

THE DEHYDRATION OF TOBERMORITE

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ABSTRACT

Tobermorite $[\text{Ca}_4(\text{Si}_6\text{O}_{18}\text{H}_2)\text{Ca}\cdot 4\text{H}_2\text{O}]$ is a hydrated calcium silicate mineral with a layer structure which in some respects resembles that of vermiculite. Its dehydration has been studied using single crystals from Ballyraigy, N. Ireland. The three most frequently encountered hydration states are characterized by basal spacings (d_{002}) of 14.0, 11.3 and 9.35 Å. Dehydration to the 9.35 Å state is complete by 300°C and is accompanied by a stacking change so that the pseudo-cell (a 5.58, b 3.66, c 18.70 Å) becomes A -face centered. The 9.35 Å structure persists up to 700°C, by which temperature all the water has been expelled, and there is some evidence that interlayer Si–O–Si bonds are formed to an increasing extent as the temperature rises.

At about 800°C, the 9.35 Å hydrate changes to β - CaSiO_3 twinned in two orientations. The b -axis of the 9.35 Å hydrate becomes b for both orientations of the product, and the (201) planes of the latter are formed parallel to the (101) and (10 $\bar{1}$) planes of the original material. The mechanism of the change is discussed and is compared with some other transformations occurring under similar conditions. An orientation-determining step is suggested in which the principal effect is a migration of silicon atoms or ions, the calcium–oxygen skeleton remaining relatively undisturbed.

INTRODUCTION

Tobermorite $[\text{Ca}_4(\text{Si}_6\text{O}_{18}\text{H}_2)\text{Ca}\cdot 4\text{H}_2\text{O}]$ is a hydrated calcium silicate which shows certain analogies to the clay minerals. The relationship has been discussed in a recent paper (Taylor and Howison, 1957), which also reviewed previous work on tobermorite. The closest similarity is perhaps to vermiculite. Like vermiculite, tobermorite can exist in several hydration states, of which the most frequently encountered are characterized by basal spacings (d_{002}) of 14.0, 11.3 and 9.35 Å. The crystal structure of the 11.3 Å form was determined by Megaw and Kelsey (1956). Dehydration to the 9.35 Å hydrate is known to occur by about 300°C. At about 800°C this hydrate is altered, giving β - CaSiO_3 ¹. The tobermorite b -axis becomes the β - CaSiO_3 b -axis, but the extent to which orientation is preserved in the sense of rotation around this axis is uncertain. The main aims of the present investigation were (i) to study the conditions of formation and stability of the 9.35 Å hydrate; (ii) to obtain preliminary structural information about this compound; and (iii) to investigate the mechanism of the transition to β - CaSiO_3 .

¹ β - CaSiO_3 is here used to include wollastonite (triclinic), parawollastonite (monoclinic), or intergrowths of the two, where it is impracticable to be more specific. For convenience, the monoclinic axes (a 15.33, b 7.28, c 7.07 Å, β 95° 24½'; Barnick, 1936), will be used throughout this paper.

MATERIAL

Crystals of tobermorite from Ballycraigy (N. Ireland) were used. X-ray oscillation and Weissenberg photographs gave results agreeing closely with the original description by McConnell (1954), who found :

Elongated flakes, cleavage (001), length b .

Unit-cell C -centered orthogonal¹, a 11.3, b 7.33, c 22.6 Å.

Strong pseudo-halving of a and b ; pseudo-cell with a 5.65, b 3.66, c 22.6 Å is body-centered.

The morphology and cell dimensions were further confirmed by electron micrographs and transmission diffraction patterns of crystals with (001) normal to the electron beam, obtained using a three-stage electron microscope. The crystals used for x-ray work all showed angular spread in the reflections, and disorder in the weak layer-lines with odd values of k , but ones up to $500 \times 100 \times 25\mu$ in size were readily found that were sufficiently near to single crystals for the present work. All showed the same grouping of multiple basal reflections: 14.0 Å (weak), 12.3 Å (weak), 11.3 Å (strong) and 9.7 Å approx. (very weak and diffuse). Except for the weaker basal reflections, the single-crystal photographs could be indexed completely on the axes given above. The proportions of hydrates with basal spacings other than 11.3 Å were therefore probably small.

EXPERIMENTAL PROCEDURE AND RESULTS

Crystals were examined using x-ray oscillation photographs to check their identities and basal spacings and were then treated by the procedures listed in Table 1, which gives also the results obtained from oscillation photographs of the treated crystals.

Several crystals that had been heated at 300°C to alter them to the 9.35 Å hydrate were examined more fully. A rotation and set of 10°-oscillation photographs about b were obtained, and also a c -rotation photograph, $h0l$ and $h2l$ Weissenbergs, and electron micrographs and diffraction patterns with the beam normal to (001). X-ray reflections, listed in Table 2, were fewer and often more diffuse than with the unheated crystals. All could be indexed on a C -centered orthogonal cell with a 11.16, b 7.32, c 18.70 Å, which resembles that of the 11.3 Å tobermorite. Reflections with h and k odd were weak; the only ones observed had hk^0 indices. The reflections with h and k even could be indexed on an A -centered pseudo-cell with a 5.58, b 3.66, c 18.70 Å. The specific gravity of a crystal heated at 300°C was found by suspension to be 2.38. The x-ray powder data reported in the literature can be indexed satisfactorily on the proposed cell (Table 3).

¹ Megaw and Kelsey (1956) showed that the true symmetry was monoclinic or triclinic. The C -centered cell, which is retained for convenience, is only geometrically orthorhombic.

TABLE 1.—TREATMENT OF CRYSTALS OF TOBERMORITE

Crystal	Treatment	Basal Spacing(s) after Treatment
All	None	14.0 w, 12.3 w, 11.3 s, 9.7 vw/d.
1	Heated at 125°C for 24 hr	11.3 vs.
2	Heated at 180°C for 24 hr	11.3 m, 9.35 ms.
3	Heated at 240°C for 15 hr	11.3 w, 9.35 s.
4	Heated at 300°C for 15 hr	9.35 s.
5	Heated at 300°C for 24 hr	9.35 s.
6	Heated at 680°C for 5 hr	9.35 vw (but 006 and 008 both present and strong).
7	Heated at 680°C for 24 hr	9.35 vw (006 and 008 as above).
8	Heated at 750–780°C for 24 hr	9.35 vw. Specimen partly altered to β -CaSiO ₃ .
9	Heated at 900°C for 1 hr	Specimen altered to β -CaSiO ₃ .
10	Heated at 930°C for 3 hr	Specimen altered to β -CaSiO ₃ .

TABLE 2.—OBSERVED REFLECTIONS ON X-RAY SINGLE-CRYSTAL PHOTOGRAPHS OF THE 9.35Å HYDRATE. INDICES AND RELATIVE INTENSITIES

<i>hkl</i>	Int.	<i>hkl</i>	Int.	<i>hkl</i>	Int.	<i>hkl</i>	Int.
002	s	20.10	vw	310	w	423	m
006	ms	20.12	vw	710	vw	425	w
008	ms	400	vs	023	ms	427	w
00.10	vw	404	w	025	m	621	s
00.12	w	600	mw	027	m	821	w
200	vw	606	m	029	w	10.21	w
202	m	800	s	02.11	w	040	s
204	ms	10.00	w	221	vvvs	440	w
206	ms	12.00	vw	227	w	840	vw
208	w	110	vwv	421	w	—	—

To study the transformation to β -CaSiO₃, a crystal of tobermorite was cemented to a silica fiber with a mixture of aluminous cement and water glass. Using a modification of Dent's (1957) method, an *h0l* Weissenberg photograph was obtained with one-half of the layer-line screen blocked out. The screen and cassette were removed and one end of the crystal heated just to redness by cautiously advancing it into a gas flame burning from a capillary jet. This was done in a darkened room and the process watched through the goniometer telescope. The layer-line screen was replaced with the other half blocked out, the cassette put back at its original setting relative to the carriage, and the film again exposed. The resulting photograph gave a double check on the relative orientations of starting material and product. The pattern from the tobermorite on one-half of the film could be compared with that of the β -CaSiO₃ on the other, and the β -CaSiO₃ pattern could be

TABLE 3.—INDEXING OF X-RAY POWDER DATA FOR THE 9.35 Å HYDRATE

Observed		Calculated (3)	
(1)	(2)	Indices	Spacings
9.67 s	9.4 s	002	9.35
	6.3 vw/d	110 (?)	6.14
4.83 s	4.80 mw	202	4.80
3.62 w	3.58 mw	204	3.58
3.16 ms	3.16 w	{ 023	3.16
		{ 006	3.12
3.04 vs	2.99 vs	221	3.03
2.79 ms	2.76 ms	{ 400	2.79
		{ 206	2.72
2.35 ms	2.4 vw/d	008	2.34
2.17 vw		208	2.16
2.10 vw	2.1 vw/d	423	2.10
2.02 vw		227	2.01
	1.93 vw	425	1.91
1.834 w	1.84 m	040	1.83
1.659 w		621	1.66
1.526 w		440	1.53
1.393 vvw		800	1.40
1.106 vvw		840	1.11
1.067 vvw		10.21	1.07

(1) McConnell (1954) ; natural mineral from Ballyeraigy.

(2) Kalousek and Roy (1957) ; synthetic material. Data derived from diffractometer trace in original paper.

(3) Indices for orthogonal cell with a 11.16, b 7.32, c 18.70Å.

compared with a superimposed weak pattern recognized as that of the 9.35 Å hydrate. The end of the crystal furthest from the flame evidently had been heated to at least 300°C.

The results confirmed that the tobermorite b -axis becomes the β -CaSiO₃ b -axis, and showed also that a single crystal of tobermorite gives one of β -CaSiO₃ twinned in two orientations with common b . The 9.35 Å hydrate is the sole intermediate stage. The relative orientations of starting material and product are shown in Fig. 1. The observed angle of 26° between the a^* -axes of the two orientations of the β -CaSiO₃ was confirmed by taking an h^0l Weissenberg photograph of another crystal of tobermorite which had been heated at 900°C.

The crystal that had been heated to redness at only one end was afterwards examined optically. It was divided into two parts by an optically sharp boundary. The part consisting of 9.35 Å hydrate had optical properties identical with those reported for this phase by McConnell (1954). The part that had been heated to redness was semi-opaque with mean refractive index 1.54 ± 0.01 ; birefringence probably below 0.005 ; elongation γ . No

twinning was detectable. This suggests that the crystal was probably composed of twin-lamellae parallel to (001), as any other composition plane would probably have been detectable.

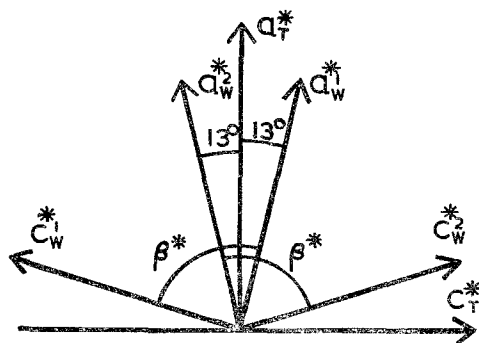


FIGURE 1.—Formation of β -CaSiO₃ from the 9.35 Å hydrate: relative orientations of starting material and product shown in reciprocal space looking along the common b^* . Suffix T denotes 9.35 Å hydrate; suffixes $\frac{1}{W}$ and $\frac{2}{W}$ denote the two orientations of the β -CaSiO₃.

DISCUSSION

Stabilities of the 11.3 Å and 9.35 Å Hydrates

Table 1 shows that 11.3 Å tobermorite is unaffected by heating at 125°C. Conversion into the 9.35 Å hydrate was partial at 180° or 240°C, but complete at 300°C. The results confirm earlier indications (Taylor, 1953) that the change in spacing is sharp and not gradual. No intermediate stage was detected.

The 9.35 Å hydrate was the only phase detected in crystals heated at 300–680°C (Table 1). From the weight-loss curve obtained by McConnell (1954), H₂O : Si can be estimated as 0.33 at 300°C and virtually *nil* at 680°C. The H₂O : Si ratio of the 9.35 Å hydrate thus appears variable at least within these limits. Independent evidence for this is provided by the data for ill-crystallized synthetic preparations [“calcium silicate hydrate (I)”]. These show basal spacings of about 9.3 Å for H₂O : Si ratios varying between 0.3–0.5 (at about 250°C) and zero (at 500°C) (Taylor, 1953; Taylor and Howison, 1957).

The Structure of the 9.35 Å Hydrate

Megaw and Kelsey (1956) showed that the layers in the 9.35 Å hydrate are stacked so that the metasilicate chains which form ribs on their surfaces abut against similar ribs of adjacent layers. This causes the body-centering of the pseudo-cell. They suggested that formation of the 9.35 Å hydrate entailed, besides loss of water, a change of stacking so that the ribs of each surface fitted into the grooves of the next.

This hypothesis is confirmed by the present observation that the pseudo-cell of the 9.35 Å hydrate is *A*-centered. This is demonstrated in Figs. 2 and 3, which show also that the stacking in the 9.35 Å hydrate is such as to bring certain tetrahedra from neighbouring layers so close together that condensation might well occur, thus forming interlayer Si–O–Si bonds. This could explain many of the known features of the 9.35 Å hydrate, viz. :

(i) Variability of H₂O : Si between 0.33 and zero without perceptible effect on cell dimensions could be explained by gradual increase in the number of interlayer Si–O–Si links with rise in temperature. Initial formation of the

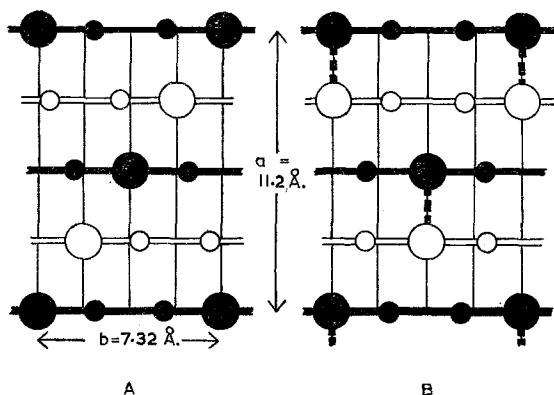


FIGURE 2.—A. Positions of silicon atoms in a single layer of tobermorite. Full lines and circles relate to the upper side and open lines and circles to the lower side of the layer. Broad lines represent metasilicate chains. Small circles represent silicon atoms in tetrahedra linked directly to the central Ca–O polyhedra. Large circles represent silicon atoms in tetrahedra not so linked, which therefore stand out above or below the layer. B. Upper side only of one layer of tobermorite with underside of the next one above it, superposed with the translations of $b/4$ and $c/2$ demanded by *A*-face centering of the pseudo-cell. Conventions as before; broken lines show positions of possible interlayer Si–O–Si bonds.

9.35 Å hydrate at 300°C may involve little or no interlayer condensation, water being lost from the molecules rather than from SiOH groups. If 11.3 Å tobermorite is tentatively written as $\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2) \cdot 4\text{H}_2\text{O}$, the 9.35 Å hydrate might be written $\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2) \cdot \text{H}_2\text{O}$ for the composition at 300°C, tending to $\text{Ca}_5\text{Si}_6\text{O}_{17}$ at 700°C.

(ii) Increased disorder in the 9.35 Å hydrate, relative to 11.3 Å tobermorite, could be explained by irregularity in the positions of interlayer links.

(iii) Kalousek and Roy (1957) showed that the 9.35 Å hydrate made from synthetic tobermorite at 650°C retains to a limited extent the 6.2 μ and 2.9 μ infrared absorption bands which they found in the unheated material. The 6.2 μ band can possibly be attributed to interlayer water molecules, and the 2.9 μ band to SiOH. This agrees with the ideas expressed above.

(iv) The 300–700°C range over which condensation is postulated, is similar to the dehydration temperatures of the two other calcium silicates known to contain SiOH. Afwillite $[\text{Ca}_3(\text{HSiO}_4)_2 \cdot 2\text{H}_2\text{O}]$ is dehydrated at about 280°C and dicalcium silicate hydrate (A) $[\text{Ca}_2(\text{HSiO}_4)\text{OH}]$ at about 425°C.

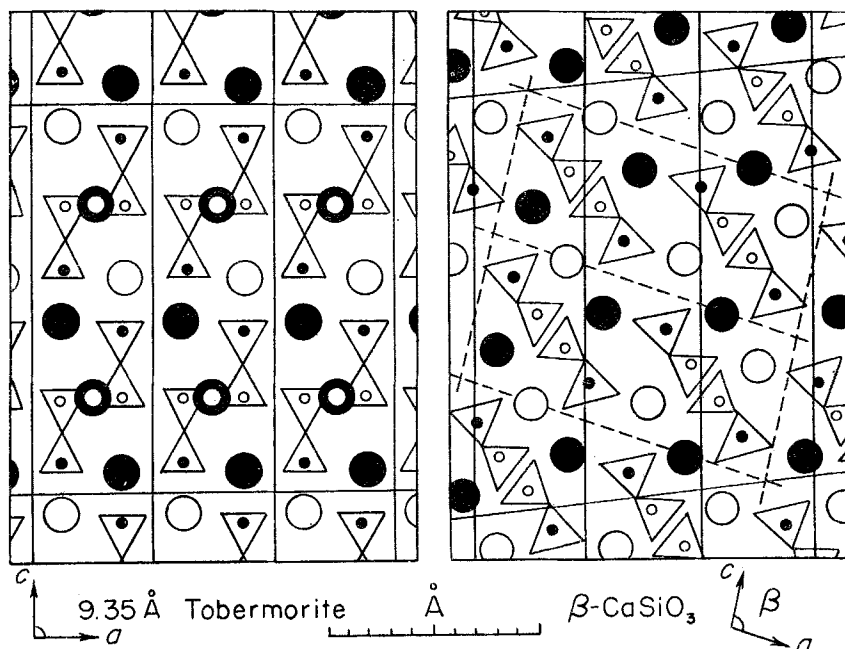


FIGURE 3.—Comparison of the probable structure of the 9.35 Å hydrate with that of $\beta\text{-CaSiO}_3$. Both figures are drawn looking down b , and the relative orientations are those found experimentally; only one orientation of the $\beta\text{-CaSiO}_3$ is shown. Large solid and open circles represent calcium ions at heights 0 and $\frac{1}{2}$ in the pseudo-cell respectively. Large circles with white centers represent interlayer calcium ions; each one shown occurs only once in every 7.3 Å along b . Triangles represent SiO_4 tetrahedra, with small circles for silicon atoms. Full and open small circles indicate that the tetrahedra occur respectively twice or once in the height (7.3 Å) of the true cell. Full lines indicate pseudo-cell boundaries; broken lines indicate boundaries of two monoclinic unit cells of $\beta\text{-CaSiO}_3$.

The Transformation to $\beta\text{-CaSiO}_3$

In Fig. 3, the structure of the 9.35 Å hydrate is compared with that of $\beta\text{-CaSiO}_3$. The relative orientations in the figure are those found experimentally. Only one orientation of the $\beta\text{-CaSiO}_3$ is shown, the other being derived from it by reflection across the (100) plane of the 9.35 Å hydrate. The structure of the 9.35 Å hydrate is highly idealized in Fig. 3. No interlayer Si–O–Si links are shown, and the interlayer calcium ions are placed approximately as their exact positions and even their numbers are not known with

certainty. They could equally well have been placed with translations $a/2$ (on the pseudo-cell) from the positions shown. It is possible that they occupy positions of both kinds, and that this is connected with the occurrence of twinning in the β -CaSiO₃.

The arrangement of calcium ions is similar in the two structures, although the 9.35 Å hydrate is defective by comparison with β -CaSiO₃. The calcium ion positions in β -CaSiO₃ can be very approximately defined using an A -centered monoclinic pseudo-cell similar to that of the 9.35 Å hydrate. This pseudo-cell is outlined by full lines in Fig. 3. The relation between the calcium patterns can be described in an alternative way. The calcium ions in the 9.35 Å hydrate all occur roughly on (101) or (10 $\bar{1}$) planes (of the true cell), while in β -CaSiO₃ they occur on (201) planes. The experimental data show that the (101) plane of the 9.35 Å hydrate becomes (201) for one orientation of the β -CaSiO₃, while (10 $\bar{1}$) becomes (201) for the other.

The ordered character of the transformation thus arises from approximate preservation of calcium ion positions, and therefore probably also to some extent of the Ca-O network. The number of metasilicate chains crossing unit area normal to b is approximately the same in the two structures, but the positions of the chains differ relative to each other and to the calcium ions. The Si-O network differs also in the probable occurrence of interlayer Si-O-Si links in the 9.35 Å hydrate. The transformation therefore probably involves considerable disturbance of the Si-O network.

Any adequate explanation of the transformation mechanism must take into account the differing Ca : Si ratios of the 9.35 Å hydrate and β -CaSiO₃. As the x-ray pattern of the β -CaSiO₃ is not noticeably anomalous, it is unlikely that the interlayer Si-O-Si links persist in the product; the process therefore involves expulsion of silica. This could happen in either of two ways. Some of the material could be converted into silica through migration of calcium and oxide ions into the rest, which would thus attain the composition and structure of β -CaSiO₃. Alternatively, silica might be expelled from all parts of the material, leaving a defective β -CaSiO₃ in which the pseudo-cell contained only two and one-half formula units instead of three. Such a defect, if it occurred in a sufficiently random way, would not noticeably affect the x-ray pattern. A migration can be envisaged, mainly of silicon atoms, in the course of which the interlayer Si-O-Si links are destroyed, the elements of silica expelled, and new though imperfect metasilicate chains produced in the positions required to form β -CaSiO₃.

This latter hypothesis is supported by the fact that closely similar mechanisms can be postulated for the dehydration reactions of at least two other calcium silicates, xonotlite and foshagite, which occur at temperatures similar to that of the present transformation (Dent and Taylor, 1956; Gard and Taylor, 1958). There is evidence from all three reactions that at 700–800°, Ca-O skeletons are relatively stable while migration of silicon occurs more easily.

Both of these mechanisms involve considerable movements of atoms. It was suggested to the author by Dr W. F. Bradley that a precise description

of such processes in terms of small displacements of atoms may apply only to the initial, orientation-determining step, in which nuclei of the product (in this case β -CaSiO₃) are formed. Following this initial step, larger migrations may occur, the bulk of the material recrystallizing on the nuclei.

There is little evidence regarding the nature of the expelled silica. The silica was not detected by x-ray or electron diffraction, but this is hardly surprising in view of its small proportion and probably poor crystallinity. The β -CaSiO₃ is optically anomalous in its abnormally low refractive index and positive (not \pm) elongation. These anomalies suggest that the β -CaSiO₃ may form thin fibers parallel to b , and it is possible that the silica is deposited in the spaces between them.

The dehydration of tobermorite from Loch Eynort (Scotland) follows a different course from that of the Ballycraig material, the 11.3 Å hydrate changing to β -CaSiO₃ without detectable intermediate formation of the 9.35 Å hydrate (Gard and Taylor, 1957). The mechanisms may therefore be quite different in the two cases. Work in progress by Mr J. W. Howison and the author shows that some ill-crystallized synthetic preparations behave differently again. They pass through a nearly amorphous state at about 600°C from which β -Ca₂SiO₄ is often the first recognizable, crystalline anhydrous product to appear. β -CaSiO₃ is formed only at a higher temperature.

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