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# REDETERMINATION OF THE CRYSTAL STRUCTURE OF EUDIDYMITE AND ITS DIMORPHIC RELATIONSHIP TO EPIDIDYMITE

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## ABSTRACT

Eudidymite, a dimorph of epididymite ($Na_2Be_2Si_6O_{15} \cdot H_2O$), crystallizes in space group $C2/c$ with $a = 12.63(1)$Å, $b = 7.38(1)$Å, $c = 14.02(1)$Å, $\beta = 103°43'(5)$ and $Z = 4$. The structure was solved by the symbolic addition method, with some difficulty due to pseudosymmetry. The full-matrix least-squares refinement yielded a final discrepancy factor of 0.080.

The structure is based on infinite double sheets of composition $[Si_6O_{15}]_\infty$, which are parallel to (001), thus producing the eminent {001} cleavage. The double sheets are formed by the "fusing" of the epididymite double–chains along the [100] direction. Individual double–sheets are bonded by interlayer Na and Be atoms.

The polymorphic transformation between the two structures is of the reconstructive type involving breakage of bonds and reorganization of cation and anion groups. The extremely high dehydration temperature is construed to be the temperature at which the Be–O bonds yield, thus allowing the trapped water molecules to escape.

## INTRODUCTION

Eudidymite and epididymite have been found only in the nepheline syenite pegmatites of Norway and Greenland (Beus, 1966). The minerals grow in cavities or in dense masses in the central portion of the zoned alkalic pegmatites and are associated with albite, neptunite, schizolite, and narsarsukite. Thus both dimorphs are products of the last stages of alkali metasomatism of the nepheline syenite pegmatites.

A structural scheme for eudidymite was first proposed by Ito (1947) based on $[Si_3O_8]_\infty$ chains. The inaccuracy of the Ito model was only partially rectified by Pobedimskaya and Belov (1962) who re–examined the structure and gave atomic coordinates on the basis of 108 $h0l$ ($R = 22$ percent) and 192 $h1l$ ($R = 24$ percent) reflections. Their paper gave no table of interatomic distances, no structure factors and only a sketchy description of the structure. Moreover, it contained two serious defects; the chemical formula given by them contained more oxygen than that shown by the chemical analysis and the structure could not be refined using their atomic coordinates.

Thus, a re–investigation was undertaken in order to correct these errors and also to explain the dimorphic relationship of the mineral with epididymite (Robinson and Fang, 1970). In addition, an attempt is made to interpret the extremely high dehydration temperature of the two minerals from the structural viewpoint.

## EXPERIMENTAL

The crystals of eudidymite were obtained from the U.S. National Museum, Smithsonian Catalogue No. 93082; locality, Langesundfiord, Norway. Precession photos and single-crystal diffractometer measurements gave the following information: $a = 12.63(1)$Å, $b = 7.38(1)$Å, $c = 14.02(1)$Å, $\beta = 103°43'(5)$, $Z = 4$ and space group $C2/c$ or $Cc$. The centrosymmetric space group $C2/c$ was confirmed by the structural refinement.

A cleavage fragment of mean dimension 0.20 mm was selected for intensity measurements with an automated Buerger diffractometer employing Ni-filtered CuK$\alpha$ radiation. Detailed procedures of data collection and reduction are given in a previous paper by Robinson and Fang (1969). No absorption correction was applied to the observed data; the corrections ($\mu = 76$ cm$^{-1}$) would have been 9 percent on a mean intensity value. Of the 1317 reflections collected, 991 symmetry independent non-zero reflections were used in the structure determination and refinement.

## DETERMINATION AND REFINEMENT OF THE STRUCTURE

As in the case of epididymite, attempts to refine the coordinates of Pobedemskaya and Belov proved futile.

Our initial effort with the symbolic addition procedure was unsuccessful. The difficulties encountered were the result of the paucity of interactions among the large $E$ values, making it necessary to accept interactions between *hkl*'s of low and high $E$ values from the outset. This, of course, led to less than desirable probabilities for the derived signs and symbols, thus engendering numerous contradictions and false solutions. After repeated trials, with different sets of origin-determining and starting reflections, we were able to determine what appeared to be reasonable symbols and signs for essentially all reflections with $E \geq 1.0$. Since there was no sign indications for the symbols, four $E$-maps with different sign conbinations were made, one of which revealed the correct structure.

From an initial $R$-index of 30.9 percent, the structure refined smoothly to 8.0 percent with individual isotropic temperature factors for all atoms, utilizing the RFINE full-matrix least-squares program of Finger (1969). A weighting scheme (Robinson and Fang, 1969) was then applied, resulting in only slightly smaller standard deviations and no improvement of the $R$ factor. The final atomic coordinates and temperature factors are given in Table 1; the observed and calculated structure factors appear in Table 2 which is on deposit.[1]

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[1] To obtain a copy of Table 2, order NAPS Document Number 01857. The present address is National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, New York 10022; and price $2.00 for microfiche or $5.00 for photocopies, payable in advance to CCMIC-NAPS. Check a recent issue of the journal for current address and price.

TABLE 1. ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR EUDIDYMITE[a]

| ATOM | $x$ | $y$ | $z$ | $B(\text{Å}^2)$ |
|---|---|---|---|---|
| Na | .0287(3) | .3405(5) | .9282(3) | 2.57(8) |
| Be | .1677(9) | .3228(12) | .4969(8) | 1.08(16) |
| Si(1) | .2038(2) | .0199(3) | .6416(2) | 0.76(4) |
| Si(2) | .2518(2) | .1027(3) | .8665(2) | 0.78(4) |
| Si(3) | .0297(2) | .0933(3) | .3618(2) | 0.82(4) |
| O(1) | .0732(5) | .0329(6) | .6266(4) | 1.07(10) |
| O(2) | .2401(5) | .1800(7) | .1152(5) | 1.49(11) |
| O(3) | .2410(5) | .1650(7) | .5715(4) | 1.19(10) |
| O(4) | .2368(5) | .4392(7) | .2447(5) | 1.65(11) |
| O(5) | .1549(4) | .4984(7) | .0558(4) | 1.16(9) |
| O(6) | .1292(5) | .0519(7) | .8755(4) | 1.12(10) |
| O(7) | 0 | .1732(10) | 1/4 | 1.51(14) |
| O(8) | .0526(5) | .2561(7) | .4373(4) | 1.31(10) |
| Ow | 0 | .4322(13) | 3/4 | 3.03(20) |

[a] Standard deviations in parentheses.

## DESCRIPTION OF THE STRUCTURE AND COMPARISON WITH THAT OF EPIDIDYMITE

A stereo pair of the structure of eudidymite is shown in Figure 1. The structure is based on double sheets of corner–sharing $SiO_4$ tetrahedra of composition $[Si_6O_{15}]_\infty$ (See also Fig. 2). The sheets are parallel to (001) and are thus responsible for the eminent {001} cleavage. The sheets are cross–linked by edge–sharing $Be_2O_6$ groups to form a complete three-dimensional framework structure characterized by low optical birefringence.

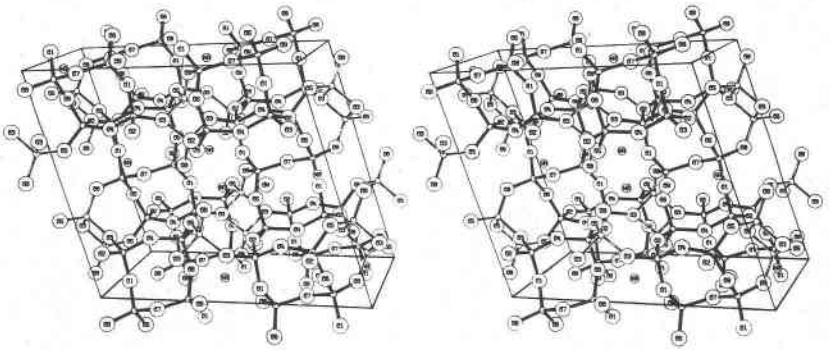

FIG. 1. Stereoscopic pairs of the crystal structure of eudidymite. The origin is at the lower left back corner with $a$ and $c$ in the plane of the paper. $+c$ is horizontal and to the reader's right, $+a$ is near vertical and $+b$ is emerging from the plane of the paper. The Be–O bonds are lightly shaded to distinguish them from the Si–O bonds.

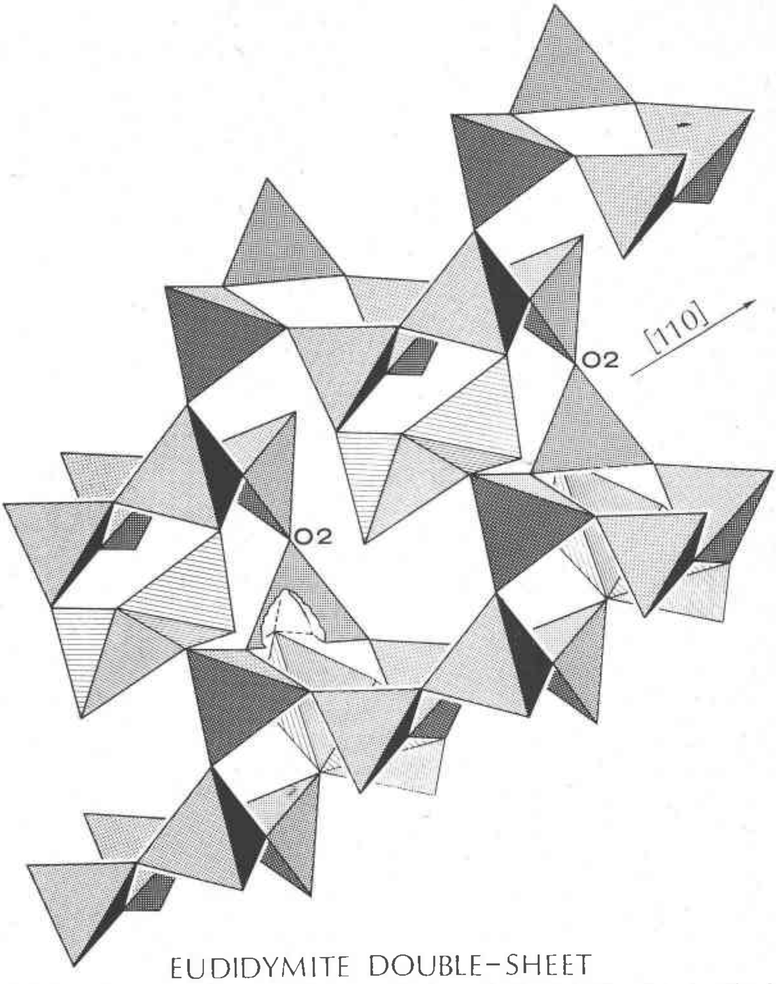

FIG. 2. A perspective polyhedral drawing of the eudidymite double-sheet which parallels (001). Stippled tetrahedra represent $SiO_4$ groups and ruled tetrahedra depict $BeO_4$ groups. The sharing of the "double chains" through O(2), in forming double sheets, can be clearly seen.

There are three crystallographically independent $SiO_4$ groups (Table 3) with one relatively short Si–O distance (below 1.600 Å) in each tetrahedron, precisely as in the epididymite structure. It is noted that O(3), O(5), and O(8) are all bridging oxygens to the Be tetrahedra. Also listed in Table 3 are the *T*–O–*T* angles in eudidymite. The preference of Si over Be in those tetrahedra with wide *T*–O–*T* angles and the dependence of *T*–O distances on *T*–O–*T* angles are clearly shown in the table (Brown, Gibbs, and Ribbe, 1969). Table 4 shows estimated bond valences as well as the various types of oxygen coordination. As expected, the values are essentially identical to those calculated for epididymite.

The polymorphic relationship between the two minerals can best be explained with the aid of two polyhedral drawings. Figure 3 shows a portion of one $[Si_6O_{15}]_\infty$ double–chain and associated $Be_2O_6$ groups in the epididymite structure. There are four of these double–chains in

Table 3. Interatomic Distances(Å) and Angles(degrees) in Eudidymite[a]

Tetrahedral coordination around Si

| | | | | | |
|---|---|---|---|---|---|
| Si(1)-O(1) | 1.616(6) | Si(2)-O(2) | 1.623(6) | Si(3)-O(1) | 1.639(6) |
| Si(1)-O(2) | 1.614(6) | Si(2)-O(4) | 1.629(7) | Si(3)-O(6) | 1.628(6) |
| Si(1)-O(3) | 1.597(6) | Si(2)-O(5) | 1.589(6) | Si(3)-O(7) | 1.633(3) |
| Si(1)-O(4) | 1.621(7) | Si(2)-O(6) | 1.628(6) | Si(3)-O(8) | 1.583(6) |
| Mean | 1.612 | Mean | 1.617 | Mean | 1.621 |
| O(1)-O(2) | 2.664(8) | O(2)-O(4) | 2.644(8) | O(1)-O(6) | 2.553(8) |
| O(1)-O(3) | 2.610(8) | O(2)-O(5) | 2.636(7) | O(1)-O(7) | 2.631(7) |
| O(1)-O(4) | 2.646(8) | O(2)-O(6) | 2.560(8) | O(1)-O(8) | 2.685(7) |
| O(2)-O(3) | 2.620(7) | O(4)-O(5) | 2.641(9) | O(6)-O(7) | 2.676(7) |
| O(2)-O(4) | 2.613(9) | O(4)-O(6) | 2.658(9) | O(6)-O(8) | 2.693(7) |
| O(3)-O(4) | 2.640(9) | O(5)-O(6) | 2.694(8) | O(7)-O(8) | 2.624(6) |
| Mean | 2.632 | Mean | 2.639 | Mean | 2.644 |
| O(1)-Si(1)-O(2) | 111.2(3) | O(2)-Si(2)-O(4) | 108.8(3) | O(1)-Si(3)-O(6) | 102.8(3) |
| O(1)-Si(1)-O(3) | 108.7(3) | O(2)-Si(2)-O(5) | 110.3(3) | O(1)-Si(3)-O(7) | 107.1(3) |
| O(1)-Si(1)-O(4) | 109.7(3) | O(2)-Si(2)-O(6) | 103.9(3) | O(1)-Si(3)-O(8) | 112.9(3) |
| O(2)-Si(1)-O(3) | 109.4(3) | O(4)-Si(2)-O(5) | 110.4(3) | O(6)-Si(3)-O(7) | 110.3(3) |
| O(2)-Si(1)-O(4) | 107.8(3) | O(4)-Si(2)-O(6) | 109.4(3) | O(6)-Si(3)-O(8) | 114.0(3) |
| O(3)-Si(1)-O(4) | 110.2(3) | O(5)-Si(2)-O(6) | 113.8(3) | O(7)-Si(3)-O(8) | 109.4(3) |
| Mean | 109.5 | Mean | 109.4 | Mean | 109.4 |

Tetrahedral coordination around Be

| | | | | | |
|---|---|---|---|---|---|
| | | O(3)-O(3') | 2.420(11) | O(3)-Be-O(3') | 92.4(6) |
| Be-O(3) | 1.687(11) | O(3)-O(5) | 2.699(7) | O(3)-Be-O(5) | 111.1(7) |
| Be-O(3') | 1.667(12) | O(3)-O(8) | 2.743(8) | O(3)-Be-O(8) | 114.5(6) |
| Be-O(5) | 1.586(10) | O(3')-O(5) | 2.746(8) | O(3')-Be-O(5) | 115.2(6) |
| Be-O(8) | 1.574(12) | O(3')-O(8) | 2.702(8) | O(3')-Be-O(8) | 112.9(7) |
| | | O(5)-O(8) | 2.587(8) | O(5)-Be-O(8) | 109.9(7) |
| Mean | 1.628 | Mean | 2.650 | Mean | 109.3 |

| T-O-T angles | | Coordination around Na | |
|---|---|---|---|
| Be-O(3)-Be | 87.6(6) | Na-O(1) | 2.632(6) |
| Be-O(8)-Si(3) | 126.3(5) | Na-O(5) | 2.398(7) |
| Be-O(5)-Si(2) | 126.7(5) | Na-O(5') | 2.661(7) |
| Si(1)-O(3)-Be | 130.3(5) | Na-O(6) | 2.671(6) |
| Si(1)-O(3)-Be' | 137.2(5) | Na-O(8) | 2.432(7) |
| Si(3)-O(7)-Si(3) | 137.6(5) | Na-O(8') | 2.992(7) |
| Si(1)-O(1)-Si(3) | 139.7(3) | Na-Ow | 2.530(5) |
| Si(1)-O(4)-Si(2) | 148.4(4) | Mean | 2.617 |
| Si(2)-O(6)-Si(3) | 149.8(4) | | |
| Si(1)-O(2)-Si(2) | 151.4(4) | | |

[a] Standard deviations in parentheses.

Table 4. Estimated Bond Valences (v.u.) in Eudidymite

| Anions | $^{iv}Si(1)$ | $^{iv}Si(2)$ | $^{iv}Si(3)$ | $^{vii}Na$ | $^{iv}Be$ | $\Sigma_C \upsilon$ | Chemistry | $\Sigma_C \upsilon$ corrected for H bonds |
|---|---|---|---|---|---|---|---|---|
| $^{iii}O(1)$ | .99 | | .96 | .13 | | 2.08 | $O^{2-}$ | 2.08 |
| $^{ii}O(2)$ | 1.00 | .99 | | | | 1.99 | $O^{2-}$ | 1.99 |
| $^{iii}O(3)$ | 1.03 | | | | .43<br>.45 | 1.91 | $O^{2-}$ | 1.91 |
| $^{iii}O(4)$ | .98 | .98 | | | | 1.96 | $O^{2-}$ | 2.03 |
| $^{iv}O(5)$ | | 1.06 | | .22<br>.13 | .56 | 1.97 | $O^{2-}$ | 1.97 |
| $^{iii}O(6)$ | | .98 | .99 | .13 | | 2.10 | $O^{2-}$ | 2.10 |
| $^{iii}O(7)$ | | | .97(*2) | | | 1.94 | $O^{2-}$ | 2.07 |
| $^{iv}O(8)$ | | | 1.08 | .21<br>.04 | .58 | 1.91 | $O^{2-}$ | 1.91 |
| $^{iv}O(9)$ | | | | .17(2*) | | 0.34 | $H_2O$ | .14 |
| Average bond length [Å | 1.612 | 1.617 | 1.621 | 2.617 | 1.629 | | | |
| (Å) $\Sigma_A \upsilon$ | 4.00 | 4.01 | 4.00 | 1.03 | 2.02 | | | |

$\Sigma_A \upsilon$ = valences of bonds emanating from cation summed over the bonded anions.

$\Sigma_C \upsilon$ = valences of bonds reaching anion.

the unit cell. Figure 4 features a corresponding portion of the eudidymite structure. In epididymite, individual double-chains are bonded only through interchain Be and Na atoms. The Be atoms are tetrahedrally coordinated to the chain oxygens in forming edge-sharing $Be_2O_6$ groups. Each $Be_2O_6$ group is bonded to all four double-chains in the unit cell. The disposition of the double chains and related $Be_2O_6$ groups gives rise to a mirror plane which passes through O(1), O(6), and O(8). However, in eudidymite (Fig. 4), the "double-chains" extend along [110] and one side of the "double chain" is broken at every third shared oxygen to accommodate a cross-linking $Be_2O_6$ group. If we consider only the silicate chains, O(3) and O(5) are shared in eudidymite but in epididymite these atoms merge into a single shared oxygen. Thus it may appear that eudidymite has two more unshared corners; however, O(2) of eudidymite is shared with an adjacent "double chain" while the corresponding oxygen of epididymite is unshared (*viz.* producing two unshared corners). Therefore, the net change in the number of shared corners in the two structures is zero. The sharing of the O(2) atom is wholly responsible for the formation of the double sheets (see Figs. 2 & 4) which characterize the eudidymite structure. Thus the transformation between the two structures is of the reconstructive type and demands a certain amount of rearrangement of Be and some oxygen atoms.

The unit cell volume difference between the two minerals is calculated to be 0.28 percent, eudidymite being more compact. However, the difference falls within the limit of the experimental error and, therefore, no conclusion regarding the paragenesis should be drawn from this. The "identical" cell volumes can easily be understood because of the identical coordination of every cation in the two structures and the close correlation between distances and angles. Since there is no field evidence suggesting the paragenetic relation of the dimorphs, the stability relation between them must await further studies of phase equilibria in this system.

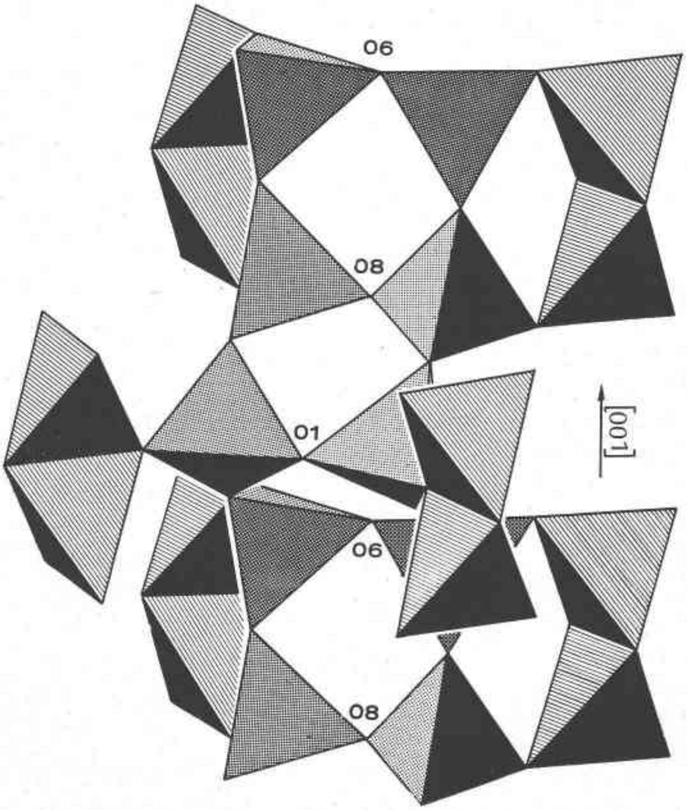

FIG. 3. A polyhedral representation of the $[Si_6O_{15}]_\infty$ double-chain of epididymite (stippled) and associated $Be_2O_6$ groups (ruled).

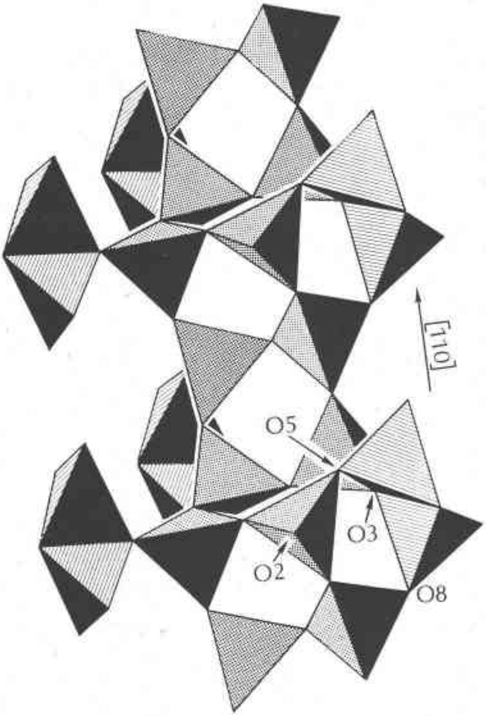

FIG. 4. A polyhedral drawing of a portion of the eudidymite "pseudo" double-chain (stippled) and associated $Be_2O_6$ groups (ruled). One side of the chain is regularly interrupted [see O(3) and O(5)]. The O(2) oxygen is shared with the next chain in forming a double-sheet which, if extended, would emerge from the plane of the paper.

## DEHYDRATION TEMPERATURE

The question of whether eudidymite (or epididymite) is a hydrated or hydroxyl silicate was discussed in our epididymite paper, in which we tentatively concluded that the structure contains $H_2O$ rather than OH, based on our bond valence calculations. Subsequently, a paper on the infrared and proton magnetic resonance study of epididymite was brought to our attention[1] (Stavitskaya *et al.*, 1967). The above cited paper confirmed the existence of water molecules in the structure. They attributed the high dehydration temperature (700 ~ 800°C) of epididymite (and eudidymite) to be the result of a covalent bond between Be and $H_2O$. However, their conclusion was based on the in-

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[1] The authors are indebted to I. I. Plyushina of Moscow State University who sent us a reprint after the publication of our epididymite paper.

correct Pobedimskaya and Belov structure which contained Be–$H_2O$ bonds. Since we have shown that Be is not bonded to $H_2O$, the explanation for the high dehydration temperature is still lacking.

In order to test the findings of Stavitskaya *et al.* concerning the presence of the $H_2O$ molecule, we took a near-infrared spectrum of eudidymite utilizing a Beckman DK–2 Ratio Reading Spectrophotometer. The spectra showed two distinct absorption bands at $1.4\mu$ and $1.9\mu$. According to Hunt and Salisbury (1970), the presence of both the $1.4\mu$ and $1.9\mu$ bands together is diagnostic of water molecules in the structure. The appearance of the $1.4\mu$ band without the $1.9\mu$ band would indicate that OH groups are present.

Thus, there is little doubt that both minerals are hydrated silicates, but how can one account for the unusually high dehydration temperature? In an attempt to explain this phenomenon, several drawings of the water environment were made and also a packing model of epididymite was constructed. (We thank Prof. G. Donnay for the suggestions.) It soon became obvious that the water is loosely situated in an inter–chain cavity and calculations showed that the dimensions of the apertures in the cavity walls are much too small to allow escape of the $H_2O$ molecule. Thus the water molecule is, in effect, locked in this cavity, even if the Na–$H_2O$ bonds are broken. However, since the Be–O bonds are weaker than those of the Si–O bonds, we believe that the "dehydration temperature" is actually the temperature at which the Be–O bonds yield and, consequently, the double chains which are linked together only by the $Be_2O_6$ groups may be titled with respect to each other, giving rise to large apertures, therefore permitting the water to escape from the structure. This postulate does not require breakage of Si–O bonds, all of which appear to be of equal strength; that is to say, there are no particular Si–O bonds which are more amendable to breakage than others. Similar reasoning may also be used to explain the dehydration of eudidymite.

Thus, we conclude that higher–than–usual dehydration temperatures cannot be taken for granted as an indication of the presence of hydroxyls.

## ACKNOWLEDGMENTS

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