

# The Crystal Structure of Brewsterite, (Sr, Ba, Ca) (Al<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>) · 5H<sub>2</sub>O

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The crystal structure of brewsterite, ((Sr, Ba, Ca) (Al<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>) · 5H<sub>2</sub>O;  $P2_1/m$ ;  $a=6.77$ ,  $b=17.51$ ,  $c=7.74$  Å  $\pm 0.05\%$ ;  $\beta=94^\circ 18'$ ) was determined by 3-D least-squares methods. The aluminosilicate framework is not in any obvious way related to those of other zeolite structures. Layers of tetrahedra formed from linked 4-, 6- and 8-membered rings are cross-linked by additional tetrahedra to produce a framework containing many tilted 5-membered rings. There are two sets of intersecting channels each defined by 8-membered rings. The strontium atom lies near the intersection of the channels in contact with five water molecules and four slightly more distant oxygen atoms. The nearest neighbour to each water molecule is a strontium atom: water molecules and oxygen atoms are found in irregular numbers and at variable distances to give a coordination number of 4 to 7 depending on the cut-off. Distances are consistent with full occupancy of Si in one tetrahedron and random occupancy of 2Si and 1Al in the other three tetrahedra. The single tetrahedron is the most distant from the Sr atom.

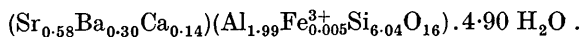
## Introduction

The structure of brewsterite was determined for two reasons: first, as part of a comprehensive study of zeolite structures in this and other laboratories in order to classify them on the basis of their aluminosilicate frameworks (see review by Smith, 1963), and secondly, to obtain information on the environment of the water molecules and exchangeable cations with the aim of delineating the nature of the bonding forces between the adsorbed molecules, cations, and the aluminosilicate framework.

Brewsterite is a rare zeolite occurring in cavities of basaltic rocks. Strunz & Tennyson (1956) have studied material from the type locality at Strontian, Argyll, Scotland, and determined the chemical composition, the cell dimensions and the powder diffraction pattern. Brewsterite has one dominant cleavage and belongs to the group of lamellar zeolites.

## Experimental

Crystals from the type locality were obtained by courtesy of Dr. D. W. Breck of the Linde Company, and can be expected to be similar to those studied by Strunz & Tennyson. Their analysis yields the formula



The physical properties were similar to those quoted in Winchell & Winchell (1951) except for a change of axes. The crystals are monoclinic with a dominant {010} cleavage and elongated along the  $x$  axis. The optical orientation is  $Z=y$  and  $\widehat{X}x=22^\circ$  in the obtuse angle. Although twinning is extremely frequent, verging on the submicroscopic for many crystals, it was possible to select a fragment, optically untwinned, of dimensions 0.2 mm along  $x$ , 0.15 mm along  $z$  and

0.1 mm along  $y$ . Single-crystal X-ray photographs gave no evidence of twinning, and the systematic absences indicated the space group to be  $P2_1$  or  $P2_1/m$ . Accurate cell dimensions were obtained from a least-squares refinement of powder data collected on a diffractometer calibrated with an internal spinel standard. The indexed powder pattern has been submitted to the Powder Diffraction File, and the parameters derived therefrom are  $a=6.772$ ,  $b=17.51$ ,  $c=7.744$  Å  $\pm 0.05\%$ ,  $\beta=94^\circ 18 \pm 3'$ .

Intensities were measured on a scintillation-counter equi-angle Weissenberg goniometer with monochromatized Mo  $K\alpha$  radiation and a stationary-counter and moving-crystal technique. The crystal was mounted along the  $x$  axis, and no correction was made

Table 1. Final atomic coordinates

	$x$	$y$	$z$	$B$
H <sub>2</sub> O(1)	0.0545	0.250*	0.4703	3.5
H <sub>2</sub> O(2)	0.9319	0.1469	0.1537	5.7
H <sub>2</sub> O(3)	0.5896	0.250*	0.0256	4.6
H <sub>2</sub> O(4)	0.0544	0.250*	0.8642	2.5
	$\pm 0.0044$	$\pm 0.0009$	$\pm 0.0021$	$\pm 0.34$
O(1)	0.3461	0.1057	0.0286	1.5
O(2)	0.4244	0.1227	0.3600	2.4
O(3)	0.7909	0.1214	0.5466	1.5
O(4)	0.4519	0.1406	0.7141	1.6
O(5)	0.0731	0.0915	0.7604	2.3
O(6)	0.2212	0.9970	0.2379	2.5
O(7)	0.3835	0.9920	0.7959	1.7
O(8)	0.0000*	0.000*	0.500*	2.6
O(9)	0.5765	0.250*	0.4986	2.1
	$\pm 0.0026$	$\pm 0.00048$	$\pm 0.0011$	$\pm 0.16$
T(A)	0.3187	0.0814	0.8220	0.95
T(B)	0.4053	0.0568	0.2105	0.84
T(C)	0.5566	0.1584	0.5345	0.86
T(D)	0.9106	0.0527	0.6412	0.88
	$\pm 0.0010$	$\pm 0.00015$	$\pm 0.00034$	$\pm 0.046$
Sr	0.2507	0.250*	0.1778	1.02
	$\pm 0.00040$	—	$\pm 0.00014$	$\pm 0.027$

\* Fixed by symmetry.



Table 3. *Interatomic distances*

Distance		Distance		Distance		
T(A)-O(1)	1.65	T(B)	O(7)-O(6)	2.72	H <sub>2</sub> O(1)-Sr	2.71
-O(4)	1.64		O(7)-O(2)	2.72	-O(3)	2.96 (2)
-O(5)	1.70		O(7)-O(1)	2.78	-H <sub>2</sub> O(4)	3.05
-O(7)	1.64		O(2)-O(6)	2.73	-H <sub>2</sub> O(2)	3.11 (2)
Average	1.66		O(2)-O(1)	2.60	-O(9)	3.26
			O(6)-O(1)	2.68	-O(2)	3.51 (2)
					-O(5)	3.57 (2)
T(B)-O(1)	1.67	T(C)	O(3)-O(9)	2.69	H <sub>2</sub> O(2)-Sr	2.81
-O(2)	1.63		O(3)-O(2)	2.78	-H <sub>2</sub> O(4)	3.02
-O(6)	1.66		O(3)-O(4)	2.74	-H <sub>2</sub> O(3)	3.04
-O(7)	1.67		O(9)-O(4)	2.72	-H <sub>2</sub> O(1)	3.11
Average	1.66		O(9)-O(2)	2.65	-O(7)	3.13
			O(2)-O(4)	2.75	-O(1)	3.24
T(C)-O(2)	1.68				-O(3)	3.29
-O(3)	1.71	T(D)	O(3)-O(6)	2.67	-H <sub>2</sub> O(2)	3.61
-O(4)	1.64		O(3)-O(8)	2.60	H <sub>2</sub> O(3)-Sr	2.66
-O(9)	1.64		O(3)-O(5)	2.49	-O(1)	3.02 (2)
Average	1.67		O(6)-O(8)	2.61	-H <sub>2</sub> O(2)	3.04 (2)
			O(6)-O(5)	2.53	-O(4)	3.17 (2)
T(D)-O(3)	1.60		O(8)-O(5)	2.59	-H <sub>2</sub> O(4)	3.47
-O(5)	1.54				H <sub>2</sub> O(4)-Sr	2.68
-O(6)	1.60		Sr, Ba-H <sub>2</sub> O(3)	2.66	-O(5)	2.90 (2)
-O(8)	1.59		-H <sub>2</sub> O(4)	2.68	-H <sub>2</sub> O(2)	3.02 (2)
Average	1.58		-H <sub>2</sub> O(1)	2.71	-H <sub>2</sub> O(1)	3.05
			-H <sub>2</sub> O(2)	2.81 (2)	-O(1)	3.40 (2)
T(A)	O(7)-O(1)	2.71	-O(2)	2.85 (2)	-H <sub>2</sub> O(3)	3.47
	O(7)-O(4)	2.73	-O(1)	2.87 (2)	-O(4)	3.57 (2)
	O(7)-O(5)	2.73				
	O(4)-O(1)	2.66				
	O(4)-O(5)	2.75				
	O(5)-O(1)	2.69				

The number in brackets is the multiplicity.

$x$  axis showed a dominant peak along  $y = \frac{1}{2}$ , which was interpreted as the vector between two Sr atoms lying in a special position on the mirror planes in  $P2_1/m$ . At no time during the structure determinations was it necessary to assume lack of a centre of symmetry, and all calculations have been based on  $P2_1/m$ . An  $F_o$  projection using only the strong  $0kl$  reflections and signs from the Sr atoms permitted location of the tetrahedrally coordinated atoms, and two more syntheses using signs calculated from Sr and the Si, Al atoms allowed recognition of the other atoms. Calculations were made on an IBM 1620 computer with programs for Fourier syntheses and structure factor calculations written, respectively, by Dr. R. Van der Helm of the Institute for Cancer Research, Philadelphia and Professor W. Macintyre of the University of Colorado.

Using spatial considerations, a framework was devised which checked with the coordinates from the Fourier synthesis. Unfortunately it was not possible to predict with sufficient accuracy the  $x$  coordinates for the Sr atom and the H<sub>2</sub>O molecules, and after several abortive cycles of least-squares refinement, it was decided to calculate the  $F_o$  projection down the  $c$  axis. The Sr-Sr vector was easily located and after adjustment of the predicted coordinates for the framework to fit the position of the Sr atom, the atomic

parameters were adjusted by several cycles of least-squares refinement. Using packing considerations,  $x$  coordinates for the water molecules were predicted, and complete refinement of the structure was obtained after four cycles with varied isotropic temperature factors by use of the program ORFLS kindly supplied by Busing, Martin & Levy. The atomic scattering factors published by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and modified arbitrarily for half ionization were used in the refinement. Averaged values for Si, Al and Sr, Ba, Ca were used in accordance with the chemical analysis. The scattering factor for oxygen was also used for the water molecules. The final atomic coordinates and isotropic temperature factors, along with the standard errors, are given in Table 1. Because fewer data were collected along the  $x$  axis than along the other two directions, the standard errors for the  $x$  fractional coordinates are about twice as large as those for the other coordinates. The experimental and calculated structure amplitudes are listed in Table 2. Including reflections below the sensitivity limit, the discrepancy index is 0.11. Interatomic distances are listed in Table 3. The standard errors of the bond lengths depend on direction because of the fewer data along the  $x$  axis. For Si-O and Sr-O the errors range from 0.02 to 0.04 Å, and for O-O from 0.03 to 0.05 Å.

## Discussion

The framework of brewsterite is complex as may be seen from Figs. 1 and 2, which show projections down the  $x$ ,  $z$  and  $y$  axes. Possibly the simplest view of the structure is down the  $y$  axis, for the majority of the tetrahedra lie in two corrugated layers near  $y=0$  and  $\frac{1}{2}$ . To simplify the situation, Fig. 3(a) shows only the

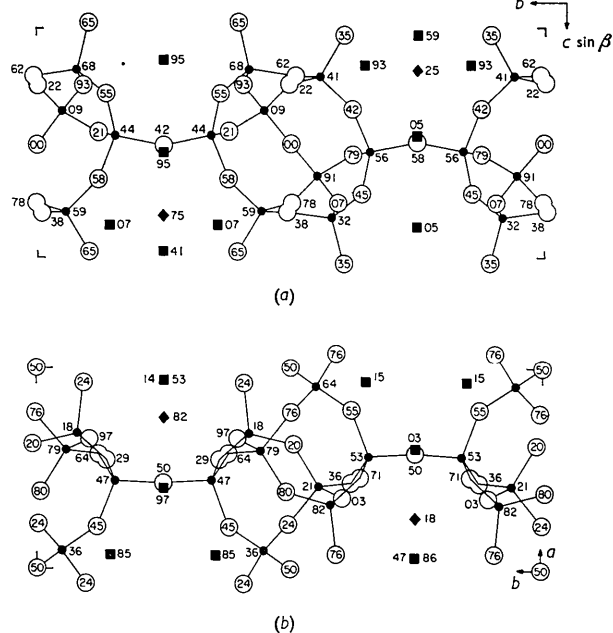


Fig. 1. The  $x$ -axis (a) and  $z$ -axis (b) projections show the paucity of tetrahedral bonds across the mirror planes at  $y = \frac{1}{4}$  and  $\frac{3}{4}$  in conformity with the observed  $\{010\}$  cleavage. The open circles, solid circles, diamonds and squares show the positions of oxygen atoms, tetrahedral atoms, strontium atoms and water molecules, respectively. The heights along the projection axes are shown as percentages of the repeat unit. In both diagrams may be seen portions of the eight-membered rings which provide the narrowest parts of the channels: the complete rings may be envisaged by extension into the adjacent unit cells.

tetrahedrally coordinated atoms. Each layer of tetrahedra is composed of linked 4-, 6- and 8-membered rings forming a 3-connected net. Thus each corner of the net can be joined once more to form a 4-connected framework. This is accomplished by bonding the layers across the mirror planes at  $y = \frac{1}{4}$  and  $\frac{3}{4}$  by  $T_2O_7$  groups, whose central oxygen atom lies on the mirror plane (T denotes Si, Al). Each bridging tetrahedron is bonded to three of the tetrahedra in the layers. Fig. 3(b), a similar simplified view down the  $x$  axis, shows that there are also 4-, 6-, and 8-connected layers of tetrahedra perpendicular to the  $x$  axis. These layers are again linked by  $T_2O_7$  groups, this time with the central oxygen atom lying on a centre of symmetry, and with each bridging tetrahedron bonded to three tetrahedra in each layer. The difference in the bonding arises from

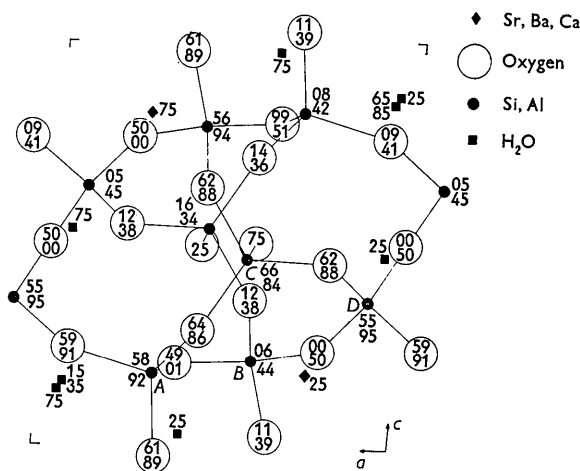


Fig. 2. The  $y$ -axis projection. Four- and five-membered rings may be found in the middle of the diagram, and six-membered rings may be discovered at the origin of the cell. These latter rings form the largest apertures in this direction.

the choice of the three tetrahedra. In Fig. 3(a) they are chosen from the same eight-membered ring, whereas in Fig. 3(b) they are chosen from the six-membered ring. There are at least three more ways in which these 3-connected nets based on 4-, 6- and 8-membered rings may be linked together by  $T_2O_7$  groups to form a framework, and these arrangements might apply to zeolites whose structures are currently unknown.

Brewsterite, in addition to the 4-, 6- and 8-membered rings, contains many 5-membered rings which cross-link the above mentioned nets. Mordenite (Meier, 1961), dachiardite (Gottardi & Meier, 1963), and the high-pressure modification of silica, coesite (Zoltai & Buerger, 1959) also contain 5-membered rings. Zoltai & Buerger (1960) have shown that the electrostatic energy of 5-rings is low, thus favouring their stability.

There are two sets of intersecting channels in brewsterite lying parallel to the  $x$  and  $z$  axes, each controlled by apertures formed from 8-membered rings (Fig. 1). The apertures perpendicular to the  $x$  axis are elliptical with a cross-section of  $5.0 \times 7.7$  Å, measured between opposing oxygen atoms. Assuming a radius of  $1.35$  Å for the oxygen atoms, the effective aperture is  $2.3 \times 5.0$  Å. Corresponding figures for the apertures perpendicular to the  $z$  axis are  $5.4 \times 5.8$  Å and  $2.7 \times 3.1$  Å. No adsorption data for brewsterite have appeared in the literature.

From Table 3 it may be seen that the mean Si, Al-O distances in tetrahedron 4 are smaller than those in the other three ( $1.58$  vs.  $1.66$ ,  $1.66$  and  $1.67$ ). Smith & Bailey (1963) have shown that in framework structures the tetrahedral distances vary from  $1.61$  for Si-O to  $1.75$  for Al-O. It appears, therefore, that

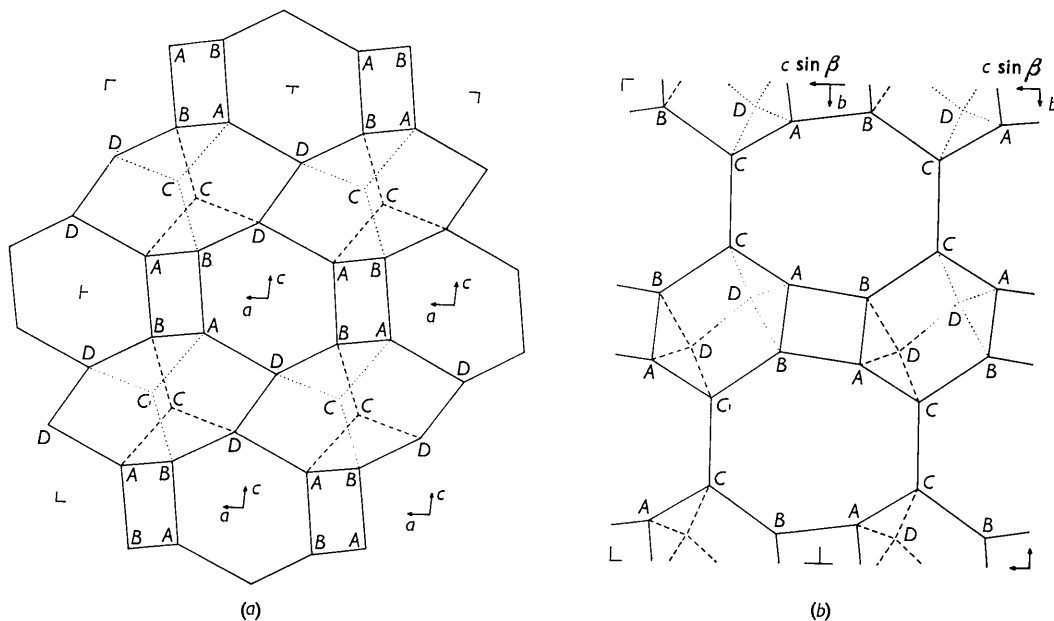


Fig. 3. (a) and (b) are schematic representations of the aluminosilicate framework viewed down the  $y$  and  $x$  axes respectively. Only the positions of the tetrahedrally coordinated atoms are shown, and they are joined together by continuous lines to show the linked 4-, 6- and 8-membered rings which form the layers. The layers are joined together by other tetrahedra. In (a) the layers  $ABD$  occur in pairs near heights  $y=0$  and  $\frac{1}{2}$ , being related by the planes of symmetry at  $y=\frac{1}{4}, \frac{3}{4}$ . Thus there are two atoms superimposed at each position  $ABD$ . The layers are linked by  $T_2O_7$  groups, with the tetrahedral atoms lying in the  $C$  positions at either  $\frac{1}{6}, \frac{2}{6}$  or  $\frac{4}{6}, \frac{5}{6}$ , approximately. The two types of  $C$  atom are distinguished by the dotted and broken lines. The central oxygen atom of the  $T_2O_7$  groups lies on the planes of symmetry. Comparison with Fig. 2 will permit further clarification of the structural relationships. The symbols  $ABCD$  are the subscripts applied to the  $T$  atoms in Table 2. In (b) the layers are again linked by  $T_2O_7$  groups so that the central oxygen atom lies on a centre of symmetry. The two tetrahedra which form the  $T_2O_7$  group are distinguished by the dotted and broken lines. Further details may be found from Fig. 1(a), but it should be noted that the axes have been re-oriented in order that the 4-, 6- and 8-membered rings of Figs. 3(a) and (b) are in the same relative orientation. By comparison with Fig. 1(a), it will be found that the layers are considerably non-planar.

the fourth tetrahedron in brewsterite is occupied solely by Si, while the other three are randomly occupied by 2Si and 1Al atom. The overall mean Si,Al-O distance for brewsterite of 1.64 fits well with the value of 1.645 expected for a framework structure of this Si,Al ratio. The fourth tetrahedron is the most distant one from the Sr atoms, and Si would be favoured for this tetrahedron because occupancy of it gives a more uniform balance of charge in the structure.

The strontium atom lies in an irregular polyhedron (Fig. 4a) with five water molecules at 2.66 to 2.81 Å and four oxygen atoms at 2.85 and 2.87 Å as nearest neighbours. Such irregularity of coordination is commonly found for Ca, Sr and Ba atoms in silicates, and the distances are reasonable. The most important feature of the coordination is the formation of an incomplete sphere of hydration about the exchangeable cation. Evidence is accumulating to show that when the cavities in zeolites are large enough, the exchangeable cations surround themselves by water molecules to form a sphere of hydration rather than bonding directly to the oxygen atoms of the framework (e.g. chabazite (Smith, Rinaldi & Dent Glasser, 1963), harmotome (Sadanaga, Marumo & Takéuchi,

1961) and gismondine (Fischer, 1963)). The bonding of the Sr atoms in brewsterite is similar to that of Ba in harmotome, bearing in mind the shorter distance to be expected for the smaller cations.

The coordination of the water molecules is complex (Fig. 4, b-e). Each has a strontium atom as its nearest neighbour, and six water molecules or oxygen atoms at distances between 2.9 and 3.4 Å. Other neighbours range on upwards from 3.5 Å and it is hardly possible to choose a cut-off to distinguish bonded from non-bonded neighbours. Such irregularity is typical of water molecules in zeolite.

The structure explains well the  $\{010\}$  cleavage, for the bonding across the symmetry planes (Fig. 1 and 3) is weak.

It is quite possible that this structure will offer a clue for the heulandite and epistilbite structure determinations which are now in progress, for heulandite has a 7.5 Å and an 18.0 Å axis similar in length to the 7.7 Å and 17.5 Å axes in brewsterite, while epistilbite has a 17.7 Å axis.

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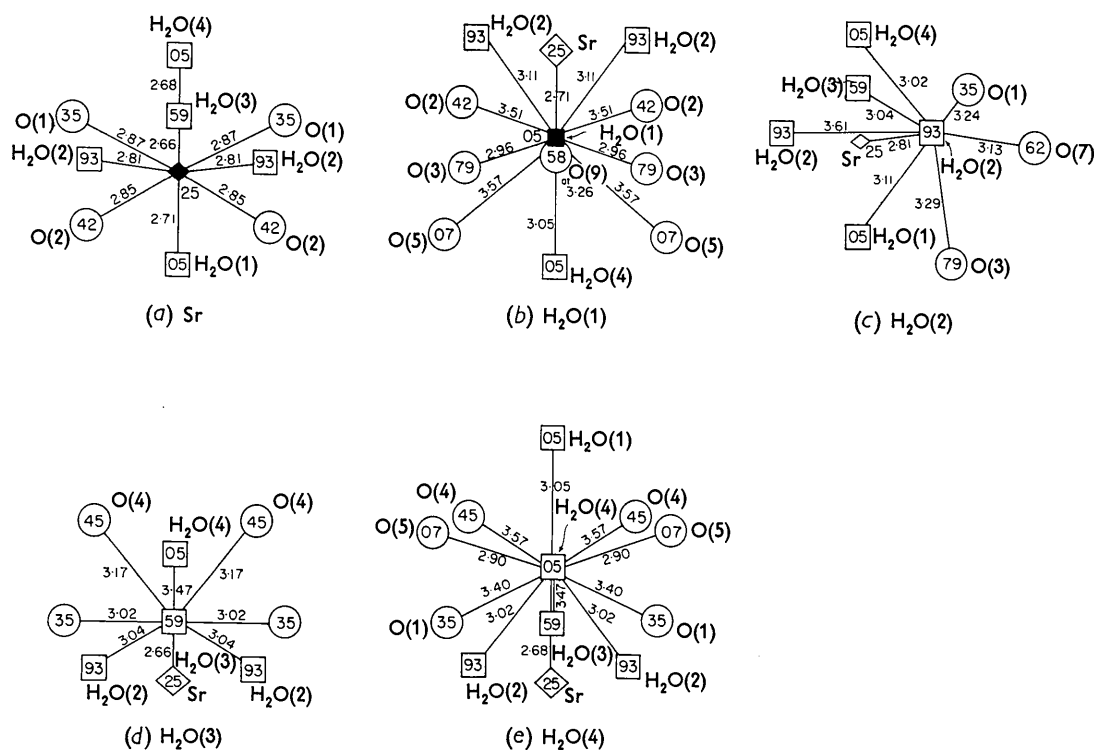


Fig. 4. (a)–(e) The environments of the Sr atom and the four water molecules respectively as viewed down the  $x$  axis. Circles, squares and diamonds denote oxygen atoms, water molecules and Sr atoms, respectively. The two-figure numbers are percentages of the  $x$ -axis repeat.

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*Note added in proof.* — Dr W. M. Meier has kindly pointed out the existence of chains parallel to the  $x$  axis and has shown that there are several other ways of cross-linking the chains.

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