

The Structure of Dicalcium Silicate α -Hydrate*

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This compound, which was prepared hydrothermally from β -dicalcium silicate, is shown to have the probable empirical formula $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$. Unit-cell dimensions are: $a = 9\cdot34$, $b = 9\cdot22$, $c = 10\cdot61$ Å. $Z = 8$. Space group, $P2_12_12_1$; pseudo space group, $Pbca$. The structure deduced, which is an idealized approximation to the true structure, contains discrete $(\text{SiO}_3\cdot\text{OH})^{3-}$ tetrahedra and has the formula $\text{Ca}_2(\text{SiO}_3\text{OH})\text{OH}$.

Introduction

Dicalcium silicate α -hydrate was first discovered in steam-cured Portland cement mortars by Thorvaldson & Shelton (1929), who also described its optical properties. It has since been prepared under hydrothermal conditions either from calcium oxide and silica gel or from anhydrous dicalcium silicates (for a review see Taylor & Bessey, 1950). Dicalcium silicate α -hydrate is readily distinguished from other hydrated calcium silicates by the fact that it crystallises in relatively large plates of rectangular outline. These show straight extinction, suggesting that the crystals are orthorhombic.

Some of the material used in the present investigation was obtained from a sample prepared by Bessey from β -dicalcium silicate (Bessey, 1938, p. 178, and private communication). Additional material was also prepared by hydrothermal treatment of mixtures of lime and silica, and of β -dicalcium silicate (Heller & Taylor, 1952). It was found that under the conditions studied the initial product was usually calcium silicate hydrate (I). Further treatment gave dicalcium silicate α -hydrate and finally hillebrandite (dicalcium silicate β -hydrate, $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$) and/or afwillite. Thus, although it was possible to select from the preparation single crystals of dicalcium silicate α -hydrate suitable for X-ray analysis, no bulk sample could be prepared which was completely free from the presence of one or both of these phases.

Composition and water content

The $\text{CaO}:\text{SiO}_2$ molar ratio of 2.0 for dicalcium silicate α -hydrate has been satisfactorily established by previous workers. The values given for the water content are, however, less certain and range between 1 and 1.25 molecules per $2\text{CaO}\cdot\text{SiO}_2$. These discrepancies are probably due to two causes. First, the samples analysed may not have been free from im-

purities, as described above. It is easily possible to underestimate the amount of a gel in the presence of a better crystallised phase, and more than negligible amounts of calcium silicate hydrate (I) may have been present in the samples analyzed, thus giving a higher water content. Secondly, different workers used different drying agents, some of non-reproducible vapour pressure, for example soda lime. Bessey (1938, p. 178) pointed out that the water content of an imperfectly crystallised calcium silicate hydrate is related to the vapour pressure of the drying agent.

Bessey's sample of dicalcium silicate α -hydrate (which had been prepared ten years previous to this investigation) was analyzed by the author and its water content was found to be 1 molecule per $2\text{CaO}\cdot\text{SiO}_2$. Bessey's original value, after drying over saturated ammonium sulphate, was between 1.1 and 1.25. The sample on standing had reached equilibrium with the moisture of the atmosphere, which has a lower vapour pressure than saturated ammonium sulphate. This suggests that water in excess of 1 molecule per $2\text{CaO}\cdot\text{SiO}_2$ is very loosely held and probably not in a state of chemical combination. The sample appeared to be free from gel but contained some hillebrandite. The water content of hillebrandite is believed to be 1 molecule per $2\text{CaO}\cdot\text{SiO}_2$ (Flint, McMurdie & Wells, 1938) so that its presence does not affect the argument.

No cases have been reported in which the water content was found to be less than 1 molecule per $2\text{CaO}\cdot\text{SiO}_2$. Kalousek (private communication), who analyzed about 100 samples of dicalcium silicate α -hydrate, concluded that the water content was 1.0 molecule per molecule of $2\text{CaO}\cdot\text{SiO}_2$, which is significant in this respect.

It was therefore considered probable that the empirical formula of dicalcium silicate α -hydrate is $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$.

Crystal data

The crystals used for the present X-ray analysis were derived mainly from sample no. 25 described by Heller

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& Taylor (1952). Single crystals from other samples, including that prepared by Bessey, were also mounted, and oscillation photographs established their identity. All the crystals were flat, rectangular plates.

The unit-cell dimensions of dicalcium silicate α -hydrate, deduced from oscillation photographs, were

$$a = 9.34, b = 9.22, c = 10.61 \text{ \AA}.$$

The crystal is orthorhombic, confirming the optical evidence previously obtained. The b axis is perpendicular to the plane of the plate. It was difficult to establish the density of the compound as it had not been obtained in a pure condition and was imperfectly crystallised. The single crystals were too small for density measurement by floatation. The values for the density given by previous workers are 2.59 and 2.80 g.cm.⁻³ (Taylor & Bessey, 1950). If it is taken as 2.76 g.cm.⁻³ the number of molecules in the cell is 8.

The only systematic absences observed were for all $0kl$ reflexions when k is odd, $h0l$ reflexions for l odd except for 209 (moderate) and 407 (weak), and $hk0$ reflexions for h odd except for 530 (moderate). Hence the true space group is $P2_12_12_1$ and there is a pseudo space group $Pbca$.

In the present work only the pseudo space group was considered. This has 8-fold general positions compared with 4-fold positions for $P2_12_12_1$. Thus the number of independent parameters is halved for the pseudo-structure, i.e. each atom is given parameters which are the average of two independent but very similar values in the true structure. The problem of the structure determination is thereby reduced to finding the parameters of one formula-unit.

Powder data

Some discrepancy occurs in the literature in the descriptions of the powder data of dicalcium silicate α -hydrate. Thus Bessey's data (Taylor & Bessey, 1950) include some spacings of hillebrandite. Table 1

Table 1

Observed spacing	Intensity	Calculated spacing	Index
5.35 Å	<i>w</i>	5.30 Å	002
4.63	<i>vwv</i>	4.56	020
4.22	<i>vs</i>	4.24	021
3.90	<i>s</i>	3.89	211
3.54	<i>s</i>	3.52	202
3.27	<i>vvs</i>	3.27	122
3.04	<i>w</i>	3.10	113
2.87	<i>s</i>	2.86	311
2.80	<i>s</i>	{2.81	131
		{2.81	222
2.77	<i>w</i>	2.79	023
2.71	<i>w</i>	{2.70	302
		{2.70	213
2.69	<i>vw</i>	2.69	123
2.65	<i>m</i>	2.65	004
2.60	<i>s</i>	2.59	312
2.56	<i>w</i>	2.56	132
2.52	<i>m</i>	2.52	321
2.47	<i>vwv</i>	2.47	114

Observed spacing	Intensity	Calculated spacing	Index
2.41	<i>vs</i>	2.41	223
2.31	<i>vw</i>	2.31	204
2.27	<i>vw</i>	2.27	410
2.24	<i>w</i>	2.25	041
2.18	<i>m</i>	2.19	141
2.16	<i>w</i>	2.15	402
2.10	<i>vw</i>	2.10	420
2.08	<i>w</i>	2.08	323
2.06	<i>mw</i>	2.06	240
2.03	<i>w</i>	2.03	332
2.02	<i>w</i>	2.02	304
1.982	<i>m</i>		
1.956	<i>w</i>		
1.926	<i>m</i>		
1.890	<i>w</i>		
1.872	<i>mw</i>		
1.842	<i>vw</i>		
1.820	<i>m</i>		
1.788	<i>s</i>		
1.737	<i>mw</i>		
1.712	<i>mw</i>		
1.687	<i>vwv</i>		
1.662	<i>mw</i>		
1.654	<i>m</i>		
1.645	<i>m</i>		
1.630	<i>m</i>		
1.608	<i>w</i>		
1.572	<i>mw</i>		
1.543	<i>mw</i>		
1.521	<i>mw</i>		
1.499	<i>vw</i>		
1.480	<i>mw</i>		
1.448	<i>w</i>		
1.407	<i>vwv</i>		
1.374	<i>vwv</i>		
1.357	<i>w</i>		
1.318	<i>vw</i>		
1.304	<i>vw</i>		
1.289	<i>vw</i>		
1.282	<i>vw</i>		
1.248	<i>vw</i>		
1.229	<i>vw</i>		
1.210	<i>vw</i>		
1.194	<i>vw</i>		
1.185	<i>vw</i>		
1.180	<i>vw</i>		
1.161	<i>w</i>		
1.152	<i>vw</i>		
1.141	<i>w</i>		

v = very, s = strong, m = moderate, w = weak.

shows a list of spacings, their intensities for copper $K\alpha$ radiation and their indices (indexing of spacings below 2 Å was not attempted as it would be too ambiguous).

Structure determination

General observations

The dicalcium silicate α -hydrate lost all its water on heating to 500° C. and the powder after cooling was identified as γ -dicalcium silicate. The primary product of decomposition may have been β -dicalcium silicate which inverted to the γ form on cooling, or γ -dicalcium silicate. In either case the product of

decomposition had a structure based on discrete SiO_4 tetrahedra. It may reasonably be expected that moderate heating and consequent loss of water would lead to association of molecules or atomic groupings rather than dissociation, and since the product consists of discrete tetrahedra it may be assumed, lacking any evidence to the contrary, that the initial compound also contained discrete SiO_4 tetrahedra.

If the structure consists of discrete SiO_4 tetrahedra, one oxygen atom per $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ is not attached to a silicon ion. This will be described as 'free oxygen'. This 'free oxygen' may be present in the form of H_2O , OH^- or O^{--} .

Most hydrates lose water present in the form of H_2O at temperatures much below 500°C . unless there is a stable framework which will trap the water molecules and prevent their escape. It is improbable that such a framework should exist in the present case, hence the 'free oxygen' probably occurs in the form of OH^- or O^{--} . In the former case one and in the latter two hydroxyl groups must be attached directly to the silicon atom, as in the case of awillite (Megaw, 1949).

Patterson projection

The intensities of all the reflexions in the $h0l$ zone were estimated visually on a complete set of oscillation photographs. A scale of six gradations only was used, ranging from absent to very strong, and the intensities were corrected for the Lorentz polarization factor. According to A. D. Booth (unpublished work) the peaks of a Patterson projection calculated on this basis should be no more than 0.1 \AA removed from the positions which would have been obtained had more accurate intensities been used. Fig. 1 shows the

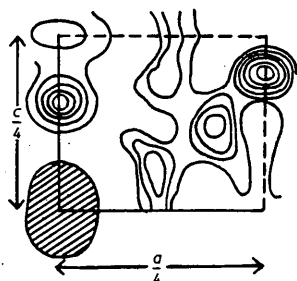


Fig. 1. Patterson map of the (010) projection.

Patterson thus obtained in the (010) projection. In this projection of the space group $Pbca$ each atom necessarily gives rise to a vector parallel to the a axis. Only two such peaks (and their repetitions) were actually observed. It was assumed that these were wholly or partly due to metal-metal vectors, i.e. due to a superposition of Ca-Ca, Ca-Si and Si-Si vectors. A limited number of possibilities for the x coordinates of the heavier atoms could therefore be deduced directly from the Patterson map.

Trial structure and comparison of observed and calculated structure factors

A trial structure was postulated, based on the usual atomic radii and built up of regular, discrete silicate tetrahedra ($\text{Si-O} = 1.63 \text{ \AA}$). These tetrahedra were assumed to be linked through calcium ions to which the 'free oxygen' groups were also coordinated. The orientation of the tetrahedra was determined only by packing considerations. No assumptions were made about the nature of the 'free oxygen' and the positions of the hydrogen atoms were neglected. Only one solution could be found which was also compatible with the Patterson projection. The approximate position of the 'free oxygen' was uniquely determined by the packing.

Structure factors were then calculated for all reflexions in the $hk0$, $h0l$ and $0kl$ projections whose $2 \sin \theta$ values were less than 1. To make the calculated structure factors F_c comparable with the observed intensities I_o (still on the basis of absent to very strong, and uncorrected), the values of F_c were first squared, then divided by the appropriate Lorentz polarization factor and by the geometric factor, G , taken from the chart described by Cox & Shaw (1930), i.e. $I_o \propto F_c^2/pG$. By taking the average of all F_c^2/pG factors for each group of observed intensities (from absent to very strong) average numerical values could be assigned to each group. These were 0, 100, 400, 800 and 1500 for absent, weak, moderate, strong and very strong reflexions respectively.

Small shifts were applied to the atomic coordinates (maintaining the size and regularity of the tetrahedra) to improve the agreement between observed and calculated intensities. The atomic coordinates finally adopted are shown in Table 2.

Table 2. Final coordinates

	Ca		Si	O				
x	4.22	3.60	7.04	4.10	5.56	7.56	8.08	6.90
y	5.90	0.20	2.80	3.30	3.10	1.60	4.00	2.50
z	8.00	4.56	10.35	7.02	9.85	9.40	10.25	1.32

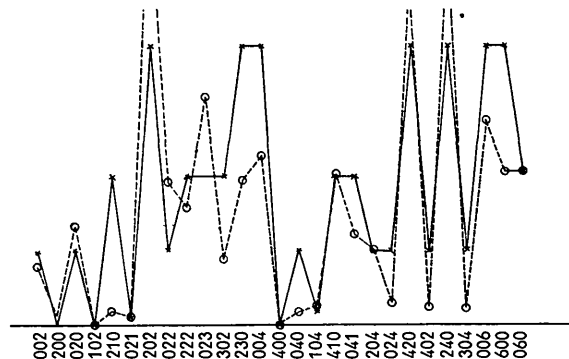


Fig. 2. Comparison of observed and calculated intensities. The full lines represent observed, the broken lines calculated structure factors.

Fig. 2 shows a comparison of the observed and calculated intensities. Fig. 3 is a plan of the (010) projection of the corresponding structure.

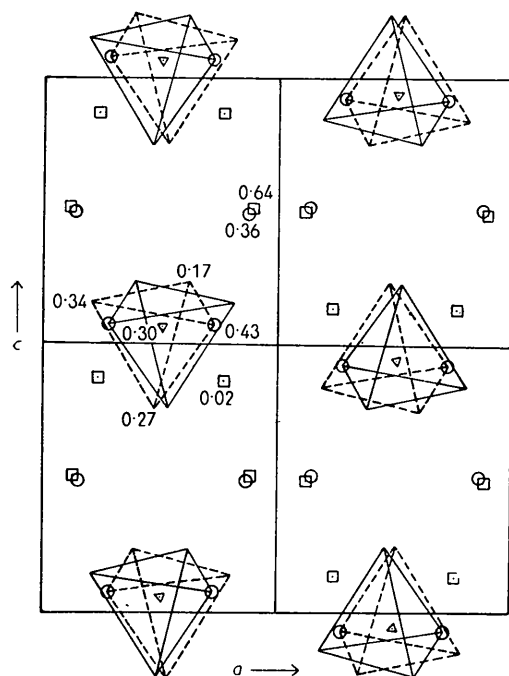


Fig. 3. Map of the ac projection. The projections of the silicate tetrahedra are shown. \square represent calcium, \triangle silicon and \circ the probable positions of hydroxyl ions. The figures represent heights in the b direction.

Discussion

The present structure is only an approximation to the true solution but the agreement between observed and calculated structure factors suggests that it provides a suitable basis for further refinement.

Inaccuracies are due to three causes: In the pseudo-structure no distinction is made between pairs of atoms whose parameters in the true structure are not identical. Moreover, it was assumed that the SiO_3OH group is a regular tetrahedron, which cannot hold exactly. Finally, and probably most important, trial-and-error is never a very accurate way of determining the parameters of a structure with many atoms, particularly those of the lighter elements. It is therefore unlikely that the interatomic distances are correct to better than 0.2 \AA , with larger errors possibly occurring in the placing of the oxygen atoms, in particular that of O V. The exact position of O V is least rigidly determined by the packing, and the effect on the structure factors of small changes in the parameters of oxygen atoms is very small.

Table 3 shows the closest neighbours of all crystallographically independent calcium and oxygen atoms.

The two calcium atoms have six oxygen neighbours at distances between $2.3\text{--}2.7 \text{ \AA}$. The 'free oxygen' (O V) has three close calcium neighbours and also four

Table 3. *Closest neighbours*

Atom	Neighbour	Distance
Ca I	O I	2.50 \AA
	O I ³	2.38
	O II ¹	2.30
	O IV	2.62
	O IV ¹	2.72
	O V	2.30
Ca II	O I ⁷	2.70
	O II ¹	2.33
	O I ¹	2.70
	O IV ⁶	2.28
	O V ¹	2.60
	O V ²	2.30
O I	Si I	1.63
	Ca I	2.50
	Ca II	2.70
	Ca II ¹	2.70
	O V ¹	2.50
O II	Si I	1.63
	Ca II ¹	2.33
	Ca I ¹	2.38
	Ca I ²	2.30
	O V ³	2.50
O III	Si	1.63
	O V ¹	2.50
	O I ¹	2.70
O IV	Si	1.63
	Ca I	2.70
	Ca I ²	2.62
	Ca II ²	2.28
	O V	2.54
O V	Ca II	2.60
	Ca II ³	2.30
	Ca I ³	2.30
	O II ³	2.50
	O IV ⁶	2.54
	O I	2.50
	O III	2.50

In column (2) Roman numerals denote crystallographically independent atoms and Arabic numerals refer to atoms which are crystallographically related.

oxygen atoms at a distance of approximately 2.5 \AA . One vertex of each tetrahedron (O III) has no close calcium neighbours, while the other three (O I, II and IV) have three close calcium neighbours each. The position of the hydrogen atoms cannot, of course, be crystallographically established at this stage. However, since O III would otherwise have one complete unsaturated valency, it is very probable that one hydrogen atom is attached to it. The most likely position for the other hydrogen atom is then on the 'free oxygen' O V, since this forms only three Ca–O bonds compared with three Ca–O and one Si–O bonds formed by the other three calcium atoms. Moreover, the environments of O III and O V are so different from the rest, that the placing of the hydrogen atoms is independent of any likely changes on refinement. Pauling's rule of electrostatic charges is completely satisfied by this arrange-

ment. Several possibilities of hydroxyl bonding arise in this structure. O III has two near oxygen neighbours other than those attached to the same Si atom: O V at a distance of 2.5 Å and O I¹ at 2.7 Å. The bond O III–O V, being the shorter, is perhaps more likely to be the hydroxyl bond, although the difference is hardly significant at this stage. O V has three close oxygen neighbours other than O III. From a consideration of the valency angles of O V, a hydroxyl bond between O II⁸ and O V can be excluded. Hydroxyl bonding of O V to either O I or O IV⁶ is, however, equally probable.

The structural formula of dicalcium silicate α -hydrate is $\text{Ca}_2(\text{SiO}_3\text{OH})\text{OH}$.

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Aluminium Monochromator with Double Curvature for High-Intensity X-ray Powder Photographs.

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The construction and performance of an X-ray monochromator using an aluminium single crystal with double curvature is described. The point-focus obtained in this way is used for taking powder photographs of the Guinier type. The gain in intensity is about 16 times as compared with a monochromator using a quartz crystal with single curvature and polished surface, all other conditions being equal.

1. Introduction

As far as we know, point-focusing monochromators using crystals with double curvature have not yet been used in practical X-ray work, although the principle and advantage of such monochromators have been recognized for many years. Shenfil, Danielson & DuMond (1951) have constructed a point-focusing monochromator using two cylindrically curved quartz crystals with their axes at right angles (the geometry of this design was described by DuMond (1950)). This monochromator was intended for the study of low-angle scattering, but its intensity is rather low for several reasons (among others, the losses at the two reflexions).

The bending of a crystal plate to a surface with double curvature can probably be effected only by means of plastic deformation, which greatly reduces the number of possible substances. It may be quite

possible to use sodium chloride, but we have chosen aluminium for our trials. We hoped to take advantage of the high intensities reported by Cauchois, Tiedema & Burgers (1950) for spectra from aluminium single crystals. For the case of transmission these authors found the intensities of spectra from aluminium single crystal lamellae to be 5–10 times as great as from quartz lamellae. For reflexion we have found that about 4 times as long an exposure is required with a quartz monochromator (plane 10 $\bar{1}$ 1 and with polished surface*) as with an aluminium monochromator (planes 100, second order, or 111) in order to obtain the same integrated intensity (estimated visually) in powder photographs, all other essential conditions being equal.

* It is known that the integrated intensity of reflexions from quartz is lower if the surface has been polished than if it has only been ground.