THE CRYSTAL STRUCTURE OF EPIDIDYMITE

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ABSTRACT

The crystal structure of epididymite——HNaBeSi$_3$O$_8$, space group *Pnma*, $a = 12.74$ Å,
$b = 13.63$ Å, $c = 7.33$ Å and $Z = 8$——has been redetermined and found to differ significantly
in its detail from that determined by Pobedimskaya and Belov (1960). The most significant
differences are: (a) the sum of O and (OH) or H$_2$O ions in the unit cell is 64, rather than
the previously reported 68, and (b) the Be[O$_3$(OH)] tetrahedra reported by Pobedimskaya
and Belov have been supplanted by Be$_2$O$_6$ groups composed of edge-sharing Be tetrahedra.
The refined structure, utilizing 738 counter intensities, yielded a final isotropic *R*-index of
8.4 percent. Average cation-oxygen distances are: Si(1)–O = 1.606 Å, Si(2)–O = 1.619 Å,
Si(3)–O = 1.618 Å, Be–O = 1.620 Å, and Na–O = 2.620 Å. The structure represents a new
type that can be envisioned as a hybrid between the framework and chain types.

INTRODUCTION

Epididymite, an orthorhombic dimorph of monoclinic eudidymite
(also under investigation in our laboratory) has the chemical composition
HNaBeSi$_3$O$_8$. A structure was first proposed by Ito (1934) but the
interatomic distances of Be–O and Si–O were so unreasonable as to
warrant re-examination. Pobedimskaya and Belov (1960) were the first
to further investigate the structure using two projections in obtaining a
final R-index of 23% for *h0l* and *0kl* film data. However, the structure still
contained some obvious flaws, namely: (1) the powder diagram intensities
could not be correlated with the atomic coordinates given (Borg, personal
communication) (2) the unit cell contained 68 O and (OH) or H$_2$O ions,
not 64 as dictated by the chemical composition, (3) there was an un-
reasonably close (1.8 Å) approach between O(1) and (OH), and finally,
(4) the Si–O distances ranged from 1.59 to 1.74 Å. Thus, a re-investiga-
tion of the structure was deemed imperative.

EXPERIMENTAL

The crystals, from Narsarsuk, Greenland, were obtained from the U. S. National Mu-
seum, Smithsonian Catalogue No. R84350. Precession photographs and measurements
with a Buerger single crystal diffractometer yielded the following cell dimensions: $a = 12.74$
$\pm .01$ Å, $b = 13.63 \pm .01$ Å, $c = 7.33 \pm .01$ Å, space group = *Pnma*, and $Z = 8$.

A nearly equant cleavage fragment of mean dimension 0.25 mm was selected for data
collection. Intensities were collected with an automated Buerger single-crystal diffractome-
ter with Ni-filtered CuK$_\alpha$ radiation. Detailed procedures during the data collection and
reduction stages are given in a previous paper (Robinson and Fang, 1969). Out of 1014 re-
flections measured, 746 spectra were "observed" for use in the structure determination.
Standard reflections were carefully monitored to insure system stability.

DETERMINATION OF THE STRUCTURE

After numerous fruitless attempts to refine the Russian coordinates, it was decided that an independent structure determination should be initiated.

Experimental normalized structure factor statistics, along with the theoretical values for centrosymmetric and noncentrosymmetric crystals calculated by Karle, Dragonette and Brenner (1965, p. 714) are given in Table 1. Centrosymmetry was strongly indicated. The structure was then solved by reiterative application of Sayre's equation using the unpublished program of R. E. Long (1965). Two possible solutions resulted, one of which proved to be correct. All atoms, with the exception of Be and H, were present in the first E map. A structure factor calcula-

TABLE 1. EXPERIMENTAL AND THEORETICAL VALUES OF
NORMALIZED STRUCTURE FACTORS

	Experimental	Centrosymmetric	Non-Centrosymmetric
Av. $\|E\|$	0.659	0.798	0.886
Av. $\|E^2-1\|$	1.153	0.968	0.736
$\|E\| \geq 3.0$	1.4%	0.3%	0.01%
$\|E\| \geq 2.0$	5.6%	5.0%	1.8%
$\|E\| \geq 1.0$	20.8%	32.0%	37.0%

tion, using the original atomic coordinates from the E map, gave an R index of 39 percent.

REFINEMENT

Several cycles of full-matrix least squares refinement, varying the scaling factor and the atomic coordinates obtained from the E map, led to an R-index of 14.7 percent. Form factors were taken from the International Tables for Crystallography (1962). At this point a difference Fourier was calculated and the Be atom was clearly visible as the area of maximum electron density. Further refinement, including the Be contribution and varying all parameters with isotropic B's, led to an R value of 9.2 percent. However, the temperature factors of the Si atoms were quite low. We then attempted to vary the temperature factors of the Si atoms anisotropically, but negative values resulted. Returning to the isotropic situation, a weighting scheme previously used by us (Robinson and Fang, 1969) was employed, resulting in a great improvement in the temperature factors of Si and yielding a final residual R of 8.4 percent. During least-squares refinement, eight strong, low-angle reflections were

Table 2. Atomic Coordinates, Temperature Factors, and Standard Errors[a]

Atom	x	y	z	$B(\text{Å}^2)$
Na	.1030(3)	.0698(3)	.5014(6)	2.2(1)
Be	.4951(8)	.0002(9)	.3433(16)	0.5(2)
Si(1)	.1589(2)	.1380(2)	.0155(3)	0.3(1)
Si(2)	.3429(2)	.1366(2)	.7314(3)	0.3(1)
Si(3)	.3317(2)	.1378(2)	.3054(3)	0.4(1)
O(1)	.1207(7)	$\frac{1}{4}$	.0005(11)	1.1(2)
O(2)	.2174(4)	.1234(4)	.2098(8)	0.9(1)
O(3)	.0603(4)	.0664(5)	.0067(7)	0.7(1)
O(4)	.2373(4)	.1142(4)	.8498(8)	1.0(1)
O(5)	.4345(4)	.0645(4)	.7907(8)	0.8(1)
O(6)	.3784(6)	$\frac{1}{4}$	.7656(11)	0.8(1)
O(7)	.3048(5)	.1239(4)	.5204(8)	0.7(1)
O(8)	.3709(7)	$\frac{1}{4}$	.2674(11)	0.8(1)
O(9)	.4151(4)	.0629(5)	.2256(8)	0.9(1)
O(10)	.0577(8)	$\frac{1}{4}$	.4890(14)	2.3(2)

[a] In parentheses referring to last decimal position given.

omitted because they were obviously suffering from secondary extinction, leaving a final total of 738 observations. The measured and calculated structure factors, including rejected reflections and those suffering from secondary extinction, are listed in Table 4 which has been deposited with The National Auxiliary Publications Service.[1] Table 2 lists the parameters from the final least squares cycle.

Possible Formulae for Epididymite

The unit cell of epididymite contains $H_8Na_8Be_8Si_{24}O_{64}$. Thus, the structural formula may be written as either $4\{Na_2Be_2Si_6O_{15}\cdot H_2O\}$ or $8\{NaBeSi_3O_7\cdot OH\}$. The latter has been adopted by both Ito (1934) and Pobedimskaya and Belov (1960) in their papers. Our difference fourier maps did not give any indication of the proton positions. However, O(10) was assumed to be a part of the (OH) or H_2O group since it is the only oxygen not bonded to a silicon atom. A recent DTA study by Shilin and Semenov (1957) indicated that epididymite does not lose water until temperatures of 810°–830° C are attained. This temperature of dehydration is supported, without reference, by Ross (1964). It is difficult to

[1] To obtain a copy, order NAPS Document No. 01111 from National Auxiliary Publications Service of A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, N. Y. 10022; remitting $2.00 for microfiche or $5.00 for photocopies, in advance, payable to CCMIC-NAPS.

TABLE 3. SELECTED INTERATOMIC DISTANCES AND ANGLES[a]

Tetrahedral coordination around Si

Si(1) Tetrahedron		Si(2) Tetrahedron		Si(3) Tetrahedron	
Si(1)–O(1)	1.606(4) Å	Si(2)–O(4)	1.630(6) Å	Si(3)–O(7)	1.624(6) Å
Si(1)–O(2)	1.619(6)	Si(2)–O(5)	1.587(6)	Si(3)–O(8)	1.633(4)
Si(1)–O(3)	1.593(6)	Si(2)–O(6)	1.629(4)	Si(3)–O(9)	1.584(6)
Si(1)–O(4)	1.605(6)	Si(2)–O(7)	1.630(6)	Si(3)–O(2)	1.629(6)
Mean	1.606 Å	Mean	1.619 Å	Mean	1.618 Å
O(3)–O(1)	2.619(7) Å	O(5)–O(7)	2.704(8) Å	O(9)–O(7)	2.708(8) Å
O(3)–O(4)	2.614(8)	O(5)–O(4)	2.638(8)	O(9)–O(2)	2.653(8)
O(3)–O(2)	2.613(8)	O(5)–O(6)	2.634(6)	O(9)–O(8)	2.629(6)
O(1)–O(4)	2.617(9)	O(7)–O(4)	2.567(8)	O(7)–O(2)	2.535(8)
O(1)–O(2)	2.617(9)	O(7)–O(6)	2.657(8)	O(7)–O(8)	2.664(8)
O(4)–O(2)	2.654(8)	O(4)–O(6)	2.653(8)	O(2)–O(8)	2.642(8)
Mean	2.622 Å	Mean	2.642 Å	Mean	2.639 Å
O(3)–Si(1)–O(1)	109.9(4)°	O(5)–Si(2)–O(7)	114.4(3)°	O(9)–Si(3)–O(7)	115.2(3)°
O(3)–Si(1)–O(4)	109.6(3)	O(5)–Si(2)–O(4)	110.2(3)	O(9)–Si(3)–O(2)	111.3(3)
O(3)–Si(1)–O(2)	108.9(3)	O(5)–Si(2)–O(6)	109.9(4)	O(9)–Si(3)–O(8)	109.6(4)
O(1)–Si(1)–O(4)	109.2(4)	O(7)–Si(2)–O(4)	108.9(4)	O(7)–Si(3)–O(2)	102.4(3)
O(1)–Si(1)–O(2)	108.4(4)	O(7)–Si(2)–O(6)	109.2(4)	O(7)–Si(3)–O(8)	109.8(4)
O(4)–Si(1)–O(2)	110.8(3)	O(4)–Si(2)–O(6)	109.0(4)	O(2)–Si(3)–O(8)	108.2(4)
Mean	109.5°	Mean	109.4°	Mean	109.4°

Tetrahedral coordination around Be

		O(9)–O(5)	2.589(9) Å	O(9)–Be–O(5)	109.0(7)°
Be–O(3)	1.649(12)Å	O(9)–O(3)	2.697(9)	O(9)–Be–O(3)	113.1(7)
Be–O(3)	1.660(12)	O(9)–O(3)	2.730(9)	O(9)–Be–O(3)	114.6(6)
Be–O(5)	1.597(12)	O(5)–O(3)	2.743(9)	O(5)–Be–O(3)	115.3(6)
Be–O(9)	1.584(11)	O(5)–O(3)	2.706(9)	O(5)–Be–O(3)	112.3(6)
		O(3)–O(3)	2.376(9)	O(3)–Be–O(3)	91.8(7)
Mean	1.622 Å	Mean	2.640 Å	Mean	109.4°

Coordination around Na

Na–O(9)	2.917(8) Å
Na–O(2)	2.688(7)
Na–O(5)	2.443(8)
Na–O(5)	2.634(8)
Na–O(7)	2.679(7)
Na–O(9)	2.455(8)
Na–O(10)	2.525(5)
Mean	2.620 Å

[a] Standard errors in parentheses refer to last decimal position given.

imagine how an H_2O could remain at these temperatures. Thus, without further evidence, the O(10) position would be considered a part of an (OH) group.

To test our argument, "estimated bond valences" were calculated, based on the method described by Donnay and Allmann (1970) which is designed to differentiate O^{2-}, $(OH)^-$ and H_2O in crystal structures determined by X rays. To our surprise, the results of our calculations

TABLE 5. PARAMETERS USED TO CONSTRUCT CURVES OF BOND
VALUES VS. BOND LENGTH FOR EPIDIDYMITE

Cation-Anion	$\bar{L}$ (Å)	ν_i(v.u.)	L_{max}(Å)	p
^{vii}Na–O	2.620	$\frac{1}{7}$	3.13	5.14
^{iv}Si(1)–O	1.606	1.00	2.13	3.06
^{iv}Si(2)– Si(3)–O	1.618	1.00	2.13	3.17
^{iv}Be–O	1.622	0.50	2.02	4.07

strongly indicated that the O(10) oxygen is a part of an H_2O molecule
with atoms O(6) and O(8) acting as acceptors (Tables 5, 6, & 7). It should
be pointed out, however, that the acceptor angle of 76° and the O(10)–
O(6) and O(10)–O(8) distances of 2.91 Å and 3.03 Å respectively would
make the hydrogen bond interaction extremely weak (Baur, 1969).

Thus, we have totally conflicting evidence as to the proton assignment

TABLE 6. ESTIMATED BOND VALENCES (V.U.) IN EPIDIDYMITE

Anions	^{iv}Si(1)	^{iv}Si(2)	^{iv}Si(3)	^{vii}Na	^{iv}Be	$\Sigma_c\nu$	Chemistry	$\Sigma_c\nu$ corrected for H bonds
^{ii}O(1)	1.00[2]*					2.00	O^{2-}	2.00
^{iii}O(2)	0.97		0.98	0.12		2.07	O^{2-}	2.07
					0.47			
^{iii}O(3)	1.00					1.97	O^{2-}	1.97
					0.50			
^{ii}O(4)	1.00	0.98				1.98	O^{2-}	1.98
				0.20				
^{iv}O(5)		1.06			0.53	1.93	O^{2-}	1.93
				0.14				
^{iii}O(6)		0.98[2]*				1.96	O^{2-}	2.09
^{iii}O(7)		0.98	0.99	0.13		2.10	O^{2-}	2.10
^{iii}O(8)			0.97[2]*			1.94	O^{2-}	2.03
				0.19				
^{iv}O(9)			1.07		0.55	1.87	O^{2-}	1.87
				0.06				
^{iv}O(10)				0.17[2]*		0.34	H_2O	0.12
Average bond length $\bar{L}$Å	1.606	1.619	1.618	2.620	1.622			
(Å) $\Sigma_A\nu$	3.97	4.00	4.00	1.01	2.05			

$\Sigma_A\nu$ = valences of bonds emanating from cation summed over the bonded anions.
$\Sigma_c\nu$ = valences of bonds reaching anion.
The coordination numbers of the anions include the hydrogen bonds of Table 7.

TABLE 7. SHORT OXYGEN–OXYGEN DISTANCES (Å) AND ESTIMATED HYDROGEN-BOND VALENCES (V.U.) IN EPIDIDYMITE

Donor Acceptor	$H_2O(10)$	$\Sigma_c\nu$
O(6)	2.907; 0.13	0.13
O(8)	3.032; 0.09	0.09
$\Sigma_A\nu$	0.22	

$\Sigma_c\nu =$ sum of valences donated by hydrogen ions of water molecules.

$\Sigma_A\nu =$ sum of valences accepted by oxygen ions.

Estimated bond valences of asymmetric, linear O_1–H–O_2 bonds taken from Lippincott and Schroeder (1955, Fig. 5).

and it would seem that a neutron diffraction study is needed to resolve the problem.

DISCUSSION OF THE STRUCTURE

The main structural feature of epididymite is the $[Si_6O_{15}]_\infty$ double chain of silicate tetrahedra paralleling the c-axis (Fig. 1). Each half-unit
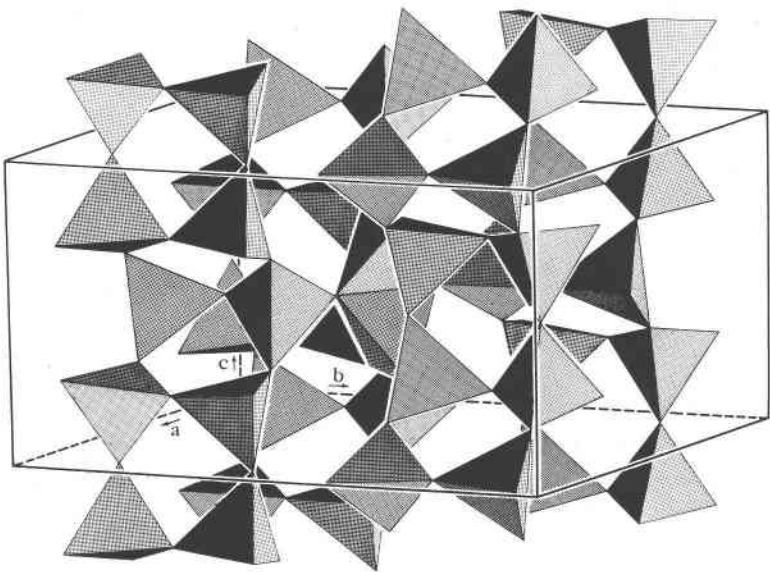
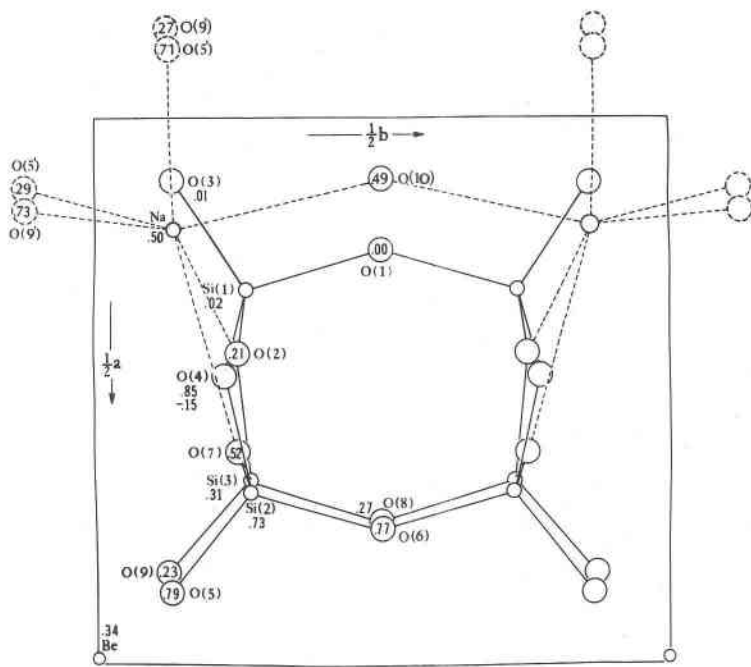FIG. 1. Polyhedral drawing of the crystal structure of epididymite (Na atoms omitted).

Fig. 2. The crystal structure of epididymite projected on (001). Numbers indicate fractional heights along *c*.

is quite similar to the single chain found in pectolite and wollastonite (Prewitt and Buerger, 1963) though different in that each is doubled by a mirror plane. The repeat distance of 7.33 Å in epididymite (3 tetrahedra along *c*) may be compared with 7.02 Å in pectolite and 7.70 Å in wollastonite. The structure, viewed normal to the chains, is shown in Figure 2. The silicate chains are joined by two edge-sharing Be tetrahedra (Fig. 3). The Be_2O_6 group shares corners with each of the three silicon tetrahedra, thereby connecting all four independent $[Si_6O_{15}]_\infty$ chains of the unit cell. Our Be–O(10) distance of > 3.5 Å negates the proposed $BeO_3(OH)$ tetrahedra of Pobedimskaya and Belov whose (OH) location is clearly incorrect as exemplified by their close (1.8 Å) approach of (OH) and O(1).

Selected interatomic distances are reported in Table 3. The Na atom has an irregular 7-fold coordination, rather than 8-fold as previously reported. There is good correlation of individual Si–O bond lengths with estimated bond valence (Tables 3 and 6). For example, the two shortest Si–O distances [Si(2)–O(5) and Si(3)–O(9)] involve the two oxygen atoms which have bond strength deficiencies. It is to be noted that the Si(2)–O
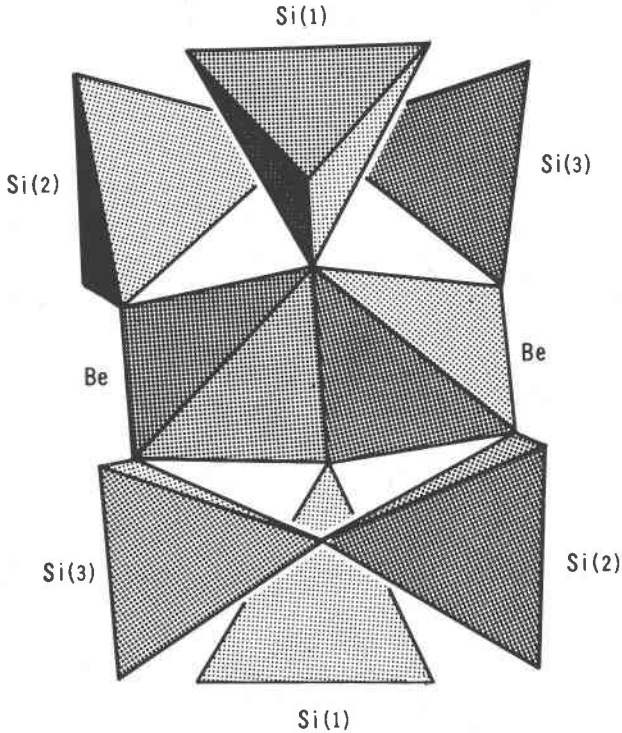
FIG. 3. Linkage of Si tetrahedra around the Be_2O_6 group (arbitrary orientation).

and Si(3)–O distances and angles are almost identical due to their analogous topological environment whereas the Si(1)–O distances are smaller. The Be_2O_6 group exhibits an extremely short O(3)–O(3') shared edge of 2.365 Å as well as a lengthening of the Be–O(3) bonds, obviously a result of the forces of repulsion acting between the two Be atoms.

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