The Structure of Epididymite ($HNaBeSi_3O_8$).

By

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(With 5 figures.)

Introduction.

Epididymite is the rhombic form of the dimorphous mineral of the composition $HNaBeSi_3O_8$, the other being monoclinic eudidymite. These crystals resemble one another and those of the felspar group. In addition to having similar chemical constitutions, these two groups of minerals are similar as regards cleavage. Whereas felspars have two perfect cleavage-faces (001) and (010), which are nearly at right angles to each other, epididymite is also perfectly cleaved along (001) and (100) and eudidymite along (001) and (110)[1]. This similarity led the writer to study the structure of epididymite, hoping to contribute to the elucidation of the structure of felspar, which at the time when he started the investigation was not yet definitely worked out[2]. The present paper gives the results of experimental work which, except for few additional photographs taken in this Institute, was done during his stay at Manchester in 1932.

1. Unit cell and space group.

The crystal specimens came originally from Greenland and were purchased from Dr. F. Krantz, Bonn am Rhein. They are colourless, transparent, tabular crystals parallel to (001) of dimensions up to 15 mm. From these crystals small cleavage pieces were made for examination.

The unit cell was found to be (Spectrometer measurements)

$$a = 12.63 \text{ Å}; \quad b = 7.32 \text{ Å}; \quad c = 13.58 \text{ Å}.$$

This gives for the axial ratio

$$a:b:c = 1.725:1:1.855$$

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1) Note the interfacial angle: (001) $\wedge$ (110) = 82° 59'. (Notation after Ch. Palache and others. vide: Z. Krist. **86**, 290. 1933.)

2) Since then W. H. Taylor's paper has appeared. Z. Krist. **85**, 425. 1933.

which agrees well with the ratio deduced crystallographically by G. Flink[1]) if the latter's c-axis is doubled.

There are eight molecules of $HNaBeSi_3O_8$ in the cell. The results of experimental work, in which oscillation photographs ($CuK\alpha$ and $MoK\alpha$ radiations) and ionization spectrometer measurements ($RhK\alpha$ radiation) were taken, indicate V_h^{16} as the only possible space group, reflexions $(h\,0\,l)$ being absent when h is odd and reflexions $(0\,k\,l)$ absent when $k+l$ is odd. This result agrees with that obtained by W. H. Zachariasen in 1929[2]). Fig. 1 shows certain essential symmetry elements of the space group. There are reflexion planes parallel to (001), and glide planes parallel to (100) and (010). There are two different sets of symmetry centres and three different sets of digonal screw axes.
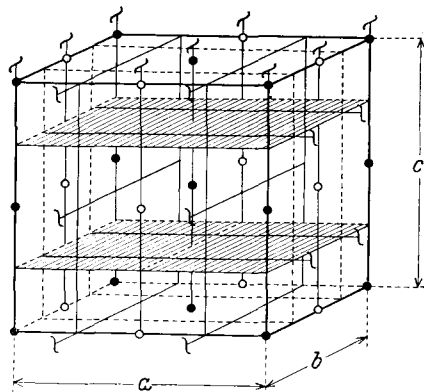

Fig. 1. Symmetry elements of the space group V_h^{16}. Small white and black circles represent centres of symmetry. Shaded planes represent reflexion planes.

An atom in the general position has eight equivalent positions. These reduce to four if the atom is either on the reflexion planes or on the centres of symmetry.

The intensity of reflexion for the plane (hkl) is proportional to the square of

$$F = \sum 8f \cos\left\{h\left(\frac{\pi}{2}+\theta_1\right)+\frac{\pi}{2}\left(k+l\right)\right\} \cos\left\{k\left(\frac{\pi}{2}-\theta_2\right)+\frac{\pi}{2}h\right\}$$
$$\cos l\left(\frac{\pi}{2}-\theta_3\right).$$

where f is the atomic scattering factor appropriate to each atom and the summation is to be taken over all atoms in the cell.

2. Analysis.

Since mineralogical data suggest that H atoms exist as OH groups in the crystal, we have to place, besides these eight OH groups, eight sodium, eight beryllium, twenty-four silicon and fifty-six oxygen atoms in

1) $a : b : c = 1.737 : 1 : 0.927$.

2) Norsk. geol. Tidsskr. **10**, 449. 1929.

the unit cell. With the methods of crystal analysis at our disposal it is not possible to determine directly the parameters of so many atoms, there being no symmetry restriction to put any of these atoms in special positions. However, we know now definitely that in silicates silicon and beryllium have each a coordination of four, while sodium has one of six or eight. It is further known that the OH group is usually associated with Be rather than with Si atoms. With this information at our disposal our first step in analysis would be to try to put in the unit cell various silicon-oxygen groups of linked SiO_4 tetrahedra as observed in other silicates, so that a silicon-oxygen arrangement of the composition Si_3O_7 is formed.
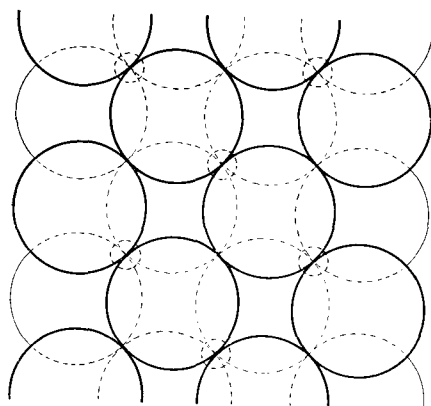

Fig. 2. Si_3O_8-chain. Large circles represent Oxygen atoms above and below the level on which silicon atoms (small circles) lie.

After several trials along these lines we chose instead as most probable the Si_3O_8 group of linked SiO_4 tetrahedra, of which the possibility in silicates has recently been pointed out by the present writer[1], and we examined whether it is not admissible in the structure in question.

A model of an arrangement corresponding to the Si_3O_8 group is reproduced in projection in Fig. 2. It should be imagined as continuing indefinitely both upwards and downwards and represents a complex chain composed of SiO_4 groups. Fig. 3 shows it as viewed from the direction of the chain. The chain is built up of two layers of oxygen atoms, a 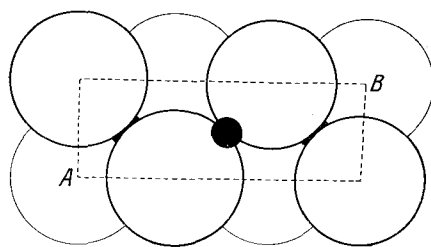silicon layer lying in the middle. Now assuming that oxygen has ionic radius of 1.3 Å the distance along the chain-direction of one oxygen atom to the next in the same layer is about 3.8 Å i. e. very nearly equal to half the length of b. Further, when projected on the plane perpendicular to the chain-direction the chain represents a

Fig. 3. Si_3O_8-chain as viewed from the chain-direction.

1) Pr. Imp. Acad. 9, 53. 1933.

rectangle, the diagonal distance of which (as marked A, B in Fig. 3) is about 5.8 Å i. e. nearly equal to half the length of a. We accordingly put the chain in a cell having V_h^{16} as the space group (in which the relative positions of symmetry elements and parametral axes are the same as specified in Fig. 1), so that the chain-direction becomes parallel to
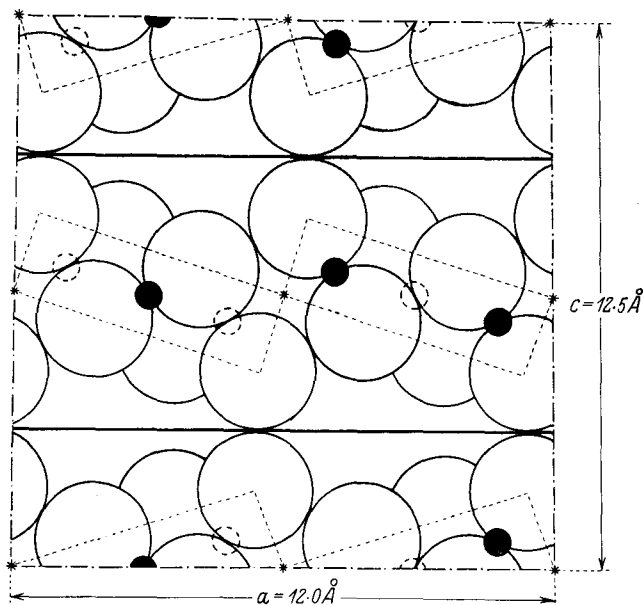

Fig. 4. Showing way in which Si_3O_8-chain are arranged in V_h^{16}. Projection on (010) or on the plane perpendicular to the chain-direction. Strong full-lines represent the traces of reflexion planes parallel to (001).

the b-axis and the points A, B lie at the centres of symmetry. The symmetry properties of the space group V_h^{16} operate then automatically and result in the formation of an arrangement illustrated in Fig. 4. If we assume that oxygen atoms are closely packed the unit cell would have the following dimensions:

$$a = 12.0 \text{ Å}; \quad b = 7.6 \text{ Å}; \quad c = 12.5 \text{ Å}.$$

It is clear that such an insertion of the chain Si_3O_8 in the cell is compatible with the space group V_h^{16} and with the dimensional relations of the unit cell of epididymite. We see moreover that a sheet is formed of Si_3O_8 groups joined side by side and has the composition Si_3O_7, two chains holding bordering oxygen atoms in common. Finally around the centres of symmetry we have spaces surrounded by six oxygen atoms where sodium atoms can be placed.

Table I. Coordinates of atoms in decimal fractions of the axial lengths. The origin is placed at a centre of symmetry.

Kind of Atom	Number in the Cell	x/a	y/b	z/c
O_I	8	.040	.0	.145
O_{II}	8	.040	.500	.145
O_{III}	8	.0	.250	.010
O_{IV}	8	.167	.0	— .040
O_V	8	.167	.500	— .040
O_{VI}	8	.182	.250	.130
O_{VII}	8	.318	.250	— .130
Si_I	8	.065	.200	.060
Si_{II}	8	.435	.200	— .060
Si_{III}	8	.335	.250	0
Na_I	4	0	0	0
Na_{II}	4	0	.50	0
Be	8	.035	.250	.052
OH_I	4	— .155	.150	.250
OH_{II}	4	.041	.250	.250

Table II. Intensity (ϱ) of Spectra. Measurements with the ionization spectrometer. ($RhK\alpha$ radiation 0.614 Å.)

Indices	Sin θ	$\varrho \times 10^6$	$F_{obs.}$	$F_{calc.}$
(020)	.0839	30.3	68	120
(040)	.1678	242.0	289	338
(060)	.2518	20.2	109	106
(080)	.3357	2.7	46	41
(10,00)	.4197	5.6	79	49
(200)	.0487	90.0	92	154
(400)	.0973	120.0	154	170
(600)	.1459	5.5	41	44
(800)	.1946	12.0	69	88
(10, 00)	.2433	23.6	111	114
(12, 00)	.2919	27.3	135	126
(14, 00)	.3405	—	—	4
(16, 00)	.3893	3.3	55	94
(18, 00)	.4379	—	—	25
(004)	.0905	198.0	191	141
(006)	.1359	64.0	136	81
(008)	.1807	56.0	143	99
(0010)	.2262	58.0	168	107
(0012)	.2714	6.1	62	23
(0014)	.3167	23.0	128	113
(0016)	.3618	21.8	135	129
(0018)	.4073	5.6	75	64

Since this ideal arrangement explains a number of spectra, we assume it to represent the fundamental framework of the structure of epididymite. We have now to place the remaining *Be* atoms and *OH* groups in the appropriate positions and, considering the dimensional relations of the unit cell and ionic radii, adjust the positions until the experimental data are satisfactorily explained.

In Table I we give the coordinates of atoms in the structure arrived at. In Table II are given the results obtained with the ionization spectrometer (*RhKα* radiation). The *F* values of $h00$, $0k0$ and $00l$ spectra were obtained from reflexions from the face (100), (010) and (001) respectively. In Table II are also given the structure factors calculated for the structure proposed.

The agreement between these and the experimental values, considering the number of parameters involved, is satisfactory. Nevertheless, the parameters given are to be considered as only tentative ones. The atoms must be displaced somewhat from the positions given in Table I.

The amount of displacement will be slight but not negligible as suggested by the discrepancy between the observed intensities from rotation photographs and calculated structure factors of the following cross-spectra, thus

	Intensity estimated	$F_{calc.}$
(110)	medium strong	0
(220)	week	64
(330)	nil	0
(440)	strong	80

No further attempt was made, however, to adjust the positions of atoms so that a better agreement between experimental and calculated values might be secured. Such an attempt would be extremely laborious in view of the many degrees of freedom of atoms in the structure. The results already obtained may be considered sufficient to establish the structure in its main features.

3. The structure.

The structure is shown in Fig. 5. It is a schematic representation projected on (010).

The structure is built up of the complex chains Si_3O_8, stretched parallel to the *b*-axis. The chain may be expressed by the constitutional formula such as,

10*

or $[SiO_3 \cdot SiO_2 \cdot SiO_3]^{4-}$.
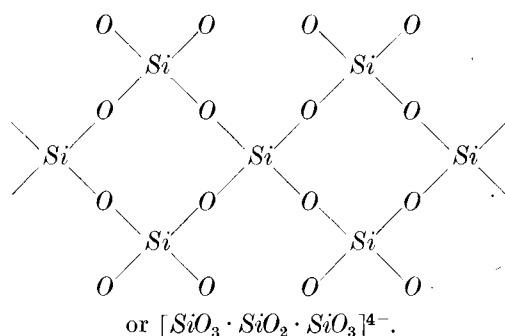
Pairs of these chains are joined side by side holding in common one half of the unsaturated oxygen atoms on the borders. The remaining similar oxygen atoms are linked by sodium atoms, which are surrounded by two such oxygen atoms and four others. These linked chains can now be regarded as forming sheets lying parallel to (001). The sheets have the composition $NaSi_3O_7$ and are heaped one upon another, linked up by beryllium atoms, which are in the centres of tetrahedra formed of two oxygen atoms and two OH groups. It is noticeable that chains are formed of these Be atoms with O atoms and OH groups, also stretched parallel to the b-axis.

In the structure thus built up Si atoms are surrounded by four O atoms, Be by two O atoms and two OH groups arranged nearly in tetra-hedral fashion, while Na atoms are at the centre of more or less distorted octahedra formed of O atoms. Each O atom is shared either by two Si
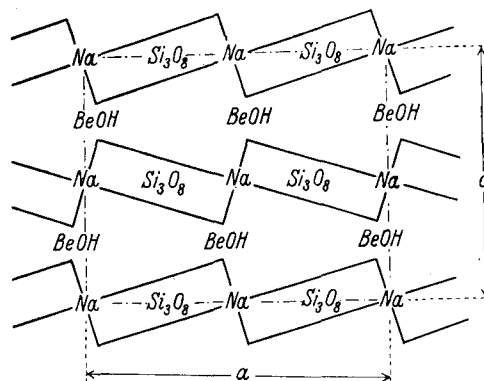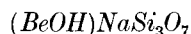

Fig. 5. Schematic representation of the structure of Epididymite projected on (010), to show how Si_3O_8-chains, represented by rectangles as in Fig. 3, are held together by Na atoms to form sheets, which in turn are linked together by Be atoms and OH groups to build up the structure.

atoms or one Si and two Na atoms or one Si, one Na and two Be atoms, while each OH group is shared by two Be atoms.

The structure will explain the two-directional perfect cleavage of epididymite. The very perfect cleavage along (001) is parallel to the sheets formed of the chains Si_3O_8 linked only by Be atoms and OH groups. The other perfect cleavage is along (100) and parallel to the planes lying inbetween and linking up two chains Si_3O_8.

The structural aspect of epididymite can be represented by the formula
$$(BeOH)NaSi_3O_7$$
or, giving an expression to the stereochemical aspect of the chain structure[1]), by the formula
$$(BeOH)_2Na_2(Si_2O_5Si_2O_4Si_2O_5).$$
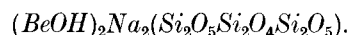
The structural relation of epididymite to eudidymite will be discussed in a paper to follow[2]).

In conclusion the writer wishes to express his sincere thanks to Prof. W. L. Bragg, F. R. S., for his constant encouragement and advice so generously given to him during his recent stay at Manchester. The writer's best thanks are also due to Dr. J. West, who has given him many valuable suggestions throughout the course of the experimental work.

Summary.

The structure of Epididymite ($HNaBeSi_3O_8$) has been determined by X-ray analysis using oscillation photographs ($CuK\alpha$ and $MoK\alpha$ radiations) and the ionization spectrometer ($RhK\alpha$ radiation).

The space group is V_h^{16} and the unit cell has dimensions $a = 12.63$ Å, $b = 7.32$ Å, $c = 13.58$ Å, containing eight molecules of $HNaBeSi_3O_8$. The structure is characterised by the presence of Si_3O_8 chains stretched parallel to the b-axis. The chains are linked up into sheets, two chains holding in common one half of the oxygen atoms on their fringe. The sheets thus formed are again joined one to another by $Be \cdot OH \cdot O$ chains, also stretched parallel to the b-axis. Na atoms are incorporated in the structure in such positions as to join the complex chains Si_3O_8 into sheets having the composition $NaSi_3O_7$.

1) Vide a discussion by P. Niggli, Z. Krist. **86**, 136. 1933.
2) Pr. Imp. Acad. **9**, 528. 1933.

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