural classification and points out structural relationships that might be useful in determining other unknown zeolite frameworks. It was suggested by Smith that the epistilbite structure might be solved by the cross-linking of columns of the mordenite type, which have a 7.5 Å repeat unit obtained from the vertical height of three linked tetrahedra, one each with the up (U), down (D), and tilted (T) orientation. Meier (1961) noted that the tectosilicates keatite, petalite, scapolite, and mordenite have one axial length of about 7.5 Å and each contain 5-membered rings of tetrahedra. On this basis he submitted the hypothesis that 5-membered rings might be found commonly in framework silicates that have this repeat distance. Recently this has been borne out by the structure determinations of

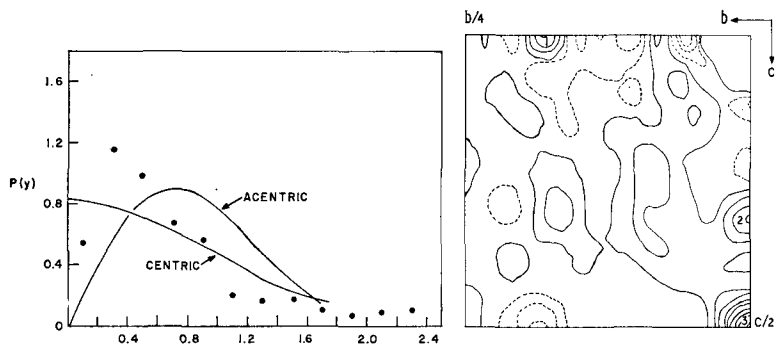
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brewsterite (Perrotta and Smith, 1964) and ferrierite (Vaughn, 1966), which also belong to the heulandite group. Kerr (1964), on this basis, predicted a structure for epistilbite and found reasonable agreement with X-ray powder data. This study confirms and extends the above predictions and hopefully will help towards a more complete structural classification. I have been informed by Slaughter (1965) that he has also confirmed the structure proposed by Kerr.

Experimental. Single crystals of epistilbite were kindly supplied by Dr. D. W. Breck of the Linde Company. The crystals are from the type locality of Teigarhorn, Iceland. The crystals were chemically analysed by Dr. I. S. E. Carmichael and gave the formula $(\text{Ca}_{2.59}\text{Na}_{1.06}\text{K}_{0.10})(\text{Al}_{6.29}\text{Si}_{17.71}\text{O}_{48}) \cdot 15.74\text{H}_2\text{O}$ (calculated to 48 oxygen atoms). Twinning is quite frequent; however, a crystal, optically untwinned and of dimensions $0.48 \times 0.32 \times 0.61$ mm, was finally selected. The cell parameters were initially determined by oscillation and precession photographs using nickel-filtered copper radiation, and were finally refined using X-ray powder data and a least-squares programme written by Dr. C. W. Burnham. The X-ray powder data were obtained using a Norelco diffractometer with nickel-filtered copper radiation, a scanning speed of $\frac{1}{4}^\circ$ per minute and a spinel internal standard calibrated to silicon ($a = 5.4301$ Å). The parameters are $a = 9.08$, $b = 17.74$, $c = 10.25$, all ± 0.01 Å; $\beta = 124.54 \pm 0.05^\circ$, which agree well with those previously given by Strunz and Tennyson (1956). The pseudo-orthorhombic cell used by Kerr may be obtained by the transformation $[201/010/001]$, which results in the change of the a -axial length to $a' = 2 \times a(\cos 34.54^\circ)$. Weissenberg and precession photographs with Ni-filtered copper radiation show the restriction $h+k = 2n$, indicating the space group to be $C2/m$, Cm , or $C2$.

Intensities were measured on a scintillation-counter equi-angle Weissenberg goniometer with zirconium-filtered molybdenum radiation, a pulse-height analyser, and a stationary-counter and moving-crystal technique. Eight layers of data, about 1200 reflections, were collected about the a -axis to the limit of the copper sphere of reflection. The intensity data were corrected for Lorentz and polarization effects and the structure amplitudes calculated using a computer programme written by Van den Hende (1963) of the Esso Research and Engineering Company. No absorption correction was applied because of the small absorption encountered with the molybdenum radiation. Since Bond (1943) recorded a piezoelectric effect for epistilbite, a computer programme was written to test for a centre of symmetry using the statistical

test introduced by Ramachandran and Srinivasan (1959). The calculated plot of points for $P(y)$ versus y drawn out by the computer is shown in fig. 1. No attempt was made to draw a curve as the results appear inconclusive.

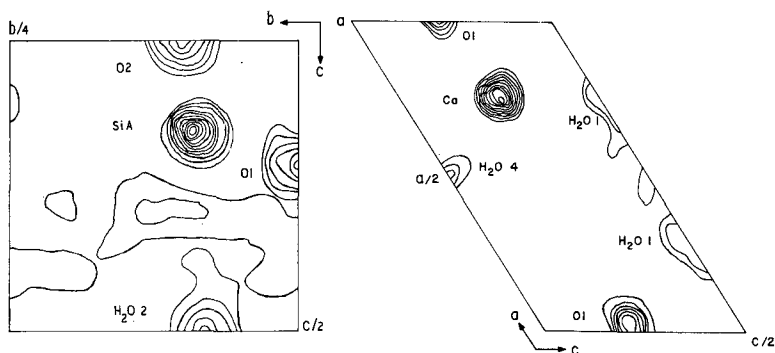


FIGS. 1 and 2: FIG. 1 (left). Statistical test for centre of symmetry. FIG. 2 (right). Section ($x = 0$) of Patterson map.

A three-dimensional Patterson synthesis was calculated using a computer programme written by Sly, Shoemaker, and Van den Hende. A likely Si-Si vector of approximately 3.2 Å in length was found at $[[0, 0.18, 0]]$ and the most reasonable orientation of these two tetrahedra would be about the mirror plane at $y = 0$. A second vector peak at $[[0, 0, 0.32]]$ was interpreted as being the vector between two tetrahedral atoms related by a two-fold axis as also was a third vector peak located at $[[0.47, 0, 0.23]]$. This allowed two of the three tetrahedra in the asymmetric unit to be oriented since the repeat distance perpendicular to the bc -plane is approximately 7.5 Å, which is reasonable for a U , D , and T orientation of the tetrahedra. According to Kerr's postulated structure, when these two tetrahedra are oriented, a fourth vector peak should exist and was indeed found at $[[0, 0, 0.50]]$ with about twice the Si-Si peak height, as expected. The prominent section ($x = 0$) of the Patterson is shown in fig. 2.

Approximate coordinates for the tetrahedral and oxygen atoms of the alumino-silicate framework gave an initial discrepancy factor of 0.31. These atomic coordinates were adjusted by eight successive three-dimensional least-squares refinements and two three-dimensional Fourier maps. The final three-dimensional Fourier was calculated using 750 of the larger structure amplitudes whose signs did not change during the remaining stages of the determination. All of the tetrahedral atoms

and oxygen atoms were located and, additionally, Fourier peaks located within the cavity were assigned to the exchangeable cation and to the water molecules. The sections through the Fourier synthesis at $x = 0$ and $y = 0$ are shown in fig. 3 and fig. 4, respectively, and illustrate typical electron densities and their interpretations. The aluminosilicate framework appears to be centric as the oxygen atoms located in special positions appear quite regular in shape in the electron-density maps.



FIGS. 3 and 4: FIG. 3 (left). Section ($x = 0$) of Fourier map. FIG. 4 (right). Section ($y = 0$) of Fourier map.

The refinement was therefore restricted to the centric space group $C2/m$. The assigned water molecule positions, however, are quite irregular in shape and had to be given varying amounts of water ranging from 0.50 to 1.0. The amount of water in each site was determined by varying the multiplier in the least squares refinement programme. The resulting amount of water in each of the four positions after refinement agreed well with their respective heights in the Fourier map. All the refinements were performed by the programme ORFLS kindly supplied by Busing, Martin, and Levy. The atomic scattering factors published by Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal (1955) and modified arbitrarily for half-ionization were used in the refinement. Averaged values for Si, Al, and for Ca, Na, K were used in accordance with the chemical analysis. The scattering factor for oxygen was also used for the water molecules. The average number of electrons for the exchangeable cation position is between twelve and thirteen; the assigned Fourier peak correlated well with the chemical analysis, being intermediate in height to those peaks assigned to (Al, Si) and oxygen atoms. The final atomic coordinates and isotropic temperature

factors, along with standard errors, are shown in table I. As in the structure of harmotome (Sadanaga, Marumo, and Takéuchi, 1961), the necessity of choosing a number of partially filled sites for the water molecules probably means that these molecules do not conform to the symmetry of the centric cell but rather have a random positioning. This could explain the piezoelectric effect. The water molecules account for

TABLE I. Final atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H ₂ O(1)	0.724	0*	0.502	4.9	0(1)	0.021	0*	0.215	0.8
H ₂ O(2)	0*	0.078	$\frac{1}{2}$ *	4.9	0(2)	0*	0.100	0*	2.0
H ₂ O(3)	0.559	0.082	0.281	4.0	0(3)	0.812	0.117	0.132	1.7
H ₂ O(4)	$\frac{1}{2}$ *	0*	0*	3.3	0(4)	0.170	0.134	0.309	1.5
	$\pm 0.054 \pm 0.018$	$\pm 0.022 \pm 0.5$			0(5)	$\frac{1}{2}$ *	0.180	0*	3.1
<i>T</i> (A)	0.001	0.088	0.161	0.6	0(6)	$\frac{1}{2}$ *	0.179	$\frac{1}{2}$ *	1.1
<i>T</i> (B)	0.293	0.208	0.390	0.8	0(7)	$\frac{3}{4}$ *	$\frac{1}{4}$ *	0*	4.6
<i>T</i> (C)	0.707	0.197	0.097	1.1	0(8)	0.773	0.233	0.261	4.7
	$\pm 0.006 \pm 0.003$	$\pm 0.006 \pm 0.1$			0(9)	$\frac{1}{4}$ *	$\frac{1}{4}$ *	$\frac{1}{2}$ *	4.6
Ca, Na	0.760	0*	0.251	2.6		$\pm 0.018 \pm 0.015$	± 0.020	± 0.3	
	± 0.018	—	$\pm 0.014 \pm 0.2$						

* Fixed by symmetry.

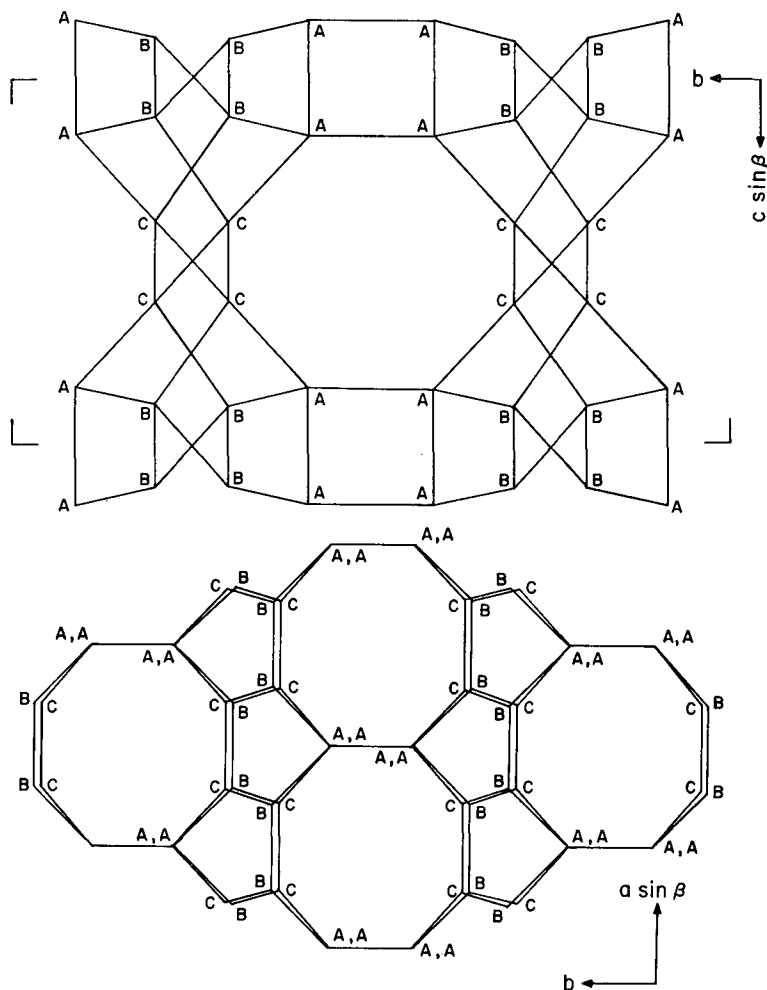
about 14 % of the total number of electrons in the structure and probably have an appreciable effect on the refinement, which was performed on the centric cell. The observed and calculated structure amplitudes are listed in the Ph.D. thesis of Anthony J. Perrotta available from the library of the University of Chicago. The weighted discrepancy factor, including those reflections below the sensitivity limit, is 0.16. The inter-atomic distances are given in table II. The computed random errors for (Al, Si)—O and (Ca, Na, K)—O distances range from 0.007 to 0.014 Å and for O—O distances from 0.015 to 0.025 Å.

Discussion. The alumino-silicate framework is shown schematically in fig. 5, viewed along the *a*-axis: the main channels, formed from 8-membered rings of tetrahedra, run parallel to the *a*-axis; the 8-membered rings are inter-linked by both 4- and 5-membered loops of tetrahedra. These 5-membered rings of tetrahedra are shown more clearly in the schematic view down the *c*-axis (fig. 6). The apertures of the cavity in this direction are also formed from 8-membered rings. Both apertures are elliptical in shape; the free aperture size, using a radius of 1.3 Å for the oxygen atoms, is 3.6×6.3 Å and 4.9×6.3 Å for the apertures perpendicular to the *a*- and *c*-directions, respectively.

The complete structure is shown in fig. 7, a view down the *a*-axis.

TABLE II. Interatomic distances (Å)

$T(A)-O(1)$	1.65	$T(B)-O(4)$	1.61	Ca, Na-H ₂ O(4)	2.31	H ₂ O(1)-H ₂ O(3)	2.38 (2)
-O(2)	1.66	-O(6)	1.63	-H ₂ O(3)	2.48 (2)	-Ca, Na	2.77
-O(3)	1.64	-O(8)	1.60	-O(3)	2.60 (2)	-O(1)	2.45
-O(4)	1.64	-O(9)	1.57	-O(1)	2.60	-O(4)	2.89
Average	1.65	Average	1.60	-H ₂ O(2)	2.61 (2)	-H ₂ O(2)	2.75 (2)
				-H ₂ O(1)	2.77		
$T(C)-O(3)$	1.62	$T(A)$	2.76	H ₂ O(2)-Ca, Na	2.61 (2)	H ₂ O(3)-H ₂ O(1)	2.38
-O(5)	1.58	O(1)-O(2)	2.65	-H ₂ O(1)	2.87	-Ca, Na	2.48
-O(7)	1.57	O(1)-O(4)	2.70	-O(3)	3.22	-H ₂ O(4)	3.00
-O(8)	1.57	O(2)-O(4)	2.62	-O(4)	3.26	-O(6)	3.10
Average	1.59	O(1)-O(3)	2.73	-H ₂ O(3)	3.29	-O(5)	3.14
		O(2)-O(3)	2.69	-O(1)	3.34	-H ₂ O(2)	3.29
		O(3)-O(4)					
$T(B)$		$T(C)$		H ₂ O(4)-Ca, Na	2.31 (2)		
O(4)-O(6)	2.60	O(3)-O(5)	2.59	-H ₂ O(3)	3.000 (4)		
O(4)-O(8)	2.66	O(3)-O(7)	2.60	-O(3)	3.14 (4)		
O(6)-O(8)	2.62	O(5)-O(7)	2.58	-O(5)	3.19 (2)		
O(4)-O(9)	2.62	O(3)-O(8)	2.58				
O(6)-O(9)	2.59	O(5)-O(8)	2.59				
O(8)-O(9)	2.59	O(7)-O(8)	2.58				



FIGS. 5 and 6: FIG. 5 (*top*). Schematic drawing of epistilbite framework projected along the a -axis. FIG. 6 (*bottom*). Schematic drawing of epistilbite framework projected along the c -axis.

This diagram, viewed in connexion with the schematic drawings, should present a clearer picture of the framework. The tetrahedra are, for the most part, in sheets parallel to the (010) plane, with two layers of tetrahedra cross-linked by 4- and 5-membered rings about the glide plane at $y = \frac{1}{4}$, which would prevent any movement of water or exchangeable

cations in the b -direction. The layered framework is extended in the b -direction by a T_2O_7 group at the mirror plane, $y = 0$. The exchangeable cation is not located in the centre but closer to the periphery of the cavity. The water molecules are located in the central part of the cavity and are aligned mainly parallel to the planes of tetrahedra.

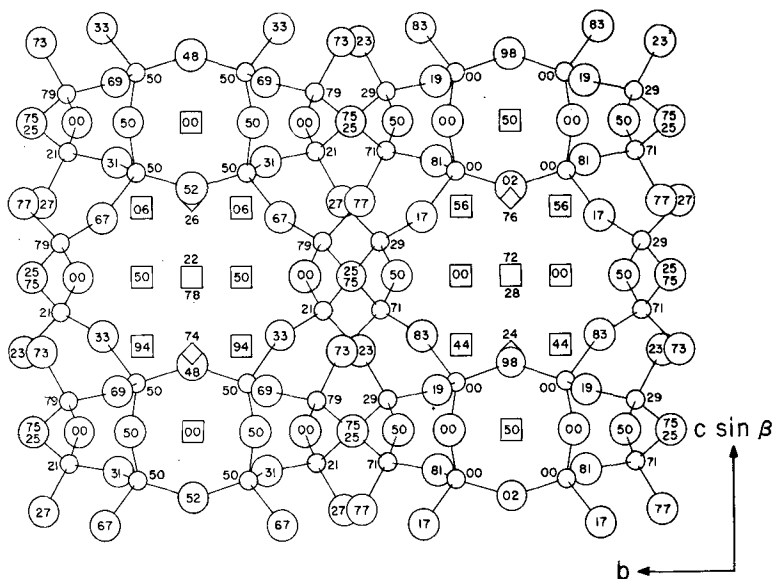


FIG. 7. Crystal structure of epistilbite viewed along a -axis (numbers represent heights along a -direction).

The coordination polyhedron of the exchangeable cation is shown in fig. 8: The three closest neighbours of the (Ca, Na) atom are water molecules while the bridging oxygen O(1) of the T_2O_7 group about the mirror plane and O(3) of the same tetrahedron are the next nearest neighbours; the rest of the nearest neighbours are water molecules with slightly greater interatomic distances giving a coordination of nine at a cut-off distance of 2.77 Å. Each of the water molecules has the exchangeable cation as one of its neighbours with the others being either water molecules or oxygen atoms. The $H_2O(3)-H_2O(1)$ distance of 2.38 Å is very short but is within the limits of distances tabulated to date.

The oxygen-oxygen distances are reasonable and quite consistent, which strengthens the hypothesis that the aluminosilicate framework

is basically centric while the water molecules and possibly the exchangeable atoms do not obey the centric space group.

The bonding of the calcium atom to the two oxygens, O(1) and O(3) of tetrahedron *T*(A), probably results in partial Al-Si ordering as shown by the larger *T*-O distance for this tetrahedron of 1.65 Å. A complete aluminum-centred tetrahedron is impossible because of a Si/Al

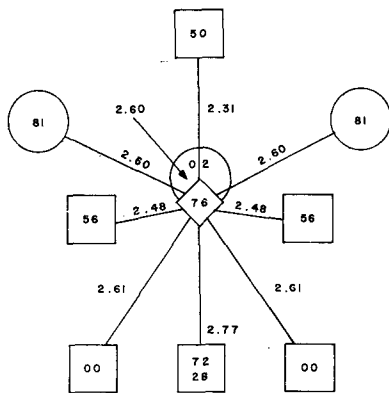


FIG. 8. Coordination polyhedra of exchangeable cation viewed along *a*-axis. Diamond = (Ca, Na, K), Square = H₂O, Circle = oxygen. Heights are shown within the elements; interatomic distances are given along join lines.

ratio of 3; however, this tetrahedron is probably occupied mainly by aluminum, which would give a more favourable distribution of charge in the structure.

As mentioned, the exchangeable cation in epistilbite is located near the periphery of the structural cavity and therefore has some oxygen atoms forming its primary coordination polyhedra, whereas the exchangeable cation in brewsterite (Perrotta and Smith, 1964) is located approximately in the centre of the cavity and is surrounded mostly by water molecules. This leads to some difficulty in accepting wholeheartedly the idea that the exchangeable cations tend to surround themselves with water molecules to form a sphere of hydration when the cavities are large enough and contain a sufficient number of water molecules since there is little difference between the water contents or the volumes of the cavities in epistilbite and brewsterite. Perhaps there is a compromise between this tendency and the electrostatic attraction to oxygen atoms of the framework. Both structures have two sets of

intersecting channels each defined by 8-membered rings and the ratio of the number of exchangeable cations to the number of water molecules is 0.21 and 0.23 for brewsterite and epistilbite, respectively. Moreover, brewsterite contains the larger strontium and barium atoms, which should make the cavity 'effectively' smaller than that of epistilbite, which contains calcium and sodium atoms. In both zeolites the determination of the water molecule positions was difficult as is evidenced by the large isotropic temperature factors. The relatively large vibration is probably due to the water molecules having weaker hydrogen bonding to framework oxygens or is caused by averaging of different sites in a lower-symmetry structure. The amount of labour that would be necessary to accurately locate the water molecules by X-ray analysis made inadvisable a more exact determination of the molecular positions. The existence of hydrogen bonding can possibly be detected by infra-red absorption spectra as shown by Yukhnevich and Senderov (1963).

The average tetrahedral distances of 1.65, 1.60, and 1.59 Å give an over-all average of 1.61 Å, lower than the expected value of 1.64 Å. The tetrahedral distances in epistilbite tend to be somewhat lower than the predicted values of Smith and Bailey (1963). It should be noted that the tetrahedral distances of natrolite (Meier, 1961) and of brewsterite are in conformity with predicted values; however, other accurately determined zeolite structures tend also to have lower distances as in epistilbite. For well-hydrated framework structures like the zeolites, this irregularity may be due to the different interactions of the cations and water molecules in the cavities and their subsequent effect on the aluminosilicate framework. By comparison with two non-zeolitic framework structures done recently, the average Al-O distance in barium aluminate (Perrotta and Smith, unpublished) is indistinguishable from the average tetrahedral distance assigned to the aluminum-centred tetrahedron in kalsilite (Perrotta and Smith, 1965); the tetrahedral distances in both structures are indistinguishable from the predicted values.

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