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## Crystal Structure of Thaumasite, $[\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}] (\text{SO}_4)(\text{CO}_3)$

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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  $[\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]^{4+}$  running parallel to  $\mathbf{c}$ , between which occur the  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  groups. The present results confirm Moenke's [*Naturwissenschaften* (1964) **51**, 239] conclusion, based on the infrared absorption spectrum, that thaumasite contains octahedral  $\text{Si}(\text{OH})_6^{2-}$  groups; it is the first structure in which these have been shown to occur. It is isostructural with jouravskite,  $[\text{Ca}_3\text{Mn}(\text{OH})_6 \cdot 12\text{H}_2\text{O}] (\text{SO}_4)(\text{CO}_3)$ , and, so far as the columns are concerned, with ettringite,  $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2 (\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ , with which it probably forms solid solutions. The  $\text{Si}(\text{OH})_6^{2-}$  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  $3\text{CaO} \cdot \text{SiO}_2 \cdot \text{SO}_3 \cdot \text{CO}_2 \cdot 15\text{H}_2\text{O}$ . 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  $\text{Ca}^{2+}$  and  $\text{SiO}_4^{4-}$  ions running parallel to the hexagonal  $c$  axis, between which occurred the  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  ions and  $\text{H}_2\text{O}$  molecules. Welin considered the constitutional formula to be

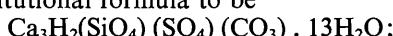


Table 1. Unit-cell parameters for thaumasite

Locality	<i>a</i>	<i>c</i>	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 (1960)
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<sup>+</sup> ions could not be satisfactorily placed, and he believed them to be most probably attached to the SO<sub>4</sub><sup>2-</sup> 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<sub>6</sub>[Al(OH)<sub>6</sub>]<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.26H<sub>2</sub>O 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<sup>+</sup> 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,



Comparison of their results with those to be described shows that thaumasite and jouravskite are isostructural, the Si<sup>4+</sup> in thaumasite being replaced by Mn<sup>4+</sup> 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 ( $\omega = 1.504$ ,  $\epsilon = 1.470$  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 *P*6<sub>3</sub> 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<sub>2</sub>·SO<sub>3</sub>·CO<sub>2</sub>·15H<sub>2</sub>O with *Z*=2. They agree less well with the formula with 14H<sub>2</sub>O.

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

	1	2	3
SiO <sub>2</sub>	9.38	Si	1.94
CO <sub>2</sub>	6.90	C	1.95
SO <sub>3</sub>	12.95	S	2.01
CaO	27.47	Ca	6.09
H <sub>2</sub> O	43.30	H	59.74
	100.00	O	60
Specific gravity	1.881		50

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<sub>2</sub>·SO<sub>3</sub>·CO<sub>2</sub>·15H<sub>2</sub>O, 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 ( $B = 8\pi^2u$ , in Å<sup>2</sup>), 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 <sub>3</sub>	Si(OH) <sub>6</sub> <sup>2-</sup>	0	0.0026 (*)	0.63 (4)
C(1)	3	CO <sub>3</sub> <sup>2-</sup>	$\frac{1}{3}$	0.456 (2)	0.9 (2)
S(1)	3	SO <sub>4</sub> <sup>2-</sup>	$\frac{1}{3}$	-0.0027 (7)	1.07 (6)
O(1)	1		{ 0.392 (3)	0.261 (1)	1.9 (1)
O(2)	1		{ 0.260 (2)	0.259 (1)	1.7 (1)
O(3)	1	H <sub>2</sub> O	{ 0.0025 (8)	0.082 (1)	2.2 (1)
O(4)	1		{ 0.0217 (7)	0.4421 (7)	1.2 (1)
O(5)	1	CO <sub>3</sub> <sup>2-</sup>	0.2014 (8)	0.4700 (9)	2.0 (1)
O(6)	1	SO <sub>4</sub> <sup>2-</sup>	0.1914 (7)	0.0431 (8)	1.5 (1)
O(7)	1		{ 0.1312 (6)	0.1150 (7)	0.86 (8)
O(8)	1	Si(OH) <sub>6</sub> <sup>2-</sup>	{ 0.1300 (6)	0.4052 (7)	0.86 (8)
O(9)	3	SO <sub>4</sub> <sup>2-</sup>	$\frac{1}{3}$	0.855 (1)	1.4 (2)
H(12)	1		{ 0.347	0.260	3.0
H(19)	1		{ 0.488	0.297	3.0
H(25)	1		{ 0.303	0.333	3.0
H(26)	1	H <sub>2</sub> O	{ 0.311	0.183	3.0
H(35)	1		{ 0.439	0.042	3.0
H(36)	1		{ 0.069	0.068	3.0
H(45)	1		{ 0.085	0.452	3.0
H(46)	1		{ 0.410	0.478	3.0
H(70)	1	Si(OH) <sub>6</sub> <sup>2-</sup>	{ 0.215	0.111	3.0
H(80)	1		{ 0.213	0.413	3.0

\*  $z$  coordinate arbitrarily held constant.

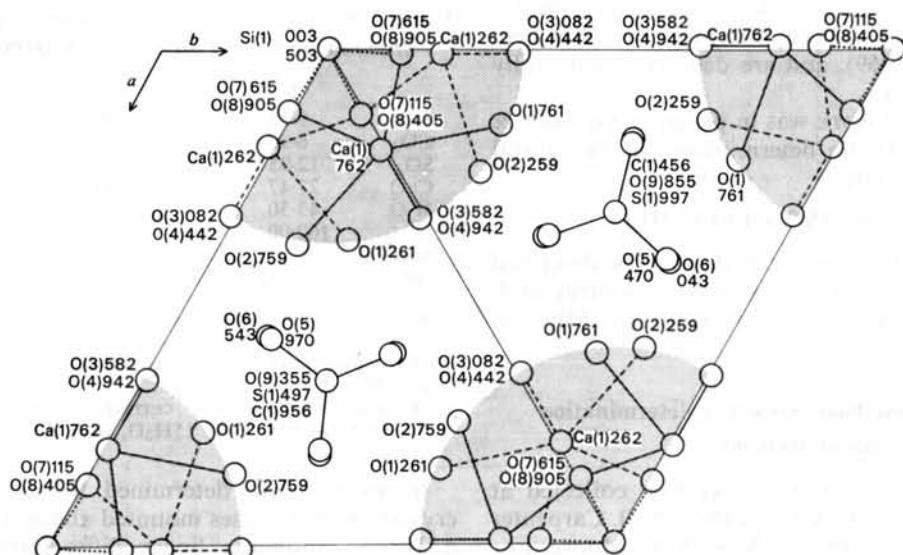


Fig. 1. The structure shown in projection along the  $c$  axis. Heights of atoms are given as  $1000 z/c$ ; hydrogen atoms are omitted. The columns, of empirical composition  $[\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]^{4+}$ , are shaded. Full and broken lines represent Ca–O bonds 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  $\times 10^3$ )

Unobserved reflexions are marked ●.

	E	FO	FC	ALPHA		E	FO	FC	ALPHA		E	FO	FC	ALPHA		E	FO	FC	ALPHA		E	FO	FC	ALPHA					
●	1, L <sup>+</sup>	0	3	305	363 322,15	10	137	146	14,38	6	299	324 120,70	●	7, L <sup>+</sup>	4	3	262	269	9,36	11	120	122	55,31	6	76	37	260,73		
●	837	817	0,00	4	367	347 26,42	11	105	110	21,30	5	297	320 24,70	●	8, L <sup>+</sup>	4	203	207	192,96	6	319	260	28,63	5	69	65	224,65		
●	290	329	180,00	6	631	567 20,71	11	4, L <sup>+</sup>	2	7, L <sup>+</sup>	133	178,44	1, 117	119	131,76	7	69	69	72,34	11	120	120	100,72	7	88	83	199,77		
●	212	215	0,02	7	342	345 177,07	11	4, L <sup>+</sup>	2	8, L <sup>+</sup>	75	36 210,85	2, 127	211	211,32	11	120	120	100,72	11	90	90	215,51						
●	324	475	0,00	7	382	414 40,43	11	193	192	100,49	1, 292	272 222,13	6	338	382 24,60	1, 167	280	153,33	11	29	111	207,42	11	242	235 245,73				
●	349	347	0,00	10	112	60 55,87	2	116	112	37,48	6	295	301 60,11	●	6, L <sup>+</sup>	3	5	73	66 301,61	0	36	42	206,56	1, 91	76	49,77	11	4, L <sup>+</sup>	8
●	378	332	0,00	11	193	192 100,49	11	193	192	100,49	6	485	530 33,93	0	98	121	146,30	7	80	51	224,30	2, 250	216	247,12	0	295	271 37,62		
●	372	387	0,00	11	198	180 181,41	7	102	102	35,87	6	164	187 187,84	2	297	297 17,84	6	92	174	187,84	3, 181	163	23,25	6	181	167 17,43			
●	70	45	0,00	11	602	551 184,21	8	370	372	2,07	6	29	45 322,52	●	8, L <sup>+</sup>	4	4, 49	126	339,74	9	355	353	221,61	2	27	71	239,20		
●	214	21	180,00	2	869	866 19,70	9	98	88	5,96	6	160	171 173,71	1, 215	195	192,91	11	80	100	122,31	9	155	154 55,27	6	137	133 36,70			
●	2, L <sup>+</sup>	0	3	482	839 11,46	11	193	192	100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	284	273	180,00	3	277	233 145,25	11	193	192 100,49	0	444	431 151,80	9	119	94	12,18	6	69	72	54,20	3, 147	125	176,20	2	107	137 355,41	11	97	86 227,26
●	185	72	180,00	6	453	421 178,86	11	193	192 100,49	1	295	324 120,70	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	422	378	182,00	7	193	71 316,43	11	193	192 100,49	1	295	324 120,70	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	377	344	0,00	9	166	180 355,71	3	123	76	7,32	●	119	120 58,69	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	
●	74	51	0,00	10	193	39 275,23	4	383	356 152,53	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	177	176	0,00	11	190	207 334,31	11	193	192 100,49	6	140	155 165,32	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	190	172	180,00	7	141	112 31,84	11	193	192 100,49	2	305	305 128,59	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	234	259	0,00	11	4, L <sup>+</sup>	1	295	324 120,70	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49			
●	205	212	0,00	11	193	192 177,64	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	73	73	42	180,00	1	103	163 185,70	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	
●	286	338	0,00	2	215	216 272,30	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	131	136	0,00	1	403	420 32,00	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	131	136	0,00	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	206	213	180,00	2	154	151 357,20	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	117	161	191,00	3	232	231 251,67	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	201	194	180,00	4	198	180 185,13	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	163	176	0,00	5	151	222 257,72	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	163	176	0,00	6	151	222 257,72	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	205	205	0,00	7	151	222 257,72	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	73	73	205	0,00	8	150	20 305,19	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	
●	129	129	180,00	9	153	153 135,87	0	249	247 349,15	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	467	570	0,00	1	537	537 155,26	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	467	570	0,00	2	267	242 343,21	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	105	121	180,00	3	231	231 251,67	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	129	129	0,00	4	150	150 155,26	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	129	129	0,00	5	151	151 155,26	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	129	129	0,00	6	151	151 155,26	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	129	129	0,00	7	151	151 155,26	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	129	129	0,00	8	151	151 155,26	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	129	129	0,00	9	151	151 155,26	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49		
●	129	129	0,00	10	151	151 155,26	11	193	192 100,49	11	193	192 100,49	11	193	192 100,49														

Table 4 (cont.)

X	FO	FC	ALPHA	X	FO	FC	ALPHA	X	FO	FC	ALPHA	X	FO	FC	ALPHA	X	FO	FC	ALPHA	X	FO	FC	ALPHA	X	FO	FC	ALPHA	X	FO	FC	ALPHA					
4 6, L <sup>+</sup> 9		5 91	64 192.23	9 36	52	42.73		3 174	151	13.63		0 33	32	66.76		7, L <sup>+</sup> 11		6 59	36 215.12	2 75	59 285.57															
4 80	102	320.26	5 150	137	225.46	NH 5, L <sup>+</sup> 10		NH 10, L <sup>+</sup> 10		2 123	244	25.24		1 123	192	72.52	0 159	173	59.03	8 78	37 20.71	4 232	225 37.63													
5 89	59	85.33	6 193	169	38.38					5 121	118	1.8		5 121	120	1.8	0 159	173	59.03	9 267	267 47.63	5 235	269 36.12													
6 219	122	172.53	7 193	151	31.66					5 131	162	74.23		2 127	123	26.65	0 151	155	67.40	3 69	75 177.54	NH 2, L <sup>+</sup> 12														
7 192	205	236.19	8 145	93	55.79	0 394	444	222.42	9 109	123	232.38	1 91	76	280.95	6 151	145	45.38	4 208	236	15.95	0 151	155	67.40	7 76	51 270.83	7 59	56 263.73									
NH 7, L <sup>+</sup> 9		9 127	107 226.22	10 23	142	251.52	NH 11, L <sup>+</sup> 10		7 145	126	15.11		7 145	131	15.11	0 145	126	214.77	5 76	123	15.11	0 47	77 255.47	NH 8, L <sup>+</sup> 12												
0 45	70	111.22	1 241	226	216.03	NH 2, L <sup>+</sup> 10		5 123	264	239.43	0 86	69	233.67	0 40	49	227.63	5 65	124	323.17	0 259	295 37.49															
1 190	117	84.04	0 223	310	34.42	7 123	62	36.05	NH 4, L <sup>+</sup> 11		1 104	115	20.23	NH 6, L <sup>+</sup> 11		0 102	173	19.92	5 59	54 331.42	1 76	51 253.15														
3 111	117	84.04	1 193	177	35.36	NH 6, L <sup>+</sup> 10		0 37	36	0.22	2 178	211	50.49	1 143	157	45.02	5 94	194 350.29	3 170	173 38.46																
4 163	150	37.53	1 193	177	35.34	3 122	128	1.11	0 100	103	307.75	2 266	250	224.53	3 155	133	215.34	6 62	86 195.74	8 145	136 14.15	0 83	81 3.35													
NH 8, L <sup>+</sup> 9		4 194	106 224.53	5 146	242	13.20	2 254	216	36.56	0 27	77	222.37	4 110	119	225.33	NH 9, L <sup>+</sup> 11		0 138	135	6.45	1 106	137 243.79	4 275	295 40.59												
0 175	184	227.26	5 246	242	13.20	5 122	128	1.11	0 27	77	222.37	3 155	133	215.34	5 95	67	49.93	9 157	104 36.37	NH 7, L <sup>+</sup> 12																
1 210	194	204.10	7 337	328	31.22	4 242	256	250.55	1 292	244	47.30	0 165	160	224.42	0 83	86	37.82	0 138	135	6.45	1 106	125 255.69	2 95	122 231.93	3 109	94 25.49										
2 61	45	21.42	8 352	165	6.64	5 122	126	22.55	2 215	243	24.55	0 165	160	224.42	2 174	111	225.75	3 152	154 229.68	3 120	94 355.61	4 97	92 17.15													
3 203	116	51.08	9 136	167	22.64	6 118	155	345.14	3 245	257	53.95	0 61	24	71.55	3 152	154 229.68	4 123	122 22.55	5 123	122 22.55	6 117	107 227.44														
5 166	126	217.88	NH 3, L <sup>+</sup> 10		7 171	147	27.37	5 73	224	24.06	NH 4, L <sup>+</sup> 11		0 131	137	72.46	NH 5, L <sup>+</sup> 11		5 85	49 267.26	0 177	137 227.44															
NH 9, L <sup>+</sup> 9		0 165	165	4.62	NH 6, L <sup>+</sup> 10		7 223	223	1.11	0 61	60	296.50	NH 10, L <sup>+</sup> 11		6 117	102	1.75	7 134	144 231.93	NH 6, L <sup>+</sup> 12																
0 76	47	220.39	2 157	166	45.70	NH 7, L <sup>+</sup> 10		0 268	267	35.45	0 61	65	4.36	1 170	171	57.74	0 125	67	72.21	8 51	43 229.16	0 75	51 335.24													
1 190	198	23.37	3 204	195	26.39	4 204	204	26.39	1 171	124	56.68	1 79	73	222.63	1 59	60	23.01	7 131	144 231.93	1 94	105 262.46															
2 232	258	49.36	4 204	195	26.39	5 110	129	26.75	1 172	125	56.68	3 77	85	258.35	NH 11, L <sup>+</sup> 11		6 117	102	1.75	7 134	144 231.93	2 95	122 231.93	3 109	94 25.49											
3 172	150	38.72	5 164	125	33.32	5 93	93	58.29	NH 2, L <sup>+</sup> 11		4 153	143	25.39	NH 12, L <sup>+</sup> 11		6 117	102	1.75	7 134	144 231.93	NH 4, L <sup>+</sup> 12															
NH 10, L <sup>+</sup> 9		7 183	140	47.58	NH 5, L <sup>+</sup> 10		8 161	156	36.48	9 116	117	7.41	0 203	250	29.71	1 310	456	54.81	3 156	133	224.66	1 233	251	25.82	4 67	46 276.35										
0 136	121	22.36	1 96	68	26.27	NH 4, L <sup>+</sup> 10		2 203	250	29.71	0 47	80	325.73	7 111	96	205.36	NH 12, L <sup>+</sup> 11		3 97	102	245.45	NH 9, L <sup>+</sup> 12														
1 92	44	36.10	NH 5, L <sup>+</sup> 10		2 202	256	27.13	5 39	52	312.31	NH 6, L <sup>+</sup> 11		0 49	23	179.07	0 120	122	42.22	4 64	63 314.72	5 106	105 36.35	6 117	122 37.37	7 205	209 35.16										
NH 11, L <sup>+</sup> 9		0 124	125	241.51	3 193	176	30.46	4 73	70	75.71	0 49	23	179.07	5 120	52	21.77	NH 1, L <sup>+</sup> 12		5 117	122 37.37	2 69	73 312.31	2 63	122 302.87												
U 95	103	226.14	1 92	154	269.53	5 137	163	12.64	0 258	259	77.32	2 220	207	58.62	3 190	125	22.57	0 174	292	35.11	6 111	118 221.77	NH 10, L <sup>+</sup> 12													
1 117	96	204.24	2 88	66	63.97	3 193	176	30.46	0 258	259	77.32	3 190	125	22.57	3 141	87	292.37	0 174	292	35.11	6 111	118 221.77														
NH 1, L <sup>+</sup> 10		4 107	121	358.41	NH 9, L <sup>+</sup> 10		0 108	172	334.50	0 98	85	235.11	0 91	55	178.73	2 45	46	306.12	NH 5, L <sup>+</sup> 12		0 223	286	44.74	NH 6, L <sup>+</sup> 10												
5 20	122	23.37	5 120	168	206.72	1 47	132	131.58	NH 5, L <sup>+</sup> 11		7 134	102	45.03	0 55	55	178.37	3 88	37	324.54	0 334	321	49.89	2 100	108 227.44												
2 212	254	35.26	7 160	193	32.47	2 134	132	45.03	NH 5, L <sup>+</sup> 11		7 134	102	45.03	0 55	55	178.37	5 312	317	46.72	1 165	164	33.23	2 100	108 227.44												

of Aberdeen. Form factors (for  $\text{Ca}^{2+}$ , Si, S, C, H and  $\text{O}^-$ ) 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  $\text{SiO}_4^{4-}$  tetrahedra which were present in this structure should be replaced by  $\text{SiO}_6^{8-}$  [or  $\text{Si}(\text{OH})_6^{2-}$ ] octahedra, and that an  $\text{H}_2\text{O}$  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  $\text{Si}(\text{OH})_6^{2-}$  octahedron and to make the remaining O

atoms coordinated to Ca into  $\text{H}_2\text{O}$  molecules; this corresponds to the formula



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  $w=1/\{1+[|F_{\text{obs}}|-30.0]/30.0]^2\}$  and analyses against  $|F_{\text{obs}}$ ,  $\sin^2 \theta$  and  $I$  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  $-5 \text{ e}\cdot\text{\AA}^{-3}$  (near the Ca and Si atoms;  $-2 \text{ e}\cdot\text{\AA}^{-3}$  elsewhere), while the extremes on the difference Fourier synthesis were  $-1.2$  and  $+0.9 \text{ e}\cdot\text{\AA}^{-3}$ . 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  $\text{Si}(\text{OH})_6^{2-}$  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  $[Ca_3Si(OH)_6 \cdot 12H_2O]^{4+}$  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 linked 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 $< 3.0 \text{ \AA}$ ), 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	O(1)—O(2)      2.93 (4) Å	O(2)—O(1)—O(9)      121 (1)°		
Ca(1)—O(2)      2.50 (2)	O(1)—O(9)      2.82 (4)			
Ca(1)—O(3)      2.43 (1)	O(2)—O(5)      2.79 (2)	O(5)—O(2)—O(6)      105.6 (6)		
Ca(1)—O(4)      2.40 (1)	O(2)—O(6)      2.78 (2)			
Ca(1)—O(7 <i>a</i> )      2.46 (1)	O(3)—O(5)      2.74 (1)	O(5)—O(3)—O(6)      89.2 (4)		
Ca(1)—O(7 <i>b</i> )      2.48 (1)	O(3)—O(6)      2.77 (1)			
Ca(1)—O(8 <i>a</i> )      2.44 (1)	O(3)—O(8)      2.98 (1)			
Ca(1)—O(8 <i>b</i> )      2.46 (1)	O(4)—O(5)      2.69 (1)	O(5)—O(4)—O(6)      90.8 (3)		
Si(1)—O(7)      1.835 (7)	O(4)—O(6)      2.75 (1)			
Si(1)—O(8)      1.731 (7)	O(4)—O(7)      2.92 (1)			
S(1)—O(6)      1.47 (1)				
S(1)—O(9)      1.48 (2)				
C(1)—O(5)      1.29 (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  $> 130^\circ$  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(7 <i>b</i> )	73.1 (7)	2.94 (4)	O(7)—Si(1)—O(8)	93.3 (3)	2.59 (1)
O(1)—Ca(1)—O(8 <i>b</i> )	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(7 <i>a</i> )	75.5 (4)	3.04 (2)			
O(2)—Ca(1)—O(8 <i>a</i> )	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(7 <i>a</i> )	86.5 (3)	3.35 (1)	Si(1)—O(8)—H(80)	135	—
O(3)—Ca(1)—O(7 <i>b</i> )	83.0 (3)	3.25 (1)			
O(4)—Ca(1)—O(8 <i>a</i> )	84.4 (3)	3.25 (1)			
O(4)—Ca(1)—O(8 <i>b</i> )	85.4 (3)	3.29 (1)			
O(7 <i>a</i> )—Ca(1)—O(7 <i>b</i> )	59.4 (3)	2.45 (1)	O(6)—S(1)—O(6)	108.9 (5)	2.41 (1)
O(7 <i>a</i> )—Ca(1)—O(8 <i>a</i> )	76.0 (3)	3.02 (1)	O(6)—S(1)—O(9)	110.1 (4)	2.40 (1)
O(7 <i>a</i> )—Ca(1)—O(8 <i>b</i> )	104.1 (3)	3.88 (1)			
O(7 <i>b</i> )—Ca(1)—O(8 <i>a</i> )	104.2 (3)	3.88 (1)			
O(7 <i>b</i> )—Ca(1)—O(8 <i>b</i> )	75.2 (2)	3.02 (1)			
O(8 <i>a</i> )—Ca(1)—O(8 <i>b</i> )	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 ( $1.731 \pm 0.007 \text{ \AA}$ ) on one side of the Si atom, and three long ones ( $1.835 \pm 0.007 \text{ \AA}$ ) on the other. Similar distortions in  $MO_6$  octahedra have been observed in corundum, with Al–O distances of  $1.86$  and  $1.97 \text{ \AA}$  (Newnham & de Haan, 1962), and in other cases. Liebau & Hesse (1969) found somewhat similar, though less symmetric, distortion in the AIV polymorph of  $SiP_2O_7$ , with Si–O distances of  $1.75$ – $1.83 \text{ \AA}$ . For the AlIII polymorph, Bissert & Liebau (1969) found a smaller range of distances ( $1.74$ – $1.79 \text{ \AA}$ ). All these Si–O distances are considerably above the range of values ( $1.57$ – $1.67 \text{ \AA}$ ) commonly observed for tetrahedral coordination, and are much nearer the sum of the single covalent radii ( $1.81 \text{ \AA}$ ). 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  $2.40$  to  $2.50 \text{ \AA}$ , agree closely with the corresponding values in jouravskite ( $2.41$ – $2.54 \text{ \AA}$ ) and less closely with those in ettringite [ $2.39$ – $2.72 \text{ \AA}$  according to Courtois *et al.* (1968) or  $2.35$ – $2.75 \text{ \AA}$  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 ( $B = 7.1 \text{ \AA}^2$ ) 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  $2.69$ – $2.93 \text{ \AA}$ . 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  $3420$ – $3560 \text{ cm}^{-1}$ , and H–O–H bending frequencies at  $1705$  and  $1660 \text{ cm}^{-1}$ . 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-

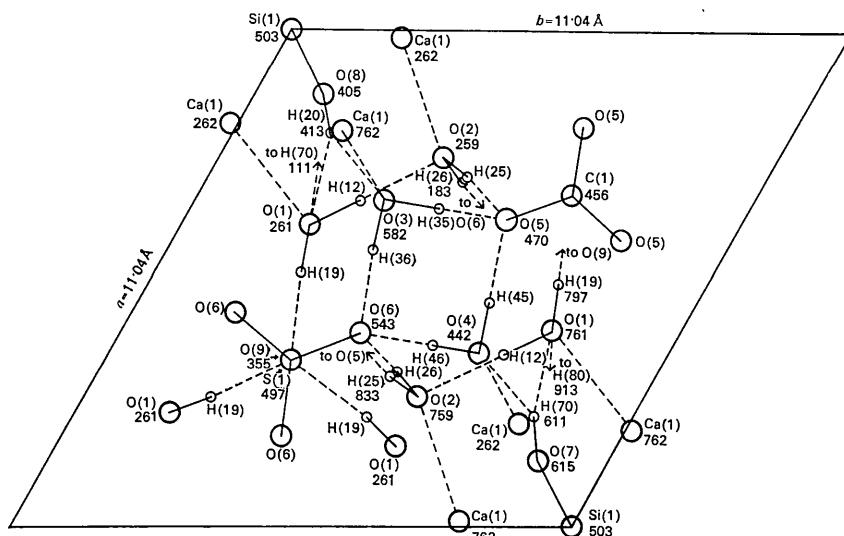


Fig. 2. Selected parts of the structure shown, as in Fig. 1, in projection along  $c$ , and chosen to illustrate the system of hydrogen bonding and coordination of the O atoms. Heights of atoms are given as  $1000 z/c$ .

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  $\text{Si}(\text{OH})_6^{2-}$  for  $\text{Al}(\text{OH})_6^{3-}$  and appropriate balancing replacements. The composition of the Franklin mineral is complicated by the virtual absence of  $\text{CO}_2$  and presence of  $\text{B}_2\text{O}_3$ ; possibly  $\text{BO}_3^{3-}$  replaces the  $\text{CO}_3^{2-}$  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  $\text{SO}_4^{2-}$ . These, too, may well form solid solutions with thaumasite, but the possibilities of this have not so far been investigated.

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