The transformation of tobermorite into xonotlite.

By H. F. W. TAYLOR, D.Sc., Ph.D.

Department of Chemistry, University of Aberdeen.

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Summary. This hydrothermal process has been studied using single crystal X-ray methods. A crystal of tobermorite ($Ca_5Si_6O_{22}H_{10}$), treated with water at 380° C. and 250 atmospheres, gives a preferred orientation aggregate of xonotlite ($Ca_6Si_6O_{17}(OH)_2$), together probably with unoriented silica. The relationship of orientations of product and starting material was established. The change occurs without intermediate dehydration of the tobermorite to the 9·35 Å. state. The structural basis of the relationship is discussed, and it is compared with those already reported for the transformations of tobermorite into β-$CaSiO_3$ and of xonotlite into β-$CaSiO_3$. A simple experimental procedure for the single-crystal study of hydrothermal reactions is described.

XONOTLITE is a hydrated calcium silicate that occurs in contact zones, and its formation is easily reproduced in the laboratory under hydrothermal conditions between about 150° and 400° C. When it is prepared from lime and silica, there is formed as an intermediate stage either tobermorite, or badly crystallized material structurally related to tobermorite. The main object of the present work was to study the mechanism of the transformation of tobermorite into xonotlite, using single crystal methods, and to find out in particular whether the process is one in which order is preserved.

Materials and methods.

Dr. J. D. C. McConnell kindly provided the tobermorite. It was part of the specimen from Ballycraigy, N. Ireland, which has previously been described (McConnell, 1954). The identity of each crystal used was checked by single-crystal X-ray methods. Relatively large crystals (up to 500μ long) were needed, and all showed both disorder and angular spread in their X-ray reflections, but they approximated well enough to single crystals for the present purpose. All gave multiple basal reflections, the strong one of spacing 11·3 Å. being accompanied by weak or very weak ones of 14·0, 12·3, and about 9·7 Å., but examination of the X-ray patterns as a whole indicated that 11·3 Å. tobermorite was by far the most important constituent. All the crystals used were irregularly shaped laths with length *b* and cleavage (001).

After it had been checked, each crystal was placed in a specially designed hydrothermal bomb of about 1 ml. capacity (fig. 1). The construction is largely apparent from the figure. The crystal was placed in the silver cup, and a measured quantity of water in the cavity below; supercritical conditions were normally employed, and the pressure was calculated from Kennedy's data (1950). The bomb was placed in an electric furnace for a length of time that had been found sufficient to bring about partial conversion of the tobermorite into xonotlite at the temperature and pressure used. It was then cooled in an air-blast, and opened. Except in one case, mentioned later, the crystal was unchanged in general appearance, though semi-opaque, and was sometimes quite dry and sometimes slightly moist. It was removed and examined by X-ray oscillation, rotation, and Weissenberg photographs. In some cases, the crystal was heated at atmospheric humidity either before or after the hydrothermal treatment; X-ray single-crystal photographs were always taken after each stage in the treatment. Attempts to treat crystals with water or saturated steam below the critical temperature (374° C.) were not very successful, as considerable contamination by atmospheric CO_2 always occurred, giving randomly oriented crystals of calcite.

Results.

Table I lists the experiments performed and gives the phases produced. In all cases, the xonotlite showed strongly preferred orientation. Fig. 2 shows a typical X-ray photograph of a crystal after hydrothermal treatment. As the crystals were in general only partly converted into xonotlite, it was easy to determine the relative orientations of product and starting material; for this purpose, rotation photographs of crystals mounted about each of the three principal tobermorite axes, and equatorial Weissenbergs about the tobermorite b-axis, were especially useful. A single crystal of tobermorite was thus found to give an aggregate of xonotlite with two preferred orientations:

Tobermorite.		Xonotlite.		
		1st orientation.	2nd orientation.	
a 11·3 Å.————→		a	16·50 kX	$\bar{a}$
b 7·33 Å.————→		b	7·32 kX	b
c 22·6 Å.————→		c	7·03 kX	$\bar{c}$
$\alpha = \beta = \gamma = 90°$		$\alpha = \beta = \gamma = 90°$		

The unit-cell data quoted above are those obtained by Megaw and Kelsey (1956) for tobermorite, and by Mamedov and Belov (1956) for

xonotlite. Two orientations are possible for the xonotlite in spite of its orthogonal cell, because the symmetry is only monoclinic (Mamedov and Belov, 1956). Weissenberg photographs in the present case showed
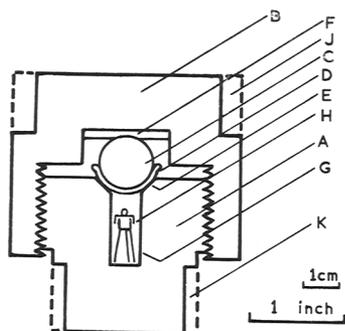
FIG. 1
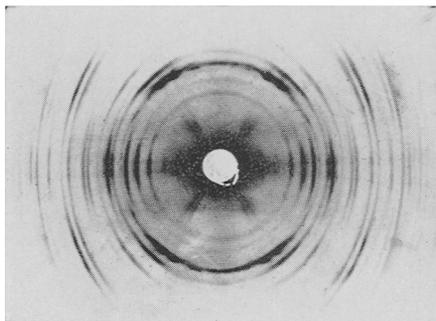
FIG. 2

FIG. 1. Bomb for hydrothermal treatment of single crystals. A, stainless steel body. B, stainless steel cap. C, steel ball. D, hardened silver gasket. E, conical surface tangential to steel ball. F, copper disk. G, cavity. H, silver cup for crystal, with lid and tripod of the same material. The body (A) and cap (B) are circular in section, with flats (J and K) to facilitate tightening and loosening.

FIG. 2. X-ray rotation photograph of crystal of 11·3 Å. tobermorite after hydro-thermal treatment; rotation about the b-axis. Sharp reflections (slightly mis-set) are from residual tobermorite; preferred orientation streaks are from xonotlite.

no differences between the intensities of corresponding $h0l$ and $h0\bar{l}$ reflections. A weak, unoriented reflection of spacing 4·2 Å. was some-times observed, and may have been due to silica.

Crystal A, which had been largely altered to xonotlite, was also examined optically. It was semi-opaque, with low birefringence and mean index about 1·53. Extinction was parallel to b, and the sign of elongation positive, in so far as measurements were possible. Crystal B was afterwards converted into β-CaSiO$_3$ (wollastonite or parawolla-stonite) by heating at 1000° C. The product was a preferred orientation aggregate with two principal orientations, as shown in fig. 3a. Crystal D, which had previously been heated at 300° C., was largely unchanged after hydrothermal treatment, but gave a few of the strongest reflections of xonotlite. The relative orientations of the 9·35 Å. tobermorite and the xonotlite seemed to be the same as with 11·3 Å. tobermorite, though this was not definitely established. Attempts to obtain a higher degree of oriented conversion of 9·35 Å. tobermorite into xonotlite (crystals E and F) were unsuccessful.

TABLE I. Hydrothermal treatments of tobermorite crystals

Crystal.	Preliminary treatment.	Principal basal spacing after preliminary treatment.	Hydrothermal treatment.	X-ray pattern after hydrothermal treatment.
A	None	11·3 Å.	380° C., 250 atm., 12 hours.	Strong, oriented pattern of xonotlite; weak pattern of residual 11·3 Å. tobermorite; powder ring 4·2 Å. (SiO_2?) No 9·35 Å. tobermorite.
B	Ditto	Ditto	Ditto	Ditto
			Crystal B afterwards heated at atmospheric humidity, 1000° C., 1 hr.	Oriented pattern of β-$CaSiO_3$.
C	Heated at 300° C. and atmospheric humidity for 3 hours.	9·35 Å.	As A	Unchanged 9·35 Å. tobermorite.
D	Ditto	Ditto	As A	Strong pattern of unchanged 9·35 Å. tobermorite: weak oriented pattern of xonotlite.
E	Ditto	Ditto	420° C., 350 atm., 12 hrs.	Oriented pattern of β-$CaSiO_3$.
F	Ditto	Ditto	370–80° C., 250 atm., approx., 6 days.	Crystal disappeared: may have dissolved and recrystallized completely.

Discussion.

The results show that conversion of 11·3 Å. tobermorite (tobermorite *sensu stricto*) into xonotlite at 380° C. and 250 atmospheres pressure occurs without intermediate formation of 9·35 Å. tobermorite (riversideite of McConnell, 1954). Had the latter been formed, it would have been detected in the hydrothermally treated crystals A and B, unless

the subsequent change to xonotlite was fast. The results with crystals C and D, however, show that this change is slow under the conditions used.

A high degree of order is preserved during the transformation. In this, and some other respects, the latter resembles those of 11·3 Å. into 9·35 Å. tobermorite (McConnell, 1954; Taylor, 1958), 9·35 Å. tobermorite into β-CaSiO$_3$ (Taylor, 1958), and xonotlite into β-CaSiO$_3$ (Dent and Taylor, 1956). These related transformations are summarized below:
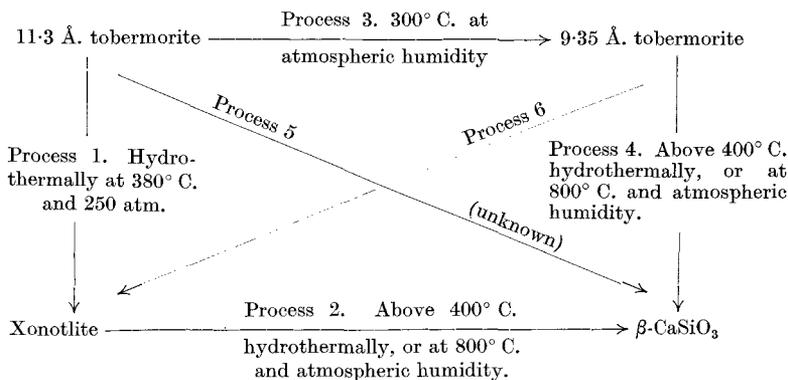
The results obtained on heating crystal B at 1000° C. after the hydrothermal treatment (table I and fig. 3a) confirm the orientation relationship previously found for the transformation of xonotlite into β-CaSiO$_3$ ($b \rightarrow b$, $c \rightarrow c$). Fig. 3 shows also that, when β-CaSiO$_3$ is formed from tobermorite, the type of twinning in the product depends on whether the process has occurred with intermediate formation of xonotlite (processes 1 and 2 above), or of 9·35 Å. tobermorite (processes 3 and 4).

Xonotlite is more easily formed from 11·3 Å. tobermorite (process 1) than from the 9·35 Å. form (process 6). In contrast, β-CaSiO$_3$ is easily obtained from 9·35 Å. tobermorite (process 4), but its direct formation from 11·3 Å. tobermorite (process 5) is not known to occur with normal specimens of tobermorite, although it apparently does happen with that from Loch Eynort, Scotland (Gard and Taylor, 1957). These facts could be explained if structural similarities existed between 11·3 Å. tobermorite and xonotlite on the one hand, and between 9·35 Å. tobermorite and β-CaSiO$_3$ on the other.

The existence of a close structural relationship in the case of 9·35 Å. tobermorite (riversideite) and β-CaSiO$_3$ has already been demonstrated,

and was shown to explain the observed orientation relationship for process 4 (Taylor, 1958). The two structures are very similar, especially as regards Ca–O packing. The structures of 11·3 Å. tobermorite and xonotlite appear to be less closely related. There is a relationship

(a). 11·3 Å. Tobermorite
→ Xonotlite → β-CaSiO₃

(b). 11·3 Å. Tobermorite
→ 9·35 Å. Tobermorite
→ β-CaSiO₃
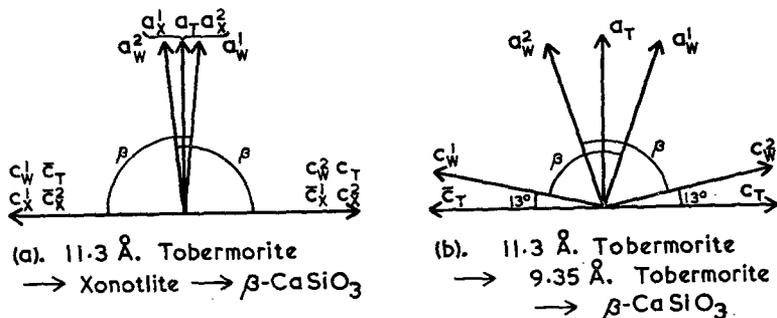
FIG. 3. Orientation relationships for transformations involving tobermorite, xonotlite, and β-CaSiO$_3$, viewed along the common b-direction. Suffixes: T = tobermorite (axial directions identical for 11·3 Å. and 9·35 Å. forms); X = xonotlite; $W = \beta$-CaSiO$_3$; 1, 2 = the two orientations for xonotlite and β-CaSiO$_3$. β-CaSiO$_3$ is referred to monoclinic axes (a = 15·417, b = 7·321, c = 7·066 Å., β = 95° 24′; Tolliday, 1958).

between the unit-cell dimensions, for (approximately) $3a_T = 2a_X$, $b_T = b_X$, and $c_T = 3c_X$, where suffixes T and X denote tobermorite and xonotlite respectively. Agreement in the c-direction would be somewhat worsened if the tobermorite was in the 9·35 Å. form. Beyond this, the similarity between the structures is not obvious; projections based on the results of Megaw and Kelsey (1956) for tobermorite and of Mamedov and Belov (1956) for xonotlite were compared in the correct relative orientations, but this did not reveal any striking resemblances. This may account for the fact that xonotlite can apparently only be formed hydrothermally, while β-CaSiO$_3$ can also be obtained by heating at atmospheric humidity, though at a much higher temperature; a more complicated rearrangement is needed to produce xonotlite, and this only occurs in the presence of high-pressure water or steam. Two complications in the change from tobermorite to xonotlite are the occurrence of twinning in the product, and the presumed segregation of silica; analogous problems have been discussed in connexion with the change from 9·35 Å. tobermorite to β-CaSiO$_3$ (Taylor, 1958). More detailed discussion of the change from tobermorite to xonotlite does not seem justified at present, especially in view of the fact that several important details

of the tobermorite structure are still uncertain. The experimental method used in the present work should be applicable to the study of other hydrothermal reactions occurring under comparable conditions, and such studies may help to elucidate the mechanism in the present case.

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