

The Crystal Structure of Tobermorite 14 Å (Plombierite), a C–S–H Phase

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The crystal structure of tobermorite 14 Å (plombierite) was solved by means of the application of the order–disorder (OD) theory and was refined through synchrotron radiation diffraction data. Two polytypes were detected within one very small crystal from Crestmore, together with possibly disordered sequences of layers, giving diffuse streaks along c^* . Only one of the two polytypes could be refined: it has $B11b$ space group symmetry and cell parameters $a = 6.735(2)$ Å, $b = 7.425(2)$ Å, $c = 27.987(5)$ Å, $\gamma = 123.25(1)^\circ$. The refinement converged to $R = 0.152$ for 1291 reflections with $F_o > 4\sigma(F_o)$. The characteristic reflections of the other polytype, $F2dd$ space group, $a \approx 11.2$ Å, $b \approx 7.3$ Å, $c \approx 56$ Å, were recognized but they were too weak and diffuse to be used in a structure refinement. The structure of tobermorite 14 Å is built up of complex layers, formed by sheets of sevenfold coordinated calcium cations, flanked on both sides by wollastonite-like chains. The space between two complex layers contains additional calcium cations and H_2O molecules; their distribution, as well as the system of hydrogen bonds, are presented and discussed. The crystal chemical formula indicated by the structural results is $Ca_5Si_6O_{16}(OH)_2 \cdot 7H_2O$.

I. Introduction

THE tobermorite phases may be classified on the basis of their different basal spacings, which are related to their degrees of hydration. Riversideite, more commonly called tobermorite 9 Å, has the chemical formula $Ca_5Si_6O_{16}(OH)_2$; tobermorite 11 Å is more hydrated, with a chemical composition ranging from $Ca_5Si_6O_{17} \cdot 5H_2O$ to $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$;¹ and finally tobermorite 14 Å, also known as plombierite, is the most

hydrated phase of the group, with the chemical formula $Ca_5Si_6O_{16}(OH)_2 \cdot 7H_2O$ (this work). These three different phases are characterized by basal spacings of 9.3, 11.3, and 14 Å, respectively.² Actually, the name plombierite was firstly used³ in 1858 to describe a gelatinous natural material, probably belonging to the “calcium silicate hydrate (I)” group.² On the basis of the chemical similarity between this nearly amorphous material and the crystalline phase described in McConnell,² the name plombierite was later also used to define the most hydrated member of the tobermorite group, and this name has been traditionally retained in the mineralogical community and widely used in mineralogical compilations. However, most researchers in cement chemistry currently apply the name “plombierite” to poorly crystalline or amorphous calcium silicate hydrates, which can vary in Ca/Si ratio from the value for tobermorite 14 Å (i.e. 0.83) to as high as about 1.5. To avoid any misunderstandings, in the following the crystalline phase we are describing will be called “tobermorite 14 Å”.

A more recently discovered mineral, clinotobbermorite, is closely related to tobermorite 11 Å as regards its structure and degree of hydration^{4,5} and transforms, by heating at 300°C, into another 9 Å phase, “clinotobbermorite 9 Å”⁵ (the structural relationships between “clinotobbermorite 9 Å” and tobermorite 9 Å will be discussed in a subsequent paper). Less characterized phases such as oyelite⁶ and tacharanite⁷ are sometimes considered as belonging to the tobermorite group, even if both display substantially different crystallographic and chemical features.⁸

The thermal behavior of tobermorite 14 Å, as well as of the other tobermorites and of their corresponding synthetic counterparts, have been carefully studied through X-ray diffraction, electron diffraction, electron microscopy, and NMR solid-state spectroscopy by several authors.^{2,9–14} According to these studies, tobermorite 14 Å transforms into tobermorite 11 Å upon heating to 80°–100°C; subsequent heating at 300°C for a few hours gives rise to tobermorite 9 Å. Actually, it was found that some specimens of tobermorite 11 Å do not shrink on dehydration and were referred to as “anomalous” to distinguish them from those specimens that shrink on dehydration (“normal” tobermorites) and decrease their basal spacing up to 9.3 Å.¹⁵ A possible reason for the occurrence of the anomalous behavior in tobermorite 11 Å has been recently hypothesized based on crystal-chemical considerations.¹

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Feature

Tobermorite 14 Å, generally associated with tobermorite 11 Å, has been found in several localities: Ballycraigy, N. Ireland;² Crestmore;¹⁶ Fuka, Japan;^{14,17} Bingham, Utah;¹⁸ Israel;¹⁹ Maqarin area, North Jordan;²⁰ Cornet Hill, Apuseni Mountains, Romania;²¹ Eastern Styria, Austria;²² Baščenov, Urals, Russia; and Zeilberg, Germany. Moreover, tobermorite 14 Å has been synthesized from different materials.^{12,23–28}

Through X-ray fiber rotation photographs of tobermorite 14 Å from Crestmore, Farmer *et al.*²⁹ found a metrically orthorhombic unit cell, with $a = 11.28$ Å, $b = 7.32$ Å, $c = 28.06$ Å, thus confirming the data presented by Heller and Taylor.³⁰ As was the case for tobermorite 11 Å, a strongly marked body-centered orthorhombic subcell has been observed in tobermorite 14 Å, with $a_S = 5.64$ Å, $b_S = 3.66$ Å, $c_S = 28.06$ Å.

The structural arrangement of tobermorite 14 Å appears particularly interesting, as the mineral is related to the so-called C–S–H(I) compound,⁸ which is one of the main products of the binding process in Portland cement. A very short abstract providing a possible structural assessment of tobermorite 14 Å, with comparison of the structural schemes for tobermorite 11 and 14 Å, has been presented by Rahman and Beyrau,¹¹ on the basis of few “subcell” data, obtained through X-ray and electron diffraction investigations.

However, until now a complete structure determination and refinement of tobermorite 14 Å has been prevented by its structural disorder, as well as by the poor quality and microscopic size of its fibers.

In our structural study the former of these difficulties was overcome by recognizing that the observed disorder phenomena can be described and adequately treated by means of the order-disorder (OD) theory,^{31–35} whereas the latter obstacle was overcome by using a high-brilliance X-ray source. The aim of this paper is to describe the structural model of tobermorite 14 Å based on OD theory, and to illustrate the results of the structural refinement on tobermorite 14 Å using X-ray diffraction data collected from a very small crystal at a synchrotron facility.

(1) Background

In their investigation of the specimen from Crestmore, Farmer *et al.*²⁹ studied the thermal behavior by means of thermal analyses and X-ray data. The transformation temperature to tobermorite 11 Å was estimated to be $55^\circ \pm 5^\circ\text{C}$. The dehydration curve they presented points to the occurrence of approximately 8 H₂O molecules pfu in the unheated sample. The infrared (IR) spectrum of the unheated sample, on the other hand, suggests the occurrence of molecular water and possibly of Si(OH) groups. More recent IR studies³⁶ confirmed the occurrence of a large amount of disordered H₂O molecules in tobermorite 14 Å, which overwhelms any other signal in the OH stretching region in the mid-IR spectra. Moreover, in agreement with NMR evidence, the IR spectra point to the occurrence of wollastonite-like single chains.³⁶ Spectroscopic investigations carried out by means of ²⁹Si MASNMR^{9,10,12,14}, in fact, clearly showed highly dominant Q_2 peaks, characteristic of single chain silicates, and few Q_1 tetrahedra in tobermorite 14 Å. During the dehydration process, and before tobermorite 11 Å is formed at approximately 250°C, an additional and possibly metastable phase was detected by Yu and Kirkpatrick,¹³ showing a basal spacing of about 12 Å.

(2) Disorder in Tobermorites

The diffraction patterns of tobermorite 14 Å are characterized by the occurrence of sharp reflections with $k = 2n$, whose positions and intensities do not change in different crystals (*family reflections* in the OD theory^{31–35}) plus a set of weak reflections, with $k = 2n + 1$, diffuse along c^* , with positions and intensities that may vary in different crystals (*characteristic reflections*). All the reflections are present only for $h + k = 2n$. The sharp reflections, moreover, can be indexed on the basis of a body-centered orthorhombic subcell with $a_S = 5.6$ Å, $b_S = 3.7$ Å, $c_S = 27.9$ Å, whereas the weak diffuse reflections or continuous streaks for

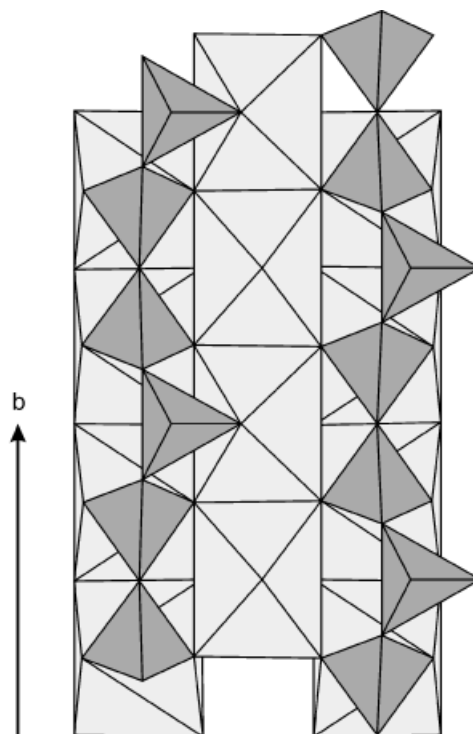


Fig. 1. Connection of silicate chains (dark gray) to the layer of calcium polyhedra (light gray), as seen down [001].

odd values of k (and h) point to the occurrence of disorder in the stacking of (001) structural layers.

Similar features (diffuse reflections, streaks, as well as non-space-group absences) occur in the diffraction patterns of all the natural and synthetic phases of the tobermorite group and are manifestations of their OD character.^{1,5,37} All of them are built by equivalent layers parallel to (001), which can stack in two different, but geometrically equivalent ways, giving rise to a potentially infinite number of ordered (polytypes) or disordered structural arrangements. The ambiguity in the stacking of adjacent layers is dependent on the peculiar crystal chemistry of the tobermorite phases, in particular, on the metrical relationships between the calcium polyhedral module, and the tetrahedral chains of wollastonite type with their typical repeats of 3.65 and 7.3 Å, respectively, along b (Fig. 1).

The family reflections ($k = 2n$) define the “subcell” and correspond to the average structure (or “family structure”, according to the OD terminology). Its determination does not consent to know the “real structure” corresponding to a definite sequence of the layers, in particular, the actual position of the wollastonite-like chains, which may equivalently occupy two positions shifted by $b/2$. Moreover, only average information on the position of H₂O molecules and Ca cations within the inter-layer space is obtainable from the family structure.

II. Structural Model

Scrutiny of the diffraction patterns of tobermorite 14 Å showed that: (i) the family reflections ($k = 2n$) are absent for $2h + 2k + l = 2n + 1$, and (ii) reflections hkl are absent for $h + k = 2n + 1$. This latter observation indicates that the equivalent layers that constitute the whole structure are C centered, as systematic absences not limited to the family reflections can only be because of symmetry elements of the single layer. By analogy with the real crystal structure of tobermorite 11 Å,^{1,37} the symmetry of this single layer was firstly hypothesized³⁸ to be $C2m(m)$, where the parentheses indicate the direction of missing (or variable) periodicity. In Fig. 2(a) this kind of layer is

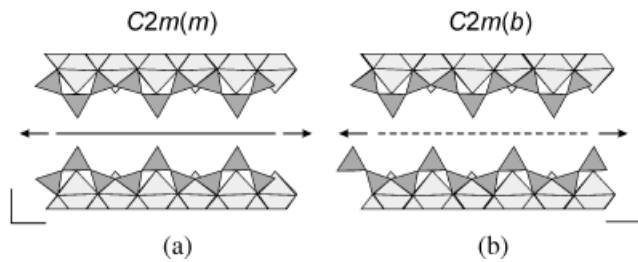


Fig. 2. The two possible layers of tobermorite 14 Å, and their symmetry elements.

sketched. However, the absence of any link between the faced wollastonite-like chains makes possible their relative displacement of $b/2$, leading to the layer symmetry $C2m(b)$ (Fig. 2(b)). These two possible layer symmetries correspond to two different OD families, which can be derived from the tabulated groupoid symbols.^{33,35} As a matter of fact, these OD families correspond to the same family structure, with space group symmetry $I2mm$, and both have been carefully tested, by deriving their main polytypes (maximum degree of order (MDO) structures in OD terminology), and comparing, for each model, the agreement between the calculated and observed intensities at the end of the refinement procedure. As the model derived for the OD family with layer symmetry $C2m(b)$ resulted in a sensibly better final reliability index, the following discussion will deal only with this last case.

In agreement with the experimental results, therefore, the OD groupoid symbol of the tobermorite 14 Å family is

$$C \quad 2 \quad m \quad (b) \\ \{2_{1/2} \quad n_{2,1/2} \quad (n_{1/2,1/2})\}$$

This means that layers with $C2m(b)$ symmetry (with translation vectors \mathbf{a} and \mathbf{b} , $a \approx 11.2$ Å, $b \approx 7.3$ Å; third vector \mathbf{c}_0 , with $c_0 \approx 14$ Å) may follow each other related either by the partial operators $n_{1/2,1/2}$ or $n_{1/2,-1/2}$, perpendicular to \mathbf{c}_0 . This corresponds to the application of two stacking vectors, $\mathbf{t}_1 = \mathbf{c}_0 + (\mathbf{a} + \mathbf{b})/4$ and $\mathbf{t}_2 = \mathbf{c}_0 + (\mathbf{a} - \mathbf{b})/4$, respectively. Infinite possible ordered or disordered sequences of layers may occur. Among them, the OD theory singles out the so-called MDO polytypes, that is, the polytypes in which not only couples but also triples, quadruples, ..., n -ples of adjacent layers are geometrically equivalent. In tobermorite 14 Å two MDO polytypes exist.

MDO₁ corresponds to the sequence $\mathbf{t}_1\mathbf{t}_2\mathbf{t}_1\mathbf{t}_2\dots$. The resulting structure has $F2dd$ symmetry and cell parameters $a \approx 11.2$ Å, $b \approx 7.3$ Å, $c \approx 56$ Å.

MDO₂ corresponds to the sequence $\mathbf{t}_1\mathbf{t}_1\mathbf{t}_1\mathbf{t}_1\dots$. The corresponding cell is C centered, with $a \approx 11.2$ Å, $b \approx 7.3$ Å, $c \approx 28$ Å, and presents additional lattice points at $1/4, 1/4, 1/2$ and $3/4, 3/4, 1/2$. A convenient cell is derived through the transformation $\mathbf{a}' = (\mathbf{a} + \mathbf{b})/2$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = -\mathbf{c}$ (Fig. 3), thus obtaining a B -cen-

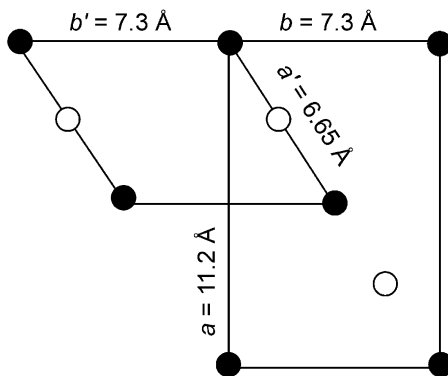


Fig. 3. Relationships between the C -centered cell, which presents additional lattice points at $1/4, 1/4, 1/2$ (empty circles), and the B -centered cell of the MDO₂ polytype of tobermorite 14 Å.

tered monoclinic cell, with parameters $a' \approx 6.65$ Å, $b' \approx 7.3$ Å, $c' \approx 28$ Å, $\gamma \approx 123^\circ$, space group $B11b$. A non-standard axial setting was used because it consents to retain the same \mathbf{b} -axis orientation of the other phases of the tobermorite group, corresponding to the direction of the silicate chains. The sequence $\mathbf{t}_2\mathbf{t}_2\mathbf{t}_2\dots$ gives rise to the twin-related structure MDO₂'.

Both MDO polytypes, with both twinned domains for MDO₂, as well as fully disordered sequences of layers, are present in the examined crystal.

III. Family Structure Refinement

A small single crystal of tobermorite 14 Å from Crestmore (0.04 mm × 0.3 mm; the width of the crystal was so small that it was not possible to measure it reliably) was selected for the data collection. It was lath-like, with (001) cleavage and elongation parallel to \mathbf{b} , similar to the crystals described by Farmer *et al.*²⁹ A preliminary study was carried out by means of long-exposed Weissenberg and precession photographs, and confirmed the occurrence of the known orthorhombic subcell of tobermorite 14 Å, $a = 5.63$ Å, $b = 3.64$ Å, $c = 27.96$ Å, with I -centered lattice. The starting data collection was performed on a Nonius Kappa CCD diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) equipped with a MoK α X-ray tube (graphite monochromatized radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Notwithstanding the high performance of the detector, at this stage only the family reflections could be measured. The orthorhombic subcell of tobermorite 14 Å was obtained through the program DIRAX,³⁹ which allows the treatment of data from disordered or twinned crystals. The reflections were integrated and scaled through the DENZO-SMN program. The starting positional parameters of the main calcium layers and of the half-occupied silicate chains were obtained from those of the substructure of tobermorite 11 Å, after proper scaling of the z coordinates, in the space group $I2mm$. Several electron maxima were detected in the interlayer space on difference Fourier maps, and they were attributed to H₂O molecules and additional calcium cations with partial occupancies and a disordered distribution. After introducing anisotropic displacement parameters for the Ca cations of the polyhedral layer, the family structure refinement (SHELXL-97⁴⁰) converged to $R = 0.127$ for 983 reflections with $F_o > 4\sigma(F_o)$.

IV. Superstructure Refinement of the MDO₂ Polytype

In order to obtain a reliable distribution of H₂O molecules and additional calcium cations, the intensities of the very weak and diffuse odd k reflections also had to be measured. These characteristic reflections were collected at the Elettra synchrotron radiation facility, using the same single crystal previously used for the family structure determination. The detector was an MAR345 Imaging Plate (Marresearch GmbH, Norderstedt, Germany) on the beamline XRD1, and the wavelength of the radiation was set to $\lambda = 1$ Å. Sixty frames were collected with $\Delta\phi = 3^\circ$. The collected frames included, in addition to the family reflections, the characteristic reflections pertaining to both the MDO polytypes. These last spots were weak and very diffuse, particularly for the MDO₁ polytype. Therefore, the indexing process had success only for the MDO₂ polytype and for its twinned counterpart MDO₂'. The data were processed with the programs XDISP, DENZO, and SCALEPACK.⁴¹

The cell parameters of the MDO₂ polytype, space group $B11b$, are $a = 6.735(2)$ Å, $b = 7.425(2)$ Å, $c = 27.987(5)$ Å, $\gamma = 123.25(1)^\circ$. Three thousand three hundred and fourteen reflections were observed, 1620 with even k and 1694 with odd k . To obtain a sufficient number of weak reflections with odd k , a high dose of radiation was allowed to reach the sample. As a consequence, a significant number of family reflections were overloaded, and their integrated intensities had to be discarded. After several trials, we decided to refine our structural model using the reflections with $k = 2n + 1$ measured with synchrotron

radiation, together with the family reflections already measured with CCD and a conventional source of X rays. A different scale factor was refined for the two sets of data.

Two structural refinements were performed: the former in the space group $B11m$ (resulting from the stacking of layers with $C2m(m)$ symmetry), and the latter in the space group $B11b$ (symmetry of the layers $C2m(b)$). The final reliability indices indicated that the latter choice was correct, even if some weak reflections $hk0$ with odd k were observed.

The starting positional parameters of the main calcium polyhedral layers and of the silicate chains were calculated on the basis of the stacking sequence of the layers hypothesized by the OD model. Additional calcium cations and H_2O molecules were located in the interlayer space through difference Fourier maps and their positions were refined under few metrical restraints suggested by the cation and H_2O distribution presented and discussed in the following section. Similarly, linear restraints were applied to the Si–O distances. After several cycles of least-square refinement, we obtained a satisfactory agreement between the observed data and the refined model ($R = 0.152$ for 1291 unique reflections with $F_o > 4\sigma(F_o)$, 983 with even k and 308 with odd k). The complexity of the disorder phenomena (presence of more polytypes as well as of disordered sequences of layers, twinning, positional disorder of the interlayer Ca cations, possible occurrence of domains with layer symmetry $C2m(m)$, etc.), and the resultant bad quality of the diffraction patterns, may account for the relatively high value of the R index.

The crystal chemical formula for tobermorite 14 Å as obtained from the refinement is $Ca_5Si_6O_{16}(OH)_2 \cdot 7H_2O$. The Ca/Si ratio is in accordance with the chemical data obtained from tobermorite 14 Å from Crestmore.¹⁵ Moreover, the occurrence of 7 H_2O molecules and two $(OH)^-$ groups in the unit formula corresponds to a weight loss on dehydration of 18.3%, in good agreement with the thermal data,^{29,13,14} which indicate weight losses of 18.2%, 18.0%, and 17%, respectively (Figs. 1, 3, and 5 in the cited papers, respectively).

In Figs. 4(a) and (b), two projections of the structure of the MDO_2 polytype are provided. Crystal and structure refinement data for tobermorite 14 Å may be found in Table I. The refined atomic and displacement parameters are reported in Table II, whereas selected bond distances are listed in Table III.

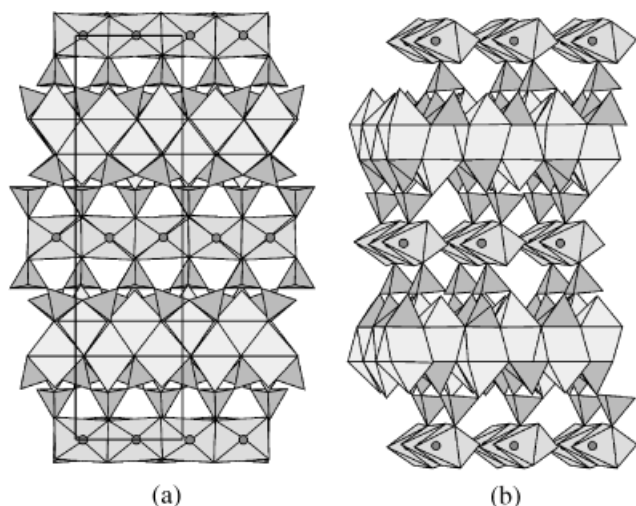


Fig. 4. Crystal structure of tobermorite 14 Å, as seen perpendicular to (100) (a), and approximately down [010] (b). The layers of Ca polyhedra are drawn in light gray, whereas the silicate chains are in dark gray. Dark gray circles indicate W4 sites, occupied by H_2O molecules with half occupancy.

Table I. Crystal and Structure Refinement Data for Tobermorite 14 Å, MDO_2 Polytype

Empirical formula	$Ca_5Si_6O_{16}(OH)_2 \cdot 7H_2O$
Crystal system	Monoclinic
Space group	$B11b$
Unit cell dimensions	$a = 6.735(2)$ Å $b = 7.425(2)$ Å $c = 27.987(5)$ Å, $\gamma = 123.25(1)^\circ$
Volume	$1170.4(5)$ Å ³
Z	2
Density (calculated)	2.23 g/cm ³
Density (measured) ²⁹	2.20 g/cm ³
Absorption coefficient	1.56 mm ⁻¹
Index ranges	$-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $-40 \leq l \leq 39$
Reflections collected	3489
Independent reflections	2077 [$R(\text{int}) = 0.0907$]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2077/14/95
Goodness-of-fit on F^2	1.081
$R = \frac{\sum F_o - F_c }{\sum F_o }$	0.152 for 1291 reflections with $F_o > 4\sigma(F_o)$

MDO, maximum degree of order.

V. Description of the Structure

The crystal structure of tobermorite 14 Å is made up of the same complex layers that constitute tobermorite 11 Å.^{1,37} They are formed by a central sheet with CaO_2 stoichiometry, connected on both sides to silicate chains with periodicity of three tetrahedra (*dreierketten*, or wollastonite-like chains, Fig. 1): the chemical composition of the complex layer is $[Ca_4Si_6O_{16}(OH)_2(H_2O)_2]^{2-}$. However, in contrast to tobermorite 11 Å, the wollastonite-like silicate chains belonging to adjacent layers in tobermorite 14 Å are not condensed to form double chains. In fact, the complex layers are moved apart and the space in between contains a larger amount of H_2O molecules compared with the 11 Å phases. Moreover, the single chains are shifted by $b/2$ with respect to each other, being related by the b glide at $z = 0$. The H_2O molecules W1, W1' (the centrosymmetrical equivalent of W1), W2, and W3 are bonded to the Ca2 cation, which partially occupies the site at (0.88, 0.99, 0.0). These H_2O molecules plus two O5 oxygen atoms of the bridging tetrahedron form an octahedron around the Ca2 cation. The W1 site is fully occupied, in contrast to the half occupancies at the W2 and W3 sites and at the Ca2 site. An additional site at (0.73, 0.43, 0.00) is half occupied by the H_2O molecule W4: the very

Table II. Occupancy Factors, Atomic Coordinates, and Displacement Parameters

Site	Occupancy	x	y	z	U_{iso} or U_{eq}
Ca1	1	0.737(6)	0.425(5)	0.2852(2)	0.0290(7)
Ca3	1	0.251(6)	0.428(5)	0.2147(2)	0.0290(7)
Si1	1	0.750(6)	0.386(5)	0.1752(3)	0.036(2)
Si2	1	0.895(6)	0.750(5)	0.1041(3)	0.046(2)
Si3	1	0.743(6)	0.961(5)	0.1751(3)	0.030(2)
O1	1	0.752(7)	0.512(6)	0.1248(6)	0.031(5)
O2	1	0.760(7)	0.189(6)	0.1542(6)	0.042(4)
O3	1	0.972(6)	0.554(6)	0.2070(6)	0.024(5)
O4	1	0.518(6)	0.301(6)	0.2065(6)	0.019(3)
O5	1	0.887(7)	0.250(6)	-0.0482(6)	0.081(8)
OH6	1	0.182(6)	0.888(6)	0.1175(9)	0.062(8)
W6	1	0.292(7)	0.445(6)	0.1296(9)	0.051(6)
O7	1	0.759(7)	0.860(7)	0.1252(8)	0.051(7)
O8	1	0.501(7)	0.824(6)	0.2067(6)	0.019(3)
O9	1	0.982(7)	0.033(7)	0.2069(9)	0.052(8)
W1	1	-0.050(8)	0.769(8)	-0.056(1)	0.10(1)
W2	0.5	0.461(7)	0.787(9)	-0.003(2)	0.07(1)
W3	0.5	0.297(8)	0.212(10)	0.003(2)	0.08(1)
Ca2	0.5	0.879(6)	0.994(6)	0.0019(8)	0.070(4)
W4	0.5	0.733(9)	0.429(9)	0.000(2)	0.070(4)

Table III. Selected Bond Distances (Å) in Tobermorite 14 Å

Si1	–O4	1.59(2)	Si2	–O5	1.57(1)	Si3	–O7	1.62(2)
	–O3	1.60(2)		–O1	1.59(2)		–O8	1.63(2)
	–O2	1.61(3)		–O7	1.63(3)		–O9	1.65(2)
	–O1	1.69(2)		–OH6	1.66(2)		–O2	1.74(3)
	Average	1.62		Average	1.61		Average	1.66
Ca1	–O9	2.27(2)	Ca3	–W6	2.39(2)	Ca2	–O5	2.26(3)
	–O8	2.29(2)		–O4	2.45(2)		–O5	2.33(3)
	–O3	2.33(2)		–O9	2.47(3)		–W2	2.36(3)
	–O4	2.38(2)		–O8	2.47(2)		–W3	2.36(3)
	–O4	2.53(2)		–O3	2.53(2)		–W1	2.36(4)
	–O3	2.56(2)		–O9	2.55(2)		–W1	2.55(4)
	–OH6	2.74(3)		–O8	2.62(2)			

short distance between Ca2 and W4 indicates that these two sites cannot be simultaneously occupied, pointing to a random distribution, with equal probabilities, of Ca(H₂O)₄O₂ octahedra on one side and H₂O molecules W4 on the other side, in the interlayer space of tobermorite 14 Å, as illustrated in Fig. 5. Moreover, the occurrence of a very short distance between the apical H₂O molecules W2 and W3 belonging to adjacent octahedral chains suggests that an ordered distribution of these octahedra and of the molecules W4 must occur.

A reasonable ordering scheme is proposed in Fig. 6: Ca2 octahedra and W4 molecules regularly alternate along [010]; as illustrated in the figure, this scheme may occur in two distinct ways in the space group *B1*, simply by inverting the positions of Ca2 octahedra and W4 molecules. The random distribution of the two ordering ways restores the *B11b* symmetry. Other ordering schemes may be sketched, but the one presented seems preferable as it corresponds to a homogeneous distribution of Ca2 octahedra and H₂O molecules W4 and allows an acceptable system of hydrogen bonds, as illustrated in the next section.

The bond valence parameters listed by Brese and O'Keeffe⁴² were used to identify the nature of the oxygen species [O²⁻, (OH)⁻, H₂O]. The corresponding calculations are shown in Table IV. The occurrence of hydrogen bonds could be deduced from the short O...O distances occurring between oxygen atoms not belonging to the same polyhedron. The disordered distribution of different atoms within the complex layer made this task quite difficult, and a full discussion of this matter will be carried out in the next section. However, it appears clear from the data of Table IV that the oxygen atom shared by the bridging Si2 tetrahedron and by the Ca1 polyhedron must actually be a hydroxyl group, as it exhibits a valence sum of 1.03 v.u. (OH6 in Tables II–IV). The occurrence of silanol groups Si(OH) in tobermorite 14 Å, already suggested by NMR¹² and IR¹³ data, is now confirmed by the structural results.

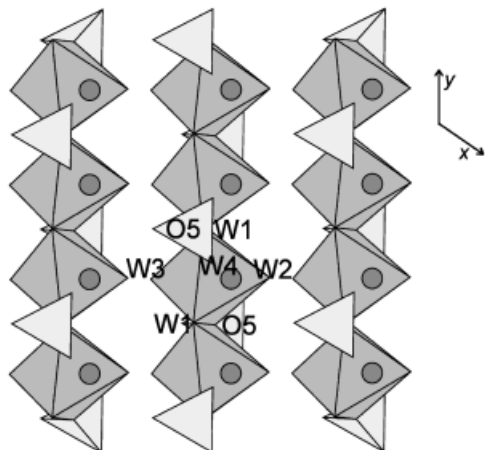


Fig. 5. Atomic distribution in the interlayer space, as seen approximately down [001]. The bridging tetrahedra of the silicate chains above and below the interlayer space are reported in light gray. The occupancies of Ca2 (within the dark gray octahedra), W4, W2, and W3 are equal to 1/2.

(1) Hydrogen Bonding Schemes

The relatively low quality of the *k* odd reflections did not allow the H-atom positions to be found directly from the diffraction data. On the other hand, any bond-valence calculation and stereo-chemical consideration is complicated by the apparently disordered atomic distribution in the interlayer space observed in our crystal of tobermorite 14 Å. However, a distribution of zeolitic calcium cations and H₂O molecules in the interlayer space has been hypothesized on the basis of crystal chemical considerations, and it is sketched in Fig. 6. A corresponding likely hydrogen bond scheme is shown in Fig. 7, whereas the O...O distances for the oxygen atoms that form hydrogen bonds are listed in Table V. The calculated bond valence sums for each oxygen atom involved in a hydrogen bond have been corrected in agreement with the parameters given by Ferraris and Ivaldi,⁴³ and are listed in the last column of Table IV.

The Ca2 cation is strongly bonded to the O5 apical oxygen atoms of the bridging tetrahedra belonging to two opposite chains. Each O5 oxygen atom is also an acceptor of a very strong hydrogen bond with one H₂O molecule W4. This strong hydrogen bond is needed to compensate the deficit of charge (valence sum of 1.57 v.u.) of the oxygen atom O5, bonded to the silicon cation Si2 and to one Ca2 calcium cation. Averaging the two slightly different configurations that statistically occur, the final bond valence sum for the O5 anion is 2.00, thus indicating that it is actually an oxygen atom. On the other hand, each W4 molecule partially compensates its deficit of charge by being an acceptor in two hydrogen bonds with the H₂O molecules W1 and in one strong hydrogen bond with the H₂O molecule W3. According to the scheme of Fig. 7, each H₂O molecule W1, which is also strongly bonded to a Ca2 cation, behaves as a donor in two hydrogen bonds with O2 and W4, respectively, whereas it receives a fraction of charge through a hydrogen bond from the H₂O molecule W6.

The overcharge on the H₂O molecules W2, resulting from the relatively short Ca2–W2 bond distance of 2.36 Å, may be

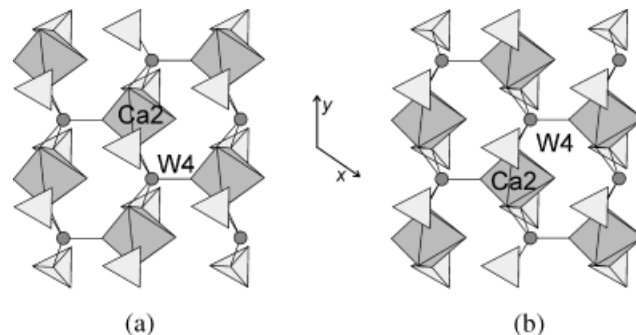


Fig. 6. Proposed ordered distribution of Ca2-centered octahedra (in dark gray) and H₂O molecules W4 (gray circles) in the interlayer space of tobermorite 14 Å. Such ordered distribution may occur in two equivalent ways, drawn in (a) and (b), respectively. The bridging tetrahedra of the silicate chains above and below the interlayer space are reported in light gray.

Table IV. Bond Valence Calculation for Tobermorite 14 Å[†]

	Ca1	Ca3	Ca2	Si1	Si2	Si3	Σ_{anions}	Σ'_{corr}
O1				0.84	1.10		1.93	2.10
O2				1.04		0.73	1.77	1.91
O3	0.37	0.22		1.07			1.86	1.86
O4	0.20 0.33			1.10			1.91	1.91
O5	0.22		0.45		1.16		1.57	2.00 (2.09)
OH6	0.12		0.37		0.91		1.03	1.03
W6		0.32					0.32	-0.02
O7					0.98	1.04	2.02	2.02
O8	0.42	0.26				0.98	1.83	1.83
O9		0.17 0.26					1.84	1.84
O10	0.44	0.21				0.93	1.84	1.84
W1			0.35				0.28	0.09
W2			0.21				0.35	0.35 (0.17)
W3			0.35				0.35	-0.08
W4			0.35				0.00	0.03
Σ_{cations}	2.10	1.70	2.07	4.04	4.14	3.69		

[†]Bond valence parameters were taken from Brese and O'Keeffe.⁴² The anionic bond valence sums were corrected by taking into account the hydrogen bonds system reported in Fig. 7.

partially compensated by assuming two weak intra-polyhedron hydrogen bonds with the two O5 anions linked to the same Ca2 cation. The bond valence balances for W2 and O5, corrected for this aspect, are given in parentheses in the last column of Table IV.

VI. Discussion and Conclusions

The structural study we performed on tobermorite 14 Å confirms the general features of this phase as summarized by Taylor,⁴⁴ as well as the occurrence of Si(OH) groups, tentatively suggested on the basis of NMR¹² and IR¹³ data. Moreover, it yields a better understanding of the local assessment of the H₂O molecules in the interlayer space and of the relationships between tobermorite 14 Å and the other phases of the group with different H₂O content.

In particular, the true nature of the dehydration product of tobermorite 14 Å at low temperatures has been a matter of debate and the presented structural results can now help in interpreting some controversial experimental data.

An early work on tobermorite 14 Å and its dehydration products,⁴⁵ carried out in order to determine the condensation degree of their silicate chains by the so-called molybdate method, indicated that both tobermorite 14 Å and its dehydration products at 80° and 450°C contain silicate single chains. These dehydration products were classified as tobermorite 11 Å and tobermorite 9 Å, respectively. In contrast, the directly synthesized tobermorite 11 Å clearly showed double chains.⁴⁵

A similar conclusion about the dehydration product of tobermorite 14 Å was reached through a ²⁹Si NMR study.⁹ The ²⁹Si NMR spectrum of the partially dehydrated phase obtained from tobermorite 14 Å upon heating to 100°C shows high noise, perhaps obscuring the subtle structural details. However, a large Q₂ peak appears as an obviously prominent feature, pointing to the occurrence of single chains in this “poorly crystallized substance”.⁹

In a more recent study¹³ the transformation of tobermorite 14 Å has been investigated through ²⁹Si and ¹H NMR spectroscopy, differential scanning calorimetry, DTA, and powder XRD techniques. XRD data confirmed the shrinking of the structure along [001], from 14 to 11.8, 11.3, and finally 9.6 Å, upon heating. The ²⁹Si NMR spectra collected from the same samples reveal that the single chain structure is substantially conserved during dehydration, even though a small Q₃ peak was detected

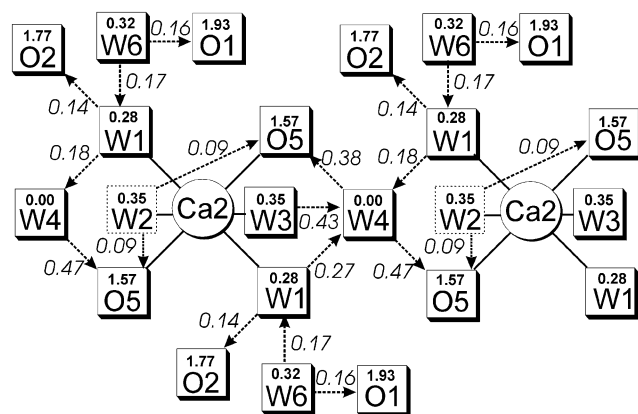


Fig. 7. Hydrogen bonding system in tobermorite 14 Å. The strength of each hydrogen bond is reported near the corresponding dashed arrow.

Table V. O...O Distances Between Oxygen Atoms Involved in Hydrogen Bonds and Corresponding Bond Valences

Donor→acceptor	O...O (Å)	v.u.
W6→O1	2.86	0.16
W6→W1	2.83	0.17
W1→O2	2.96	0.14
W4→O5	2.42	0.47
W4→O5'	2.49	0.38
W1→W4	2.63	0.27
W1→W4'	2.80	0.18
W3→W4	2.45	0.43
W2→O5	3.29	0.09
W2→O5'	3.35	0.09

The arrows point towards the acceptor oxygen atoms.

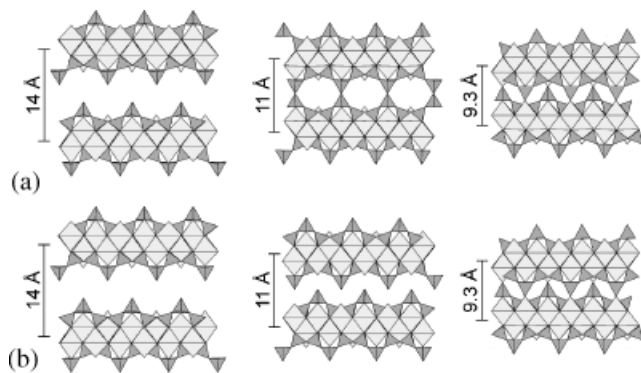


Fig. 8. (a) Schematic drawing of the stable phases with decreasing basal spacing and H₂O content, corresponding to tobermorite 14 Å (with single silicate chains), tobermorite 11 Å (double chains), and tobermorite 9 Å (single chains). (b) The suggested metastable path resulting from heating tobermorite 14 Å. Here, a metastable phase with a basal spacing of approximately 11 Å, and single silicate chains, is proposed.

for the sample heated up to 250°C and showing a (002) spacing of 11.3 Å.

All these experimental results point to the occurrence of a partially dehydrated 11 Å phase that shows single silicate chains. On the contrary, all the natural and directly synthesized samples of tobermorite 11 Å (and clinotobermorite, too) display silicate double chains, regardless of their normal or anomalous thermal behavior, as evidenced from structural refinements,^{1,5,37,46} as well as from NMR data.^{9,14,47} Therefore, it can be postulated that the 11 Å phase obtained upon heating of tobermorite 14 Å is a metastable phase that preserves the same mutual orientation of the silicate chains of the parent phase. In Fig. 8 the sequences of the structural transformations in passing from tobermorite 14 Å to tobermorite 9 Å (its structure type will be discussed in a forthcoming paper by Bonaccorsi, Merlino, and Taylor (in preparation)) are drawn both for the equilibrium process and for the alternative metastable path, proposed here.

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