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CRYSTAL STRUCTURE OF ELPIDITE, $Na_2Zr[Si_6O_{15}]\cdot 3H_2O$

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The two-storied three-membered oxygen–silicon rings of formula $[Si_6O_{15}]$ which have been suggested for pseudohexagonal elpidite, $Na_2Zr[Si_6O_{15}]\cdot 3H_2O$ (on analogy with the strictly hexagonal catapleite, $Na_2Zr[Si_3O_9]\cdot 2H_2O$), have been unrolled and joined together as a result of x-ray structure analysis into infinite $[Si_{4+2}O_{15}]_\infty$ ribbons, in which two $[Si_{2+1}O_9]_\infty$ wollastonite chains are joined together "flatwise." These ribbons were first discovered four years ago in epididymite. The double oxygen–silicon chains present are the reason for the close relationship between elpidite and the amphiboles; this is shown in its acicular habit, cleavage along the pseudohexagonal prism, and positive optical sign.

The structure of this orthorhombic Na zirconium silicate, with a dimetasilicate Si : O ratio of 2 : 5, was solved by us[*] and described [1] in a centrosymmetric approximation within the space group Pbmm:

$$a = 7.4,\ b = 14.4,\ c = 7.05\ \text{Å},\ Z = 2\ (\text{s.g.}\ \ 2.615).$$

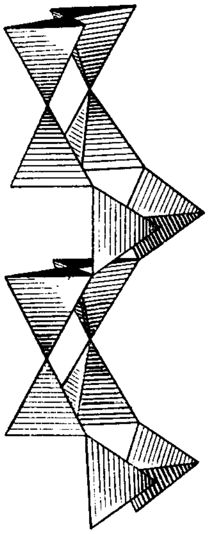

Fig. 1. An epididymite ribbon, $[Si_{4+2}O_{15}]_\infty$, as the product of condensing two $[Si_{2+1}O_9]_\infty$ chains related by a longitudinal plane of symmetry.

The most characteristic feature of the silicate structural arrangement was the "epididymite" ribbon [3], two tetrahedra wide and with a repeat distance along the axis of three tetrahedra, giving a "link" consisting of a 2 × 3 block (Fig. 1).[†] The discrete $[Si_{4+2}O_{15}]_\infty$ ribbons lie in ranks parallel to (100) in such a way that along [100] all the "odd" members face in the opposite direction to the "even" members (Fig. 2). They are inverted by the twofold axis of rotation passing between the ribbons, and also by the glide plane (100) = b, in which these ribbons lie. The unit cell constant a = 7.4 A corresponds to one such rank (or "wall") of the oxygen–silicon ribbons, which are connected both to one another and to the Zr octahedra lying between the walls; these octahedra lie on "derived" twofold axes passing between the walls in the unit cell, on the "median" derived glide plane b' (see diagram of space group Pbm2 in Fig. 3).

The Zr octahedra and the oxygen–silicon ribbon together make up a three-dimensional anionic framework. Between the Zr octahedra, in both the

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[*] From material donated by E.I. Semenov, one of the first discoverers of this mineral in the USSR.

[†] These ribbons (Fig. 1), discovered (in 1959) in the Be silicate epididymite [3], were described as wollastonite chains [4] related in pairs by a plane of symmetry in such a way that the chains lay "flatwise," sharing one O atom from each Si tetrahedron, $2[Si_{2+1}O_9] - 3O = [Si_{4+2}O_{15}]$, unlike the situation in the xonotlite ribbon [4], where only every third Si tetrahedron takes part in the pairing of two wollastonite chains.

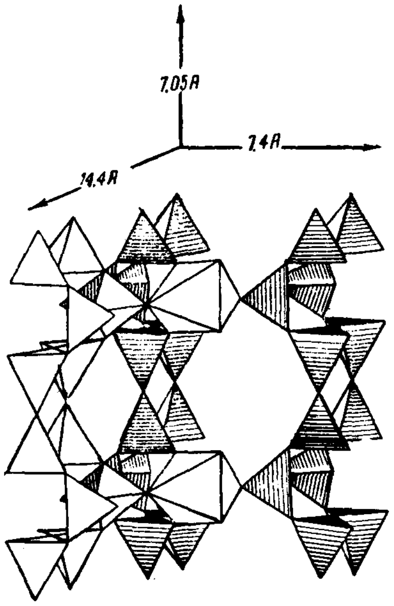

Fig. 2. Structure of elpidite. The anionic framework consists of epididymite ribbons in two orientations, connected by Zr octahedra. The light ribbons are in the foreground along the axis b = 14.4 A and the shaded ribbons are in the background.

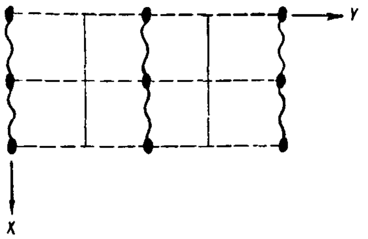

Fig. 3. Diagram at the space group Pbm2, with two nonequivalent glide planes (100): b and b'.

vertical direction (parallel to the c axis) and the horizontal (parallel to the b axis), lie twice the number of Na cations; on the twofold axes in large, somewhat deformed octahedra, and on the vertical symmetry planes in the simplest type of seven-cornered figure (heptaverticon) is a trigonal prism with a semioctahedron on one of the square faces. All the corners of the Na polyhedra which are not joined to silica are occupied by H_2O molecules of two types.

The first structural model was obtained by the use of the heavy Zr atom, which was of great value in the three-dimensional Patterson synthesis, which was based on a massive set of about 1000 reflections from 0kl, hk0, hk$l$ (l = 1-5).

After having fixed the positions of the heavier Zr and Si atoms only, we obtained from yz and xy Fourier patterns all the other maxima which did not contradict the suggested model and which were identified as O or Na atoms or H_2O molecules. The pattern was spoiled only by two peaks on the yz projection, corresponding firstly to unresolved O_{IV} and Na_I, and secondly to the molecule $(H_2O)_I$ (Fig. 4). Both peaks showed "creep" and were bifurcated by the mirror plane perpendicular to the twofold axis in the Pbmm space group.‡

In the subsequent stages of the analysis all the atoms were used in constructing electron density projections, whereupon the positions of O_{IV}, Na_I, and $(H_2O)_I$ were improved, as follows: they were placed in twofold positions on the twofold axes on the lines of intersection of the two mirror planes (in the group Pbmm). However, the corresponding maxima, while remaining in the plane of symmetry perpendicular to the y axis, invariably moved off the other mirror plane into a fourfold position. Putting half the Na and O atoms in each of these positions, we carried out a series of Fourier syntheses, resulting in the table of coordinates given in [1]. The reliability factors turned out to be the same for both the xy and yz projections. They were equal to about 24% (without taking the zero reflections and temperature factor into account). The

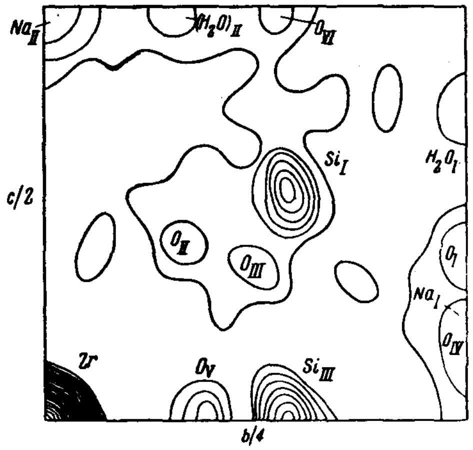

Fig. 4. Elpidite. Projection of electron density on yz (1/4 unit cell) in the centrosymmetric approximation (space group Pbmm).

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‡ The molecules $(H_2O)_I$ and $(H_2O)_{II}$ in Tables 1 and 2 of [1] were denoted by O_{VII} and O_{VIII}.

discrepancy over the H_2O molecules, with the a priori small probability of finding them in the two mirror planes, forced us to assume that there was no true mirrorplane perpendicular to z in the elpidite structure, but only a pseudoplane, so that the symmetry was lowered to Pbm2. To fix the coordinates in this more flexible version of the structure, the method of least squares was used (the refining was carried out on a BÉMS computer using Brusentsev's program [5]). Figure 5 shows a contour map of the electron density projection on yz for a quarter of the unit cell. The plane of pseudosymmetry relates the peaks Si_I, O_I, O_{II}, and O_{III} to the peaks marked Si_{II}, O_{VII}, O_{VIII}, and O_{IX}, respectively. The peaks Na_I and $(H_2O)_I$ do not have mirror "reflections."

The coordinates listed in Table 1 were averages from projections on yz and xy and from three-dimensional electron density syntheses. The reliability factors, after introducing the isotropic factors β, taking the thermal movement of the atoms into account in the calculation of least squares and also considering the systematic error in the measurement of the intensities, fell to the values R_{0kl} = 14.5%, R_{hk0} = 15.6%, R_{hkl} = 20.7%. The average values for β, evaluated by Wilson's method, were taken as $\beta_{xy0} = 0.49$ and $\beta_{xyz} = 0.4$ for all atoms. In the yz projection the values of β were found for individual atoms; they varied from 0.2 to 2.0.

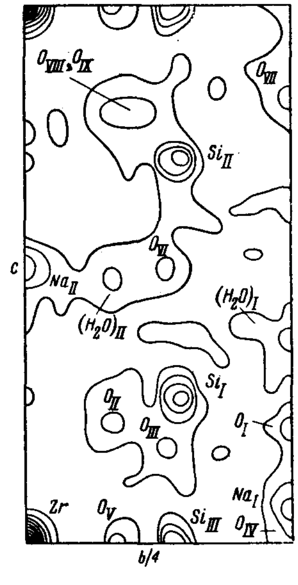

Fig. 5. Elpidite. The same projection (¼ unit cell) in the noncentrosymmetric approximation (space group Pbm2).

TABLE 1. Coordinates of the Principle Atoms in the Elpidite Structure

Atom	100x/a	100y/b	100z/c
Zr (2)	0	0	0
Si_I(4)	27	15	25
Si_{II}(4)	29	14	71
Si_{III}(4)	59	14	0,2
O_I (2)	24	25	23
O_{II}(4)	10	8	23
O_{III}(4)	48	12	16
O_{IV}(2)	63	25	3
O_V (4)	78	9	1
O_{VI}(4)	30	13	52
O_{VII}(2)	22	25	82
O_{VIII}(4)	14	8	81
O_{IX}(4)	47	12	79
$(H_2O)_I$(2)	87	25	37
$(H_2O)_{II}$(4)	72	8	49
Na_I (2)	97	25	8
Na_{II} (2)	0	0	51

From the viewpoint of "second-chapter" silicate crystal chemistry [4], the architectural basis of the elpidite structure is a layer parallel to the x = 0 plane (in our description), which is made up of Zr octahedra and twice as many Na polyhedra (Fig. 6).** Between the two adjacent "heavy" layers of this type lies a "reinforcement" (Figs. 2 and 7) of infinite oxygen–silicon ribbons arranged so that the large Na polyhedra in both directions match up with (are "commensurable" with) vertical and horizontal Si_2O_7 diorthogroups slightly protruding from the ribbons, while each Zr octahedron is the same height as one third of a link of the ribbon of SiO_4 tetrahedra.

The "seventh" H_2O molecule in the polyhedron around Na_I, and also the pair of H_2O molecules around Na_{II}, each of which is bound to a single Na atom (see Table 2 for the balance of valences) provide a satisfactory explanation for the zeolitic character of elpidite.

The interatomic distances in elpidite are shown in Table 3.

Due to the loss of the solitary satisfactory crystal fragment of elpidite (cf. [2] concerning the mass of twinned material), we have as yet been unable to obtain more precise values of the unit cell

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**In the description of Fig. 2, our attention was focused on the glide plane along which the oxygen–silicon ribbons are placed. In a general description of the structure, it is natural to place the origin at the Zr atom, which lies at a pseudocenter of symmetry on the other glide plane, on which the Na atoms also lie together with the entire heavy layer of large cations. The oxygen-silicon "reinforcement" lies, of course, in the "second" glide plane (100).

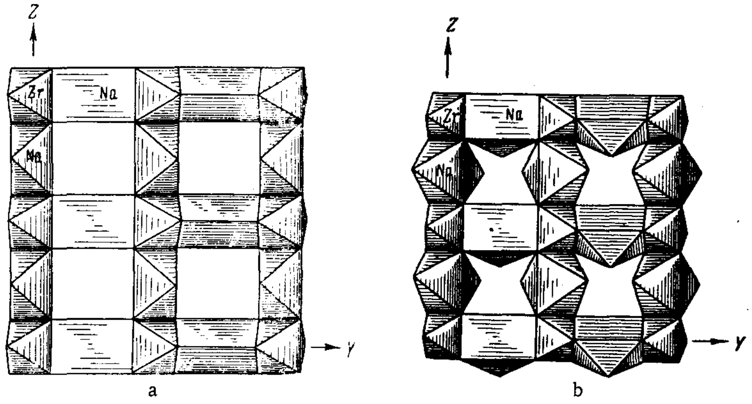

Fig. 6. Structure of elpidite. The architecture is based on heavy "walls" of Zr octahedra and two types of Na polyhedra. a) The idealized case without the seventh H_2O molecule; b) the actual case with the seventh zeolitic molecule.

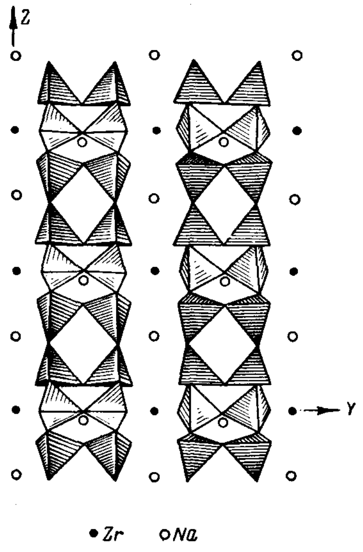

Fig. 7. Structure of elpidite. The silicate reinforcement of parallel but oppositely orientated epididymite ribbons (at the same level $x = \frac{1}{2}$) which packs out the basic layers of cation polyhedra (on the level $x = 0$).

constants, and to provide sufficiently accurate values of the atomic coordinates and interatomic distances (Tables 1 and 3).

Being a chain (ribbon) silicate with a predominance of vertical columns of Zr octahedra and Na polyhedra, elpidite has the typical positive optical sign and tendency to form needles of the amphibole type with a generally prismatic habit, with striations parallel to the c axis along the appropriate faces. As the axial ratio is $a : b \approx 1.9$, it is fair to call the crystals pseudohexagonal (of prismatic habit). The cleavage (110), as in amphiboles, cuts off one oxygen–silicon ribbon. Since the bond between the ribbons is provided by the highly charged Zr^{4+} ion, the corresponding fracture is uneven and hackled [2].

The same basic mineralogical article [2] provides a certain amount of support for the closeness of elpidite, $Na_2Zr[Si_6O_{15}] \cdot 3H_2O$, to catapleite, $Na_2Zr[Si_3O_9] \cdot 2H_2O$ [6]. The relationship expected had to be of the same type as that relating beryl, $Be_3Al_2[Si_6O_{18}]$, to milarite, $K(Be_2Al)Ca_2 \cdot [Si_{12}O_{30}]$ [4]. The former is characterized by single-storied six-membered oxygen–silicon rings, while the latter has similar rings, but they are two-storied. With a completely identical cationic part (Na_2Zr) the three-membered catapleite ring $[Si_3O_9]$ should correspond to a similar, but two-storied, $[Si_6O_{15}]$ elpidite ring. We persistently searched for this ring in the (001) projection until the three-dimensional Patterson synthesis unrolled it into a ribbon–the double chain depicted in Fig. 8. It was therefore particularly pleasant to note epididymite among the paragenetic minerals of elpidite, since this was the mineral in which the double $[Si_6O_{15}]_\infty$ chain was first located.

As noted in [2], an elpidite grain is to a large extent made up of polysynthetic twins. This twinning may apparently be connected with the naturally insufficient supply of Zr in the forming crystal, which forces the oxygen–silicon chains along (100) into direct contact with one another. If, in such a case, a bond is formed between the protruding third tetrahedron in each link, this gives the eight-membered ring so characteristic of the structures of feldspars, in particular albite, a mass of which

TABLE 2. Balance of Valences in the Elpidite Structure

O, H_2O	Si_I	Si_I^*	Si_{II}	Si_{II}^*	Si_{III}	Si_{III}^*	Zr	Na_I	Na_{II}	Σ
O_I	$^4/_4$	$^4/_4$								2
O_{II}	$^4/_4$						$^4/_6$	$^1/_7$	$^1/_6$	$1^{41}/_{42}$
O_{III}	$^4/_4$				$^4/_4$					2
O_{IV}					$^4/_4$	$^4/_4$				2
O_V					$^4/_4$		$^4/_6$	$^1/_7$		$1^{34}/_{42}$
O_{VI}	$^4/_4$		$^4/_4$							2
O_{VII}			$^4/_4$	$^4/_4$						2
O_{VIII}			$^4/_4$				$^4/_6$	$^1/_7$	$^1/_6$	$1^{41}/_{42}$
O_{IX}			$^4/_4$							2
$(H_2O)_I$					$^4/_4$			$^1/_7$		$^1/_7$
$(H_2O)_{II}$									$^1/_6$	$^1/_6$

TABLE 3. Interatomic Distances in Elpidite (in A)

Zr-octaverticon

$Zr - O_{II} = 2.1\ (1)$
$- O_{VIII}^* = 2.0\ (7)$
$- O_V = 2.0\ (6)$

$O_{II} - O_{II}^* = 2.6\ (9)$
$- O_V = 2.8\ (2)$
$- O_V^* = 2.9\ (7)$
$- O_{VIII}^* = 2.9\ (9)$

$O_V - O_{VIII}^* = 3.0\ (1)$
$- O_{VIII}^{**} = 2.9\ (4)$
$O_{VIII}^* - O_{VIII}^{**} = 3.1\ (4)$

Na-heptaverticon

$Na_I - O_{II} = 2.8\ (9)$
$- O_V = 2.7\ (2)$
$- O_{VIII}^* = 3.3\ (4)$
$- (H_2O)_I = 2.1\ (8)$

$O_{II} - O_{II}^* = 3.4\ (6)$
$- O_V = 2.8\ (2)$
$- O_{VIII}^* = 2.9\ (9)$
$- (H_2O)_I = 3.2\ (1)$

$O_V - O_V^* = 3.2\ (1)$
$- O_{VIII}^* = 3.0\ (1)$
$- (H_2O)_I = 3.4\ (8)$
$O_{VIII}^* - O_{VIII}^{****} = 3.3\ (4)$

Na-octaverticon

$Na_{II} - O_{II} = 2.3\ (9)$
$- O_{VIII} = 2.6\ (1)$
$- (H_2O)_{II} = 2.3\ (9)$

$O_{II} - O_{II}^* = 2.6\ (9)$
$- O_{VIII} = 4.0\ (8)$
$- (H_2O)_{II} = 3.3\ (9)$
$- (H_2O)_{II}^* = 3.1\ (9)$

$O_{VIII} - O_{VIII}^{***} = 3.1\ (4)$
$- (H_2O)_{II} = 3.8\ (3)$
$- (H_2O)_{II} = 3.4\ (1)$

Si_I-tetrahedron

$Si_I - O_I = 1.4\ (9)$
$- O_{II} = 1.6\ (1)$
$- O_{III} = 1.7\ (1)$
$- O_{VI} = 1.9\ (4)$

$O_{II} - O_{II}^* = 2.6\ (9)$
$- O_{III} = 2.6\ (5)$
$- O_{VI} = 2.6\ (5)$

$O_{II} - O_{III} = 2.8\ (7)$
$- O_{VI} = 2.6\ (4)$
$O_{III} - O_{VI} = 2.8\ (6)$

Si_{II}-tetrahedron

$Si_{II} - O_{VII} = 1.7\ (6)$
$- O_{VIII} = 1.5\ (2)$
$- O_{IX} = 1.5\ (3)$
$- O_{VI} = 1.4\ (3)$

$O_{VII} - O_{VIII} = 2.4\ (9)$
$- O_{IX} = 2.6\ (1)$
$- O_{VI} = 2.7\ (9)$

$O_{VIII} - O_{IX} = 2.5\ (6)$
$- O_{VI} = 2.4\ (9)$
$O_{IX} - O_{VI} = 2.3\ (3)$

Si_{III}-tetrahedron

$Si_{III} - O_{III} = 1.4\ (3)$
$- O_{IV} = 1.6\ (1)$
$- O_V = 1.6\ (1)$
$- O_{IX}^* = 1.7\ (2)$

$O_{III} - O_{VI} = 2.4\ (3)$
$- O_V = 2.5\ (1)$
$- O_{IX}^* = 2.5\ (6)$

$O_{IV} - O_V = 2.5\ (7)$
$- O_{IX}^* = 2.7\ (1)$
$O_V - O_{IX}^* = 2.8\ (1)$

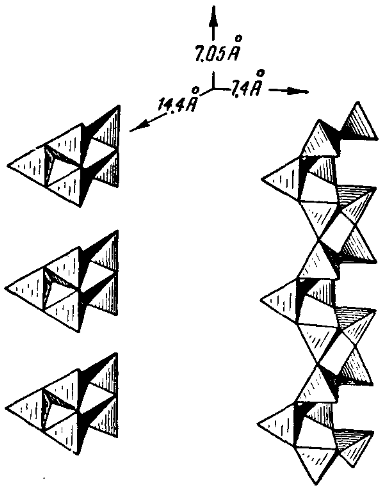

Fig. 8. The unrolling of a rank of two-storied three-membered $[Si_{3+3}O_{15}]$ rings to form an elpidite (epididymite) ribbon of the same formula.

always surrounds a grain of both elpidite and epididymite.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.