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Crystal Structure of Thaumasite, [Ca₃Si(OH)₆.12H₂O](SO₄)(CO₃)

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Thaumasite (hexagonal, $P6_3$, a 11·04, c 10·39 Å, $Z=2$) has a structure based on columns of empirical composition $[Ca_3Si(OH)_6.12H_2O]^{4+}$ running parallel to c, between which occur the CO_3^{2-} and SO_4^{2-} groups. The present results confirm Moenke's [*Naturwissenschaften* (1964) 51, 239] conclusion, based on the infrared absorption spectrum, that thaumasite contains octahedral $Si(OH)_6^{2-}$ groups; it is the first structure in which these have been shown to occur. It is isostructural with jouravskite, $[Ca_3Mn(OH)_6.12H_2O](SO_4)(CO_3)$, and, so far as the columns are concerned, with ettringite, $[Ca_3Al(OH)_6.12H_2O]_2(SO_4)_3 2H_2O$, with which it probably forms solid solutions. The $Si(OH)_6^{2-}$ octahedra in thaumasite are somewhat distorted, with Si–O distances of 1·731 and 1·835 Å; the conditions under which octahedral coordination of Si by O can arise in phases produced at ordinary pressures are discussed.

Introduction

Thaumasite is a mineral of approximate composition $3CaO.SiO_2.SO_3.CO_2.15H_2O$. There has been some uncertainty as to whether the number of moles of water in the formula should be 15 or 14; the results to be presented support the value of 15. The only previous investigation of the crystal structure was made by Welin (1956), who found a structure based on chains of Ca^{2+} and SiO_4^{4-} ions running parallel to the hexagonal c axis, between which occurred the SO_4^{2-} and CO_3^{2-} ions and H_2O molecules. Welin considered the constitutional formula to be
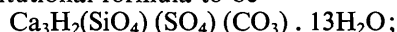
$$Ca_3H_2(SiO_4)\,(SO_4)\,(CO_3)\,.\,13H_2O;$$

Table 1. *Unit-cell parameters for thaumasite*

Locality	a	c	Reference
Långban, Sweden	10·90 Å	10·29 Å	Aminoff (1933)
Långban, Sweden	10·95	10·30	Welin (1956)
Ballyalton, N. Ireland	11·03	10·40	Knill & Young (1960)
Centerville, Virginia, U.S.A.	10·992	10·311	Font-Altaba (1060)
Paterson, New Jersey, U.S.A.	11·06*	10·54	Murdoch & Chalmers (1960)
Paterson, New Jersey, U.S.A.	11·04	10·39	This investigation

* a axis incorrectly given as 22·12 Å in original paper; see Berry (1963).

the two H^+ ions could not be satisfactorily placed, and he believed them to be most probably attached to the SO_4^{2-} ions. The determination was evidently approximate, and no R index was given. Moenke (1964) investigated the infrared absorption spectrum, from which he concluded that the silicon atom was octahedrally coordinated. Kirov & Poulieff (1968) disputed this conclusion, but their argument seems to have rested on the untenable assumption that the silicon coordination in the thermal dehydration product was necessarily the same as in the unheated mineral.

As was noted by McConnell & Murdoch (1962), thaumasite shows close crystallographic similarities to ettringite ($Ca_6[Al(OH)_6]_2(SO_4)_3.26H_2O$ approximately), the crystal structure of which has recently been determined (Moore & Taylor, 1968, 1970; Courtois, Dusausoy, Laffaille & Protas, 1968). Although Moore & Taylor used Welin's structure for thaumasite as a starting point for their work, the structure for ettringite which they obtained differed more from that of thaumasite than appeared consistent with the close similarities that exist between the X-ray patterns of the two minerals. For this reason, and also because of the unsatisfactory features of Welin's structure (the apparent disagreement with the infrared evidence and improbable placing of the two H^+ ions), a redetermination of the thaumasite structure seemed to be required. The results have been briefly reported elsewhere (Edge & Taylor, 1969), and are described more fully in the present paper.

While the present work was in progress, Granger & Protas (1969) reported a determination of the crystal structure of jouravskite,

$$Ca_3[Mn(OH)_6] (SO_4) (CO_3).12H_2O.$$

Comparison of their results with those to be described shows that thaumasite and jouravskite are isostructural, the Si^{4+} in thaumasite being replaced by Mn^{4+} in jouravskite.

Experimental methods, structure determination and refinement

Crystals were selected from a specimen collected at Paterson, New Jersey, U.S.A., by Prof. A. B. Carpenter and kindly made available by Miss A. E. Moore. For preliminary work, an irregularly shaped crystal (A) of approximate maximum dimension 0·2 mm was used. Later, a well-formed hexagonal prism (B) of approxi-

mate length 0·6 mm and greatest cross-section 0·16 mm was found. Refractive index determinations ($\omega = 1·504$, $\varepsilon = 1·470$ in Na light) and X-ray oscillation, rotation and Weissenberg photographs about the a and c axes confirmed the identity of the material, and gave results compatible with the space group $P6_3$ reported by Welin (1956). The unit-cell parameters obtained with Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å) were $a = 11·04 \pm 0·02$, $c = 10·39 \pm 0·02$ Å. Similar, though rather widely varying results have been reported previously for specimens from the same and other localities (Table 1).

Table 2, column 1, gives the chemical analysis and specific gravity reported for thaumasite from Paterson; closely similar data have been reported for specimens from other localities. The analytical results represent the mean of three analyses, corrected for the presence of about 1·2% of alkali sulphates and normalized to a total of 100·0%. The specific gravity is the mean of an observed range (1·875 − 1·887). Column 2 gives atomic cell contents calculated from these data and the cell parameters found in the present work. The results agree satisfactorily with the idealized cell contents given in column 3, which correspond to the formula $3CaO.SiO_2.SO_3.CO_2.15H_2O$ with $Z = 2$. They agree less well with the formula with $14H_2O$.

Table 2. *Chemical analysis and atomic cell contents for thaumasite from Paterson, New Jersey, U.S.A.*

	1		2	3
SiO_2	9·38	Si	1·94	2
CO_2	6·90	C	1·95	2
SO_3	12·95	S	2·01	2
CaO	27·47	Ca	6·09	6
H_2O	43·30	H	59·74	60
	100·00	O	49·77	50
Specific gravity	1·881			

1. Chemical analysis and specific gravity, Penfield & Pratt (1896).
2. Atomic cell contents calculated from (1), assuming $a = 11·04$, $c = 10·39$ Å.
3. Atomic cell contents corresponding to the formula $3CaO.SiO_2.SO_3.CO_2.15H_2O$, with $Z = 2$.

Intensities were determined for each of the two crystals, in both cases mounted about the c axis, using a Hilger automatic linear diffractometer with Mo radiation, balanced filters, and six measuring cycles per reflexion. Measurements were made over approximately a hemisphere of reciprocal space, and in general

the results for six equivalent reflexions were averaged to obtain the data for each independent reflexion. For preliminary work, data were thus collected for 375 independent reflexions, using crystal A; later, data were similarly collected for 1163 independent reflexions using crystal B. Except for 13 very weak reflexions for which the data were very doubtful in quality, and to which $|F|$ values of approximately 2·0 were arbitrarily assigned, all reflexions were treated as observed. No absorption corrections were applied as such, but empirical adjustments of the layer scale factors made during refinement probably amounted in part to the application of partial absorption corrections.

Computing was carried out largely using an ICL 4/50 computer, with programs kindly supplied by Dr F. R. Ahmed and collaborators of the National Research Council, Canada, and adapted by Mr J. S. Knowles of the Department of Computing, University

Table 3. *Atomic coordinates (fractional) and isotropic temperature factors ($B, = 8\pi^2 u$, in Å^2), with e.s.d.'s on last digit in parentheses*

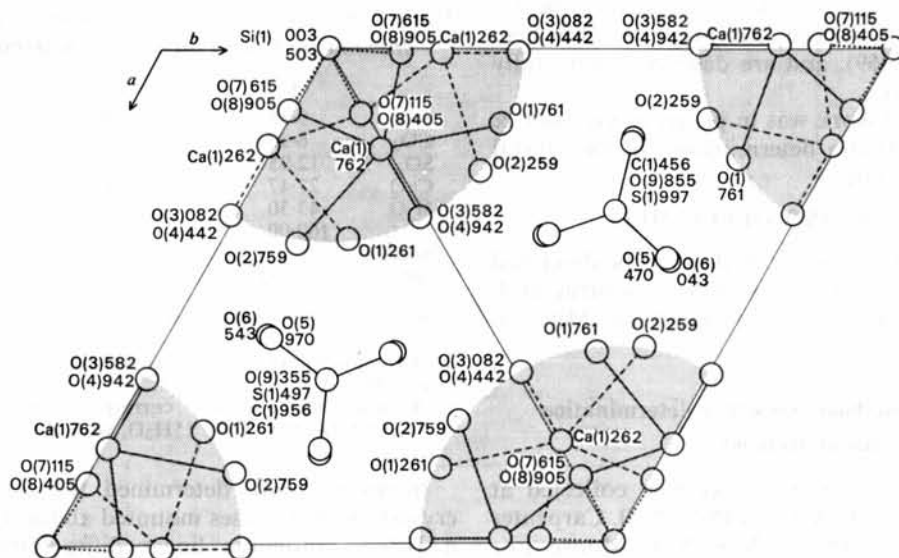|	Symmetry	Present in (group)	x/a	y/b	z/c	B
Ca(1)	1		0·1947 (6)	−0·0116 (6)	0·2619 (3)	0·72 (2)
Si (1)	6_3	$Si(OH)_6^{2-}$	0	0	0·0026 (*)	0·63 (4)
C(1)	3	CO_3^{2-}	$\frac{1}{3}$	$\frac{2}{3}$	0·456 (2)	0·9 (2)
S(1)	3	SO_4^{2-}	$\frac{1}{3}$	$\frac{2}{3}$	−0·0027 (7)	1·07 (6)
O(1)	1	⎫	0·392 (3)	0·228 (3)	0·261 (1)	1·9 (1)
O(2)	1	⎬ H_2O	0·260 (2)	0·401 (2)	0·259 (1)	1·7 (1)
O(3)	1	⎪	0·0025 (8)	0·3411 (9)	0·082 (1)	2·2 (1)
O(4)	1	⎭	0·0217 (7)	0·3467 (7)	0·4421 (7)	1·2 (1)
O(5)	1	CO_3^{2-}	0·2014 (8)	0·6223 (8)	0·4700 (9)	2·0 (1)
O(6)	1	SO_4^{2-}	0·1914 (7)	0·6229 (8)	0·0431 (8)	1·5 (1)
O(7)	1	⎫ $Si(OH)_6^{2-}$	0·1312 (6)	0·1249 (6)	0·1150 (7)	0·86 (8)
O(8)	1	⎭	0·1300 (6)	0·1242 (6)	0·4052 (7)	0·86 (8)
O(9)	3	SO_4^{2-}	$\frac{1}{3}$	$\frac{2}{3}$	0·855 (1)	1·4 (2)
H(12)	1	⎫	0·347	0·290	0·260	3·0
H(19)	1	⎪	0·488	0·265	0·297	3·0
H(25)	1	⎪	0·303	0·465	0·333	3·0
H(26)	1	⎬ H_2O	0·311	0·462	0·183	3·0
H(35)	1	⎪	0·439	0·079	0·042	3·0
H(36)	1	⎪	0·069	0·441	0·068	3·0
H(45)	1	⎪	0·085	0·444	0·452	3·0
H(46)	1	⎭	0·410	0·053	0·478	3·0
H(70)	1	⎫ $Si(OH)_6^{2-}$	0·215	0·178	0·111	3·0
H(80)	1	⎭	0·213	0·180	0·413	3·0

* z coordinate arbitrarily held constant.

Fig. 1. The structure shown in projection along the c axis. Heights of atoms are given as 1000 z/c; hydrogen atoms are omitted. The columns, of empirical composition $[Ca_3Si(OH)_6.12H_2O]^{4+}$, are shaded. Full and broken lines represent Ca–O bonds between atoms at $z > \frac{1}{2}$ and $z < \frac{1}{2}$ respectively; dotted lines represent Si–O bonds.

Table 4. *Observed and calculated structure factors (all × 10)*

Unobserved reflexions are marked ●.

The table is arranged in multiple columns, each headed by the labels:

K	FO	FC	ALPHA

with successive blocks introduced by headings of the form H= n, L= m.

Table 4 (cont.)

of Aberdeen. Form factors (for Ca^{2+}, Si, S, C, H and O^-) were taken from *International Tables for X-ray Crystallography* (1962).

Using the data for crystal A, Welin's structure was taken as a starting point; it gave $R = 0.57$ on all 375 independent reflexions. Three-dimensional electron-density and difference electron-density distributions were calculated; they indicated that the SiO_4^{4-} tetrahedra which were present in this structure should be replaced by SiO_6^{8-} [or $Si(OH)_6^{2-}$] octahedra, and that an H_2O molecule which was placed on a threefold axis did not exist. In addition, they suggested considerable shifts of most of the other atoms. When they had been made, the structure refined to $R = 0.11$ on block-diagonal least-squares treatment with empirical adjustments of layer scale factors. Individual, isotropic temperature factors were used. No attempt was made at this stage to introduce the H atoms, but the structure did not differ in any other important respect from that finally obtained. It was much nearer than Welin's structure to that of ettringite.

The more extensive data for crystal B were now collected. When used with the parameters found with crystal A, they gave an initial R index of 0.26. Refinement by block-diagonal least-squares treatment and adjustment of layer scale factors produced convergence at $R = 0.096$ on 1155 independent reflexions. Three-dimensional electron-density and difference electron-density distributions were now calculated, and also interatomic distances and angles; from O–O distances and other crystal-chemical considerations possible sites for the H atoms were deduced. Most corresponded, at least approximately, with positive peaks on the difference distribution, but not all the features of the latter could be explained in this way and it was evident that the limitations imposed by the data were being reached. The H atoms were distributed so as to produce an $Si(OH)_6^{2-}$ octahedron and to make the remaining O

atoms coordinated to Ca into H_2O molecules; this corresponds to the formula

$$3CaO.SiO_2.SO_3.CO_2.15H_2O$$

and to the situations that have been proposed for ettringite and jouravskite. When the H atoms were added, the R index did not change significantly, but the agreement was markedly improved for several moderately strong low-angle reflexions for which it had been rather poor. Attempts at further refinement failed. The intensities of a few weak reflexions which were incorrect or doubtful were amended, and the final R index was 0.094 on all 1163 independent reflexions.

The weighting scheme used in the later stages of refinement was $w = 1/\{1 + [(|F_{obs}| - 30.0)/30.0]^2\}$ and analyses against $|F_{obs}|$, $\sin^2\theta$ and l index showed that it was satisfactory. Final electron-density and difference electron-density distributions were calculated. The minimum values on the electron-density map were around -5 e.$Å^{-3}$ (near the Ca and Si atoms; -2 e.$Å^{-3}$ elsewhere), while the extremes on the difference Fourier synthesis were -1.2 and $+0.9$ e.$Å^{-3}$.

Tables 3–5 give respectively the final parameters, the observed and calculated structure factors, and the more important interatomic distances and angles. The coordinates of the H atoms are tentative, and their temperature factors were arbitrarily assigned. It is nevertheless considered unlikely that the coordinates could be seriously in error, except perhaps those for H(70) and H(80) [the H atoms of the $Si(OH)_6^{2-}$ groups], which were little more than plausible guesses.

Description of the structure

Fig. 1 shows the structure, with the H atoms omitted, in projection along the c axis; Fig. 2 shows selected parts of it, in the same projection, chosen to indicate the H atom positions and the system of hydrogen

bonding. The structure is based on columns of empirical composition $[Ca_3Si(OH)_6.12H_2O]^{4+}$ running parallel to **c**, between which occur the SO_4^{2-} and CO_3^{2-} groups. It is isostructural with jouravskite and, so far as the columns are concerned, with ettringite. The following description therefore deals only with some specific points; for a fuller description of other aspects of the structure, reference should be made to the papers on jouravskite (Granger & Protas, 1969) and ettringite (Moore & Taylor, 1970).

The $Si(OH)_6^{2-}$ octahedra

The results confirm Moenke's (1964) conclusion that thaumasite contains $Si(OH)_6^{2-}$ groups; it is the first structure in which these have been proved to exist. It has been suggested that they occur in aqueous solutions (Iler, 1955), but there appears to be no substantial evidence for or against this view. Until recently, it has generally been assumed that octahedral coordination of Si by O occurs only in phases produced at high pressures. However, strong chemical evidence has long existed for the occurrence of octahedral SiO_6 in complexes of Si with such ligands as acetylacetone (Dilthey,

1903) or pyrocatechol (Rosenheim, Raibmann & Schendel, 1931), while Levi & Peyronel (1935) showed that it also occurred in one of the polymorphs of SiP_2O_7. More recently, Bissert & Liebau (1969) and Liebau & Hesse (1969) have shown that it occurs in two further polymorphs of this composition. The SiP_2O_7 polymorphs, as well as the complexes mentioned above, are all formed at ordinary pressure. Thaumasite does not appear to have been synthesized, but its mode of occurrence in nature and low density make it most unlikely that it is a high-pressure phase.

These examples suggest that octahedral coordination of Si by O is liable to occur in phases produced at ordinary pressure whenever the only other atoms coordinated to the O atoms are ones of relatively high electronegativity, such as C, H or P. These relatively electronegative atoms draw electrons out of the Si–O bonds, thus lengthening them, decreasing their mutual repulsion, and allowing the increase in Si coordination number to occur. Under these circumstances, the O atoms behave similarly to F, and the $Si(OH)_6^{2-}$ group can be linkened to the SiF_6^{2-} group, which is readily formed at ordinary pressures.

Table 5. *Interatomic distances and angles, with e.s.d.'s in parentheses*

To distinguish between equivalent O atoms within the CaO_8 polyhedron, the suffixes *a* and *b* are used, O(7*a*) having approximately the same *x* and *y* coordinates as O(8*a*), while O(7*b*) is similarly related to O(8*b*).

M–O distances within polyhedra		O–O distances between polyhedra (given only where < 3·0 Å), and O–O–O angles (given only where the central O atom is assumed to occur in an H_2O molecule which is H-bonded to the outer ones)			
Ca(1)–O(1)	2·45 (3) Å				
Ca(1)–O(2)	2·50 (2)				
Ca(1)–O(3)	2·43 (1)				
Ca(1)–O(4)	2·40 (1)	O(1)–O(2)	2·93 (4) Å	O(2)–O(1)–O(9)	121 (1)°
Ca(1)–O(7a)	2·46 (1)	O(1)–O(9)	2·82 (4)		
Ca(1)–O(7b)	2·48 (1)	O(2)–O(5)	2·79 (2)	O(5)–O(2)–O(6)	105·6 (6)
Ca(1)–O(8a)	2·44 (1)	O(2)–O(6)	2·78 (2)		
Ca(1)–O(8b)	2·46 (1)	O(3)–O(5)	2·74 (1)	O(5)–O(3)–O(6)	89·2 (4)
Si(1)–O(7)	1·835 (7)	O(3)–O(6)	2·77 (1)		
Si(1)–O(8)	1·731 (7)	O(3)–O(8)	2·98 (1)		
S(1)–O(6)	1·47 (1)	O(4)–O(5)	2·69 (1)	O(5)–O(4)–O(6)	90·8 (3)
S(1)–O(9)	1·48 (2)	O(4)–O(6)	2·75 (1)		
C(1)–O(5)	1·29 (1)	O(4)–O(7)	2·92 (1)		

O–M–O and Si–O–H angles. For O–M–O angles, the corresponding O–O edge distance of the polyhedron is also given; O–Ca–O angles > 130° are excluded.

O(1)—Ca(1)–O(3)	74·9 (8)°	2·97 (3) Å	O(7)–Si(1)–O(7)	83·8 (3)°	2·45 (1) Å
O(1)—Ca(1)–O(4)	79·8 (8)	3·11 (3)	O(7)–Si(1)–O(8)	93·5 (3)	2·60 (1)
O(1)—Ca(1)–O(7b)	73·1 (7)	2·94 (4)	O(7)–Si(1)–O(8)	93·3 (3)	2·59 (1)
O(1)—Ca(1)–O(8b)	73·6 (7)	2·94 (4)	O(7)–Si(1)–O(8)	176·3 (3)	—
O(2)—Ca(1)–O(3)	80·0 (5)	3·17 (2)	O(8)–Si(1)–O(8)	89·3 (3)	2·43 (1)
O(2)—Ca(1)–O(4)	77·1 (5)	3·05 (2)			
O(2)—Ca(1)–O(7a)	75·5 (4)	3·04 (2)			
O(2)—Ca(1)–O(8a)	76·5 (4)	3·06 (2)			
O(3)—Ca(1)–O(4)	102·1 (3)	3·75 (1)	Si(1)–O(7)–H(70)	134	—
O(3)—Ca(1)–O(7a)	86·5 (3)	3·35 (1)	Si(1)–O(8)–H(80)	135	—
O(3)—Ca(1)–O(7b)	83·0 (3)	3·25 (1)			
O(4)—Ca(1)–O(8a)	84·4 (3)	3·25 (1)			
O(4)—Ca(1)–O(8b)	85·4 (3)	3·29 (1)			
O(7a)–Ca(1)–O(7b)	59·4 (3)	2·45 (1)	O(6)–S(1)–O(6)	108·9 (5)	2·41 (1)
O(7a)–Ca(1)–O(8a)	76·0 (3)	3·02 (1)	O(6)–S(1)–O(9)	110·1 (4)	2·40 (1)
O(7a)–Ca(1)–O(8b)	104·1 (3)	3·88 (1)			
O(7b)–Ca(1)–O(8a)	104·2 (3)	3·88 (1)			
O(7b)–Ca(1)–O(8b)	75·2 (2)	3·02 (1)			
O(8a)–Ca(1)–O(8b)	59·6 (3)	2·43 (1)	O(5)–C(1)–O(5)	118 (1)	2·22 (1)

The present results indicate a definite distortion of the $Si(OH)_6^{2-}$ octahedron, which gives rise to three relatively short Si–O bonds ($1\cdot731 \pm 0\cdot007$ Å) on one side of the Si atom, and three long ones ($1\cdot835 \pm 0\cdot007$ Å) on the other. Similar distortions in MO_6 octahedra have been observed in corundum, with Al–O distances of $1\cdot86$ and $1\cdot97$ Å (Newnham & de Haan, 1962), and in other cases. Liebau & Hesse (1969) found somewhat similar, though less symmetrical distortion in the AIV polymorph of SiP_2O_7, with Si–O distances of $1\cdot75$–$1\cdot83$ Å. For the AIII polymorph, Bissert & Liebau (1969) found a smaller range of distances ($1\cdot74$–$1\cdot79$ Å). All these Si–O distances are considerably above the range of values ($1\cdot57$–$1\cdot67$ Å) commonly observed for tetrahedral coordination, and are much nearer the sum of the single covalent radii ($1\cdot81$ Å). This agrees with the theory mentioned above.

The CaO_8, SO_4^{2-} and CO_3^{2-} polyhedra

With one possible exception, these show no abnormal features. The Ca–O bond distances, which range from $2\cdot40$ to $2\cdot50$ Å, agree closely with the corresponding values in jouravskite ($2\cdot41$–$2\cdot54$ Å) and less closely with those in ettringite [$2\cdot39$–$2\cdot72$ Å according to Courtois et al. (1968) or $2\cdot35$–$2\cdot75$ Å according to Moore & Taylor (1970)]. The SO_4^{2-} tetrahedra are nearly regular, with normal bond lengths and temperature factors; in jouravskite, Granger & Protas (1969) found an abnormally high temperature factor ($B = 7\cdot1$ Å^2) for the atom corresponding to O(9) in the present structure, which, they suggested, might be due to partial replacement of SO_4^{2-} by CO_3^{2-}. There is no evidence for this in the Paterson thaumasite; if anything, the analysis (Table 2) suggests that the reverse substitution is more likely to occur. The CO_3^{2-} groups have normal bond lengths and temperature factors,

but show a slight deviation from planarity. This may not be significant, but possible explanations might lie in the presence within the crystal of regions in which the positions of the CO_3^{2-} and SO_4^{2-} ions are interchanged, or, less probably, in minor replacement of CO_3^{2-} by SO_4^{2-} as mentioned above.

Hydrogen bonding and oxygen coordination

The suggested orientations of the H_2O molecules are similar to those proposed for ettringite by Moore & Taylor (1970). All the H atoms of the H_2O molecules take part in forming hydrogen bonds, which have O–O distances of $2\cdot69$–$2\cdot93$ Å. The H atoms of the $Si(OH)_6^{2-}$ groups, in contrast, each appear to be directed between the O atoms of two different H_2O molecules, of which one is in the same, and the other in a different CaO_8 polyhedron. The $Si(OH)_6^{2-}$ molecules are thus, at the most, only weakly hydrogen bonded. Although this distribution of the H atoms is tentative, it appears consistent with the infrared spectrum (Moenke, 1964), which shows four O–H stretching frequencies at 3420–3560 cm^{-1}, and H–O–H bending frequencies at 1705 and 1660 cm^{-1}. The O–H stretching frequencies are all in a range consistent with weak to moderately strong hydrogen bonding, and which suggests that both strong hydrogen bonds and completely non hydrogen bonded OH are absent. A system of hydrogen bonds between the H_2O molecules and the SO_4^{2-} and CO_3^{2-} ion similar to that proposed here seems also to exist in jouravskite (Granger & Protas, 1969).

Oxygen atoms O(2)–O(4), which occur in H_2O molecules, have a tetrahedral environment, as do those of the CO_3^{2-} ions [O(5)] and SO_4^{2-} ions [O(6) and O(9)]. The environment of the remaining H_2O molecule, containing O(1), is less regular: Ca(1), O(2) and O(9) sur-
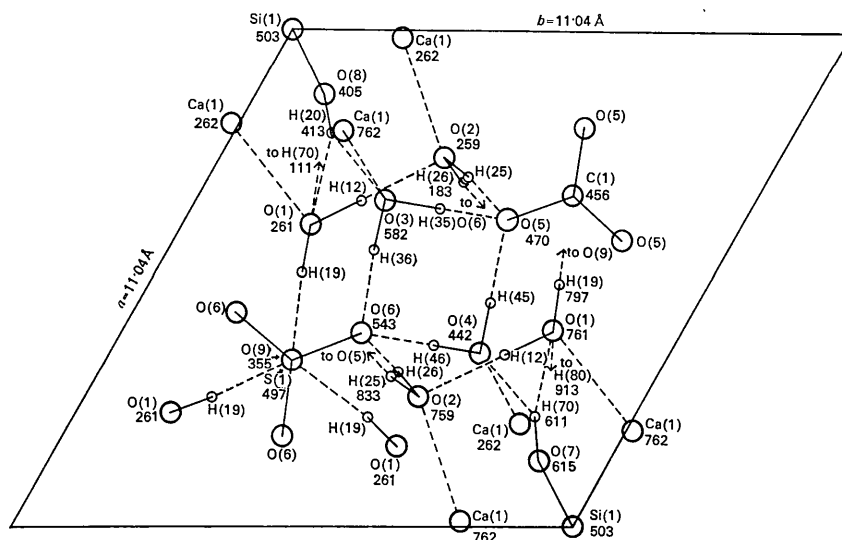

Fig. 2. Selected parts of the structure shown, as in Fig. 1, in projection along c, and chosen to illustrate the system of hydrogen bonding and coordination of the O atoms. Heights of atoms are given as 1000 z/c.

round it roughly in plane triangular configuration, while O(7) and O(8) lie out of the plane and only slightly further away. There are no O–O distances below 3·0 Å in the structure that do not appear to involve hydrogen bonding, other than ones along the edges of polyhedra.

Possible solid solutions in the ettringite–thaumasite group

Carpenter (1963) described oriented overgrowths of thaumasite on ettringite, and noted that both minerals when present in them had anomalous refractive indices. He concluded that a limited solid solution series might exist. In conformity with this suggestion, at least two other mineral specimens have been reported that have compositions, optical properties and cell parameters broadly intermediate between those of ettringite and thaumasite; one was found at Crestmore, California (Murdoch & Chalmers, 1960) and the other at Franklin, New Jersey (Hurlbut & Baum, 1960). The close similarity between the two structures that is indicated by the present results is entirely consistent with the existence of solid solutions, while the difference in space group and doubling of the c axis in ettringite necessarily imply the existence of at least a discontinuity, if not a gap, in the series.

The specimens described by Murdoch & Chalmers (1960) and by Hurlbut & Baum (1960) both have the doubled c, and should probably be described as ettringites with some substitution of $Si(OH)_6^{2-}$ for $Al(OH)_6^{3-}$ and appropriate balancing replacements. The composition of the Franklin mineral is complicated by the virtual absence of CO_2 and presence of B_2O_3; possibly BO_3^{3-} replaces the CO_3^{2-} of the thaumasite structure, but infrared or other evidence would be needed to substantiate this. Both were reported as having doubled a axes, but Berry (1963) pointed out that this arose from wrong indexing of the X-ray patterns. In addition to these natural specimens, several synthetic phases have been described that are similar to ettringite but which have other anions in place of SO_4^{2-}. These, too, may well form solid solutions with thaumasite, but the possibilities of this have not so far been investigated.

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