The real structure of tobermorite 11Å: normal and anomalous forms, OD character and polytypic modifications

STEFANO MERLINO1, *, ELENA BONACCORSI1 and THOMAS ARMBRUSTER2

1 Università di Pisa, Dipartimento di Scienze della Terra, Via S. Maria 53, I-56126 Pisa, Italy
* e-mail: merlino@dst.unipi.it
2 Universität Bern, Laboratorium für chemische und mineralogische Kristallographie, Freierstrasse 3, CH-3012 Bern, Switzerland

Abstract: Specimens of tobermorite 11Å from Wessels mine, South Africa, an ‘anomalous’ tobermorite, and from Bašcenov, Urals, Russia, a ‘normal’ tobermorite, have been studied through X-ray diffraction. Their structural disorder, evidenced by the diffuseness of the reflections with k odd, has been dealt with through an OD approach, which allowed us to derive a reliable model of the structure, to define the two main polytypes (MDO structures), which were subsequently refined, revealing the distinctive structural details of the two specimens.

The MDO1 polytype of tobermorite 11Å from Wessels mine [orthorhombic, space group F2dd, a = 11.265(2), b = 7.386(1), c = 44.970(9) Å] was refined to $R = 0.128$, whereas the refinement carried on the MDO2 polytype [monoclinic, space group B11m, a = 6.735(2), b = 7.385(1), c = 22.487(4) Å, $\gamma = 123.25(1)^\circ$] converged to $R = 0.051$. Two refinements were carried out for the MDO2 polytype of the specimen from the Urals [space group B11m, a = 6.732(2), b = 7.368(1), c = 22.680(4) Å, $\gamma = 123.18(1)^\circ$] with data collected with conventional source ($R = 0.089$) and with synchrotron radiation ($R = 0.110$).

Common structural features are the infinite layers of calcium polyhedra, parallel to (001), with tetrahedral chains of wollastonite-type running along b and attached on both sides of these layers. The composite layers are stacked along c and connected through formation of double tetrahedral chains, with ‘ideal’ composition [Si₆O₁₅(OH)₂] and [Si₆O₁₆(OH)] in the specimens from Wessels mine and Urals respectively. The most distinctive feature of the two specimens is the content of the structural cavities: whereas only water molecules were found in the specimen from Wessels mine, ‘zeolitic’ calcium cations and water molecules were found in that from Urals. These structural aspects are compared and their relevance in explaining the different thermal behaviour of the two types of tobermorite 11Å is indicated.

Key-words: tobermorite 11Å, crystal structure, OD theory, double chains, thermal behaviour, normal tobermorite, anomalous tobermorite.

Introduction

Tobermorite was firstly described by Heddle (1880) from Tobermory (island of Mull in the Hebrides Archipelago) and from a quarry near Dunvegan in the island of Skye. Afterwards it was found in several other localities, generally in cavities of basic rocks or at the contact between limestone and dolerite, or granodiorites.

It was found that three distinct phases exist, corresponding to three degrees of hydration, tobermorite 9Å (riversideite), tobermorite 11Å (tobermorite s.s.), tobermorite 14Å (plombierite) (McConnell, 1954), characterised by different $d_{002}$ values in the powder diffraction pattern, 9.3 Å, 11.3 Å, 14.6 Å, from the least to the most hydrated form, respectively.

Most specimens are poorly crystalline or microcrystalline, not suitable for structural studies with single-crystal X-ray diffraction techniques. More-
over also the best crystallised specimens constantly display structural disorder, manifested as diffuse streaks or diffuse spots in the X-ray or electron diffraction patterns.

Notwithstanding the severe difficulties which were caused by the existence of multiple hydration states, poor crystallinity and extensive disorder, a wide series of studies were carried on with various techniques to acquire at least partial knowledge of the structural features of tobermorite minerals, especially when it was realised they are closely related with CSH (hydrated calcium silicates) compounds that form in the hydration processes of the Portland cement (Taylor, 1964, 1992, 1997) and play a central role as the main binding agent.

Tobermorite 14Å transforms to tobermorite 11Å by heating at 80 to 100°C; subsequent heating at 300°C for few hours gives rise to tobermorite 9Å: the progressive dehydorization may be easily tested and followed through the variation of the $d_{002}$ value. Some specimens of tobermorite 11Å, at difference from those obtained from tobermorite 14Å, do not shrink on dehydorization and are called ‘anomalous’ to distinguish them from those specimens that shrink on dehydorization (‘normal’ tobermorites) (Mitsuda & Taylor, 1978).

The first thorough crystallographic, chemical and thermal study on natural tobermorite has been carried by McConnell (1954) on specimens from Ballycraigy, County Antrim, North Ireland, where tobermorite 11Å was found as fibrous aggregates, each fibre being elongated along [010] and platy parallel to (001). The results of a single crystal X-ray diffraction study pointed to orthorhombic symmetry, space group C222₁, with unit cell dimensions $a = 11.3$, $b = 7.33$, $c = 22.6$ Å. ‘Reflections with $h$ and $k$ odd were found to be weak and diffuse, and the direction of spread of these spots was found to be along the $c$*-axis in reciprocal space, indicating that the mineral is built of perfect structural slabs normal to $c$ with structural mistakes occurring between these slabs’ (McConnell, 1954). The strong and sharp reflections (even $h$, $k$) define a smaller cell with $A = a/2$, $B = b/2$, $C = c$, with body centred lattice and possible space groups $Immm$, $I222$, $I2₁2₁₂₁$, $Imm$ (namely $I2mm$, or $Im2m$, or $Imm2$).

At Ballycraigy tobermorite 11Å is associated with tobermorite 14Å, which, according to McConnell, has been formed through the hydration of it. On the other side tobermorite 9Å has been experimentally formed by dehydorization of tobermorite 11Å (McConnell, 1954) which is therefore of ‘normal’ type. The composition of tobermorite 11Å has been indirectly determined by following the cumulative dehydorization curve of a mixture of ‘11Å’ and ‘14Å’ hydrates, thus obtaining the crystal chemical formulas $Ca₅Si₆O₁₇·5H₂O$ or $Ca₅Si₆O₁₆(OH)₂·4H₂O$.

A first structural model of tobermorite 11Å was proposed by Megaw & Kelsey (1956) on the basis of single crystal data (Weissenberg and rotation photographs) collected using a specimen from Ballycraigy. According to their description, the ‘pseudorhombohedral’ structure is based on layers parallel to (001) (with reference to the unit cell parameters determined by McConnell, 1954), 11.3 Å thick, built up by a central sheet which has $CaO₂$ stoichiometry. This sheet is condensed, on both sides, with silicate chains of wollastonite type, which may be described, following the use in cement chemistry, as built up by ‘paired’ $Si₃O₉$ groups connected by a ‘bridging’ tetrahedron. The chains are grasped to the sheet through the paired groups and form ridges running along [010]. The complex layers, with $Ca₅Si₆O₁₈$ stoichiometry, are stacked in such way that the ridges of each layer are precisely facing those of the adjacent layers. The authors maintain that the remaining calcium atom and the water molecules are placed in the cavities between the ridges and that some hydrogen atoms are attached to the silicate chains (Megaw & Kelsey, 1956). The most probable crystal chemical formula that may be derived from their model is: $Ca₅Si₆O₁₆(OH)₂·4H₂O$. It must be emphasised that Megaw & Kelsey (1956) did not present quantitative structural data, as atomic coordinates and bond distances, but only outlined the main modules of the average structure.

A further step towards the understanding of the structure of tobermorite 11Å has been made by Hamid (1981) who, working on samples from Zeilberg (Germany), determined unit cell dimensions $a = 11.172$, $b = 7.392$, $c = 22.779$ Å, and, as in the case of the specimen from Ballycraigy, observed diffuse spots for odd $h$, $k$ values, in addition to sharp reflections (even $h$, $k$ values). By considering only the sharp reflections he determined the subcell structure in the space group $Immm$ and refined it to $R = 0.085$ for 513 independent reflections.

The structure is now more precisely characterised as built up by a continuous sheet of seven-coordinated calcium polyhedra, flanked on both sides by Dreiereinfachketten (Liebau, 1956), which may occupy two alternative positions displaced by $b/2$. Besides the disorder dependent on the twofold position of the silicate chains, two other causes of disordering are presented by Hamid (1981): the bridging tetrahedra of each chain may assume two oppo-
site orientations, related by the mirror plane \( m \) normal to the \( a \) axis; moreover a calcium cation placed in the cavities between the complex layers presents half occupancy, the actual occupancy being correlated with the orientation of the bridging tetrahedra. The results of the structural investigation point to the crystal chemical formula \( \text{Ca}_4.5[\text{Si}_{6}\text{O}_{15}(\text{OH})_{3}] \cdot 2\text{H}_2\text{O} \). As regards the general aspects of the structural arrangement, Hamid (1981) assumes, as it was already made by Megaw & Kelsey (1956), that the tetrahedral chains are single chains and no condensation occur between chains facing each other along \( c \).

A new natural species, clinotobermorite, closely related to tobermorites, in particular to tobermorite 11Å, and presenting the same disordering as the other phases of the group, has been recently found, firstly at Fuka (Japan) by Henmi & Kusachi (1989, 1992) and subsequently at Wessels mine, Kalahari manganese field, South Africa (Hoffmann & Armbruster, 1997). At Wessels mine not only clinotobermorite, but also tobermorite 11Å was found, both as crystals sufficiently large for X-ray diffraction studies through single-crystal techniques. The second main obstacle for a structural investigation, namely the extensive disordering, was easily overcome as soon as it was realised that the disorder displayed by clinotobermorite and tobermorite 11Å (as well as by the other hydration forms of tobermorite) was of OD type (Dornberger-Schiff, 1956, 1964, 1966). Through the application of an OD approach (Merlino, 1997) we succeeded in defining their real structures and shedding light upon their polytypic features. The results obtained with tobermorite 11Å from Wessels mine (an ‘anomalous’ tobermorite), clinotobermorite and its dehydration product have been presented in a comprehensive account (Merlino et al., 1999) dealing with the main structural aspects of those compounds and suggesting an explanation for the different behaviour of ‘normal’ and ‘anomalous’ tobermorite, based on the presence or absence, respectively, of ‘zeolitic’ calcium cations in the cavities of the structure. Successively we have carried out a structural study on a specimen of ‘normal’ tobermorite 11Å from Baščenov, Urals, Russia, to define the precise structural relationships between the two kinds of tobermorite 11Å. The aim of the present paper is to give a full account of the OD character and polytypic modifications of tobermorite 11Å in general and to present a detailed description and discussion of the structural arrangements of the ‘normal’ and ‘anomalous’ types of tobermorite 11Å.

### OD character of the structural family of tobermorite 11Å

The power of OD theory in revealing the real structure of the various phases in tobermorite group has been already presented (Merlino, 1997; Merlino et al., 1999, 2000). Here we simply recall that the various phases, and tobermorite 11Å among them, present OD structures consisting of layers of one kind. In these structures, adjacent layers may be arranged in two geometrically equivalent ways, which gives rise to a family of possible structures, differing in the stacking of the layers. The common symmetry features of the whole family are defined by the \( \lambda \)-operations (symmetry operations of the single layer, namely one of the 80 layer groups) and the \( \sigma \)-operations, which convert a layer into the adjacent one and are fully described by the OD groupoid family symbol (Dornberger-Schiff & Fichtner, 1972).

It seems proper to recall that the various possible structures (ordered or disordered members of the whole OD family) present common diffraction features, namely reflections which always appear sharp, in the same position and with the same intensity (family reflections), and differ in the position, intensity, shape (sharp spot, diffuse spot, continuous streak) of the other reflections. The family reflections correspond to the so-called family structure, more loosely denoted as subcell structure.

The symmetry properties of the building layers, as well as the symmetry operations relating adjacent layers, may be sometimes derived through a careful consideration of the diffraction patterns, paying due attention to the systematic absences in the family reflections and in the whole pattern. As regards tobermorite 11Å, McConnell (1954) has shown that the \( C \) centring condition is valid for the whole diffraction pattern; it is therefore a character of the single layer, which consequently should present a layer group symmetry with \( C \) centred lattice. This aspect, together with the metric relationships between clinotobermorite and tobermorite 11Å, and the results obtained in our study of clinotobermorite, as well as the orthorhombic symmetry of the ‘average’ structure of tobermorite 11Å, immediately suggests a reliable structure for the single layer of tobermorite 11Å. It has layer group symmetry \( C2m(m) \) (Fig. 1), with \( a \) and \( b \) as translation vectors \( (a = 11.3, b = 7.33 \text{ Å}) \) and third basis vector (not a translation vector) \( c_0 \) \( (c_0 = 11.3 \text{ Å}; \text{cell parameters taken from McConnell, 1954}) \). At difference from the corresponding layer in clinotobermorite, the double chain is obtained from the single
chain through the action of a mirror plane normal to c, instead than through the action of a twofold axis parallel to b, the mirror plane normal to b being still active.

For a layer with symmetry $C2m(m)$ there are two possible OD groupoid families\(^1\) (Dornberger-Schiff, 1964; Dornberger-Schiff & Fichtner, 1972):

$$C \ 2 \ m \ (m) \ \{n_{r,2} \ 2r \ (2)\} \ \{2r \ n_{2,2} \ (n_{r,})\}$$

The second is the correct one. In fact, the $\lambda$- and $\sigma$-operations should correspond to the operators of the family structure, once the translational components of any glide and screw are modified in agreement with the passing from the dimensions of the single layer $(a, b, c_0)$ to those of the subcell $(A = a/2, B = b/2, C = 2c_0)$; therefore the translational components which refer to the a and b axes must be doubled and those which refer to the c axis must be halved. In this way, with $r = s = \frac{1}{2}$, the operators of the second OD groupoid family in (1) exactly reproduce the operators of the space group $I2mm$. This is just one of the possible space groups listed by McConnell (1954) for the subcell structure of tobermorite 11Å. Actually Hamid presented the results of his refinement of the ‘superposed disordered structure’, namely the ‘family structure’, in the space group $Imm2$, but it seems proper to observe that the ‘family structure’ determined by him may be described also in the space group $I2mm$; in fact, looking at Table 1 of his paper, we may realise that the atoms are arranged in pairs having the same x and y coordinates; the corresponding z values become opposite (z and -z) through a translation of the origin by 0.21c.

\(^1\) The symbols which describe the $\sigma$-operators are in keeping with those generally used for normal space-group operators (Dornberg-Schiff, 1964; Dornberg-Schiff & Fichtner, 1972; Merlino et al., 1999). For example the symbol $n_{r,2}$ in the first position indicates an n glide normal to a, with translational components rb/2+rc. The symbol 2, in the second position indicates a screw parallel to b with translation component rb/2. The parentheses in the third position of each line indicate that c0, the third basis vector of the single layer, is not a translation vector.

In conclusion, the OD groupoid family of tobermorite 11Å is:

$$C \ 2 \ m \ (m) \ \{2s_{1/2} n_{2,1/2} (n_{3,1/2})\}$$

Layers with $C2mm$ symmetry may follow each other in the c direction, related by the operator $n_{1/2,1/2}$ (due to the C centring of the single layer) normal to e or by the operator $n_{1/2,-1/2}$ (due to the C centring of the single layer). Pairs of layers related in both ways are geometrically equivalent. It is worth to note that layers related by the operators $n_{1/2,1/2}$ and $n_{1/2,-1/2}$ are translationally equivalent and stacked according to the vectors:

$$t_1 = c_0 + (a + b)/4$$
$$t_2 = c_0 + (a - b)/4$$

respectively. Infinite possible ordered or disordered sequences of layers may occur, corresponding to the infinite possible sequences of the indicated operators. According to the OD theory, there are two MDO polytypes (homogeneous and distinct sequences of operators):

MDO\(_1\) – corresponds to the sequence in which the operators $n_{1/2,1/2}$ and $n_{1/2,-1/2}$ regularly alternate, or,
equivalently, to the regular alternation of \( t_1 \) and \( t_2 \) stacking vectors.

MDO\(_2\) – corresponds to the sequence in which the \( n_{\frac{3}{2}, \frac{3}{2}} \) is constantly applied, or, equivalently, to the constant application of \( t_1 \) stacking vector (the constant application of \( t_2 \) vector gives rise to the twin related structure MDO\(_2\)').

**Symmetry of the two MDO polytypes**

MDO\(_1\) – Fig. 2a shows that:

a) the \( \sigma\)-operator \( n_{\frac{3}{2}, \frac{3}{2}} \) normal to \( b \) is continuing in the succeeding layers, becoming a total glide \([d\]) in a structure with \( c = 4c_0 \);

b) the translation operator \( \frac{a}{2} + \frac{b}{2} \) is valid for all the layers and the operators \( n_{\frac{3}{2}, \frac{3}{2}} \) and \( n_{\frac{3}{2}, -\frac{3}{2}} \) become total \([d]\) glides;

c) the twofold axes parallel to \( a \) of the single layers are total operators.

Therefore the whole structure has \( F2dd \) symmetry, with cell parameters: \( a = 11.3, b = 7.33, c = 45.2 \) Å.

MDO\(_2\) – Fig. 2b shows that the application of two successive operators \( n_{\frac{3}{2}, \frac{3}{2}} \) corresponds to a translation \( 2c_0 + \frac{(a + b)}{2} \). As all the layers are \( C \) centred, the third layer is translated by \( c = 2c_0 \) relatively to the first one; the \( \lambda\)-operator \([d\]) is total operator, valid for the whole structure. The corresponding \( C \) cell with \( a = 11.3, b = 7.33, c = 22.6 \) Å, \( \gamma = 90^\circ \), presents additional lattice points at \( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \) and \( \frac{3}{4}, \frac{1}{4}, \frac{1}{2} \) (Fig. 3). A convenient cell is derived through the transformations \( a' = (a + b)/2, b' = -b, c' = -c \), thus obtaining a \( B \) centred monoclinic cell, space group symmetry \( B11m \) and cell parameters: \( a' = 6.73, b' = 7.33, c' = 22.6 \) Å, \( \gamma = 122.9^\circ \). These values correspond to those determined by Hamid (1981) for one of the ‘possible ordered phases’. For it Hamid (1981) indicates a space group \( P2_1 \) (obviously it stands for \( P112_1 \)); however it is proper to observe that reflections \( 00l \) are family reflections and therefore are present only for \( l = 2n \), thus suggesting a screw \( 2_1 \), which actually does not occur.

A partial drawing of the reciprocal lattice of tobermorite 11Å, with the positions of the family reflections and of the reflections corresponding to the MDO polytypes, is illustrated in Fig. 4.

**Experimental**

An exceptionally well-crystallised specimen of tobermorite 11Å were found at Wessels mine, Kalahari Manganese Field, South Africa. For the structural study we have selected a thin crystal, elongated along [010] and platy (001), with dimensions \( 0.16 \times 0.26 \times 0.80 \) mm\(^3\). We carried out two data collections with a Siemens P4 automatic four-circle diffractometer, and monochromatized MoK\(\alpha\) radiation. In the former we collected the reflections of both the MDO\(_2\) and MDO\(_2\)' polytypes, in a \( C \) centred monoclinic cell with parameters \( a = 11.265(3), b = 7.385(1), c = 22.487(4) \) Å, \( \gamma = 90.00(1)^\circ \), refined on the basis of 20 reflections with \( 24^\circ < 2\theta < 32^\circ \). The separation of the reflections pertaining to the different individuals was performed successively, applying the transformation matrices \( \frac{1}{2} \frac{1}{2} 0, 0 1 0, 0 0 1 \) and \( \frac{3}{4} \frac{3}{4} 0, 0 -1 0, 0 0 -1 \), respective-
Table 1. Unit cell, data collection and refinement parameters for the two MDO polytypes of anomalous tobermorite and for MDO2 polytype of normal tobermorite.

<table>
<thead>
<tr>
<th></th>
<th>Anomalous tobermorite from Wessels mine</th>
<th>Normal tobermorite from Urals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MDO1 (Conventional X-ray source)</td>
<td>MDO2 (Synchrotron radiation source)</td>
</tr>
<tr>
<td>Crystal dimensions (mm)</td>
<td>0.16 × 0.26 × 0.80</td>
<td>0.08 × 0.08 × 0.20</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.265(2)</td>
<td>6.735(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.386(1)</td>
<td>6.739(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>44.970(9)</td>
<td>22.487(4)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>123.25(1)</td>
<td>123.18(1)</td>
</tr>
<tr>
<td>Space group</td>
<td>F2dd</td>
<td>B11m</td>
</tr>
<tr>
<td>20 max</td>
<td>60°</td>
<td>60°</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>1880</td>
<td>1722</td>
</tr>
<tr>
<td>Observed reflections</td>
<td>[with F_{obs} &gt; 4σ(F_{obs})]</td>
<td>-</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>psi-scan</td>
<td>-</td>
</tr>
<tr>
<td>R_{obs.}</td>
<td>0.128</td>
<td>0.051</td>
</tr>
<tr>
<td>Equipment</td>
<td>P4 Siemens four-circle automatic diffractometer</td>
<td>345 mm Imaging plate from MarResearch®</td>
</tr>
<tr>
<td>Wavelength of radiation</td>
<td>0.71069 Å (graphite monochromatized MoKα)</td>
<td>1 Å *</td>
</tr>
<tr>
<td>Scan mode</td>
<td>ω-20</td>
<td>ω-20</td>
</tr>
<tr>
<td>Scan width</td>
<td>1° in ω</td>
<td>3°/min</td>
</tr>
<tr>
<td>Scan speed</td>
<td>4°/min</td>
<td>3°/min</td>
</tr>
<tr>
<td>Refinement</td>
<td>Full-matrix least squares against F² with SHELXL-97 (Sheldrick, 1997)</td>
<td>-</td>
</tr>
<tr>
<td>Chemical formula (Z = 2)</td>
<td>Ca₄Si₆O₁₅(OH)₂·5H₂O</td>
<td>Ca₄Si₆O₁₆(OH)·5H₂O</td>
</tr>
</tbody>
</table>

* 60 frames were collected, with Δφ = 3°; the exposition time corresponded to a dose of 500.

Monoclinic polytype MDO₂

**Anomalous tobermorite from Wessels mine.** The refined cell parameters were a’ = 6.735(2), b’ = 7.385(1), c’ = 22.487(4) Å, γ = 123.25(1)°. The starting positional parameters of the atoms belonging to the complex layers were calculated on the basis of the corresponding OD model, in the space group B11m as described in the preceding paragraph. Few cycles of least-square refinement (SHELXL program; Sheldrick, 1997) confirmed the correctness of the model. The examination of the Fourier map revealed the presence of three additional maxima of electron density, located on the mirror plane within the structural cavities. The height of each maximum was compatible with the presence of either an oxygen atom or about half calcium cation. Taking into account that the three maxima are located far from each other and from the oxygen atoms of the complex layers (at distances longer than 2.93 Å), and that the chemical data we have collected on this sample pointed to...
Table 2. Tobermorite 11 Å, monoclinic polytype MDO₂, space group B11m: atomic coordinates and isotropic or equivalent displacement parameters.

<table>
<thead>
<tr>
<th></th>
<th>Anomalous tobermorite from Wessels mine</th>
<th>Normal tobermorite from Urals conventional X-ray tube</th>
<th>synchrotron radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>y</td>
<td>z</td>
</tr>
<tr>
<td>Si1</td>
<td>0.758(4)</td>
<td>0.386(2)</td>
<td>0.157(3)</td>
</tr>
<tr>
<td>Si2</td>
<td>0.908(4)</td>
<td>0.753(3)</td>
<td>0.071(7)</td>
</tr>
<tr>
<td>Si3</td>
<td>0.759(4)</td>
<td>0.969(7)</td>
<td>0.157(8)</td>
</tr>
<tr>
<td>O1</td>
<td>0.771(1)</td>
<td>0.505(8)</td>
<td>0.094(2)</td>
</tr>
<tr>
<td>O2</td>
<td>0.759(1)</td>
<td>0.178(1)</td>
<td>0.132(7)</td>
</tr>
<tr>
<td>O3</td>
<td>0.985(1)</td>
<td>0.536(9)</td>
<td>0.198(2)</td>
</tr>
<tr>
<td>O4</td>
<td>0.519(1)</td>
<td>0.306(8)</td>
<td>0.194(2)</td>
</tr>
<tr>
<td>O5</td>
<td>0.894(2)</td>
<td>0.746(1)</td>
<td>0.0</td>
</tr>
<tr>
<td>O6</td>
<td>0.188(1)</td>
<td>0.893(1)</td>
<td>0.094(2)</td>
</tr>
<tr>
<td>W6</td>
<td>0.270(2)</td>
<td>0.434(2)</td>
<td>0.093(3)</td>
</tr>
<tr>
<td>O7</td>
<td>0.770(1)</td>
<td>0.860(1)</td>
<td>0.095(2)</td>
</tr>
<tr>
<td>O8</td>
<td>0.523(1)</td>
<td>0.811(8)</td>
<td>0.195(2)</td>
</tr>
<tr>
<td>O9</td>
<td>0.987(1)</td>
<td>0.045(9)</td>
<td>0.198(5)</td>
</tr>
<tr>
<td>Ca1</td>
<td>0.265(2)</td>
<td>0.432(8)</td>
<td>0.205(7)</td>
</tr>
<tr>
<td>Ca3</td>
<td>0.7499(2)</td>
<td>0.922(8)</td>
<td>0.294(5)</td>
</tr>
<tr>
<td>W1*</td>
<td>0.427(5)</td>
<td>0.219(5)</td>
<td>0.0</td>
</tr>
<tr>
<td>W2</td>
<td>0.879(3)</td>
<td>0.237(3)</td>
<td>0.0</td>
</tr>
<tr>
<td>W3*</td>
<td>0.422(5)</td>
<td>0.800(5)</td>
<td>0.0</td>
</tr>
<tr>
<td>Ca2*</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* In normal tobermorite W1 and W3 have occupancy 1/2, whereas Ca2 has occupancy 1/4.
Table 3. Selected bond distances (in Å) in monoclinic MDO$_2$ tobermorite 11Å from Wessels mine (first column) and Urals (data obtained with conventional X-ray tube and synchrotron radiation source are in second and third column, respectively). e.s.d. are reported in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>Si1 O1</th>
<th>1.649(5)</th>
<th>1.64(2)</th>
<th>1.67(2)</th>
<th>Si2 O1</th>
<th>1.614(5)</th>
<th>1.67(2)</th>
<th>1.64(2)</th>
<th>Si3 O2</th>
<th>1.639(6)</th>
<th>1.67(2)</th>
<th>1.69(2)</th>
<th>O2</th>
<th>1.637(6)</th>
<th>1.64(2)</th>
<th>1.65(2)</th>
<th>O5</th>
<th>1.603(2)</th>
<th>1.614(6)</th>
<th>1.638(8)</th>
<th>O7</th>
<th>1.646(5)</th>
<th>1.62(2)</th>
<th>1.69(2)</th>
<th>O7</th>
<th>1.602(6)</th>
<th>1.60(2)</th>
<th>1.61(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca1 O4</td>
<td>2.368(6)</td>
<td>2.36(2)</td>
<td>2.38(2)</td>
<td>Ca3 O4</td>
<td>2.398(5)</td>
<td>2.43(2)</td>
<td>2.42(2)</td>
<td>Ca2 O6</td>
<td>2.35(3)</td>
<td>2.32(3)</td>
<td>2.35(3)</td>
<td>O8</td>
<td>2.356(5)</td>
<td>2.42(2)</td>
<td>2.44(2)</td>
<td>O2</td>
<td>2.284(4)</td>
<td>2.41(4)</td>
<td>2.44(2)</td>
<td>O2</td>
<td>2.498(8)</td>
<td>2.39(5)</td>
<td>2.44(2)</td>
<td>O2</td>
<td>2.44(6)</td>
<td>2.39(6)</td>
<td>2.44(2)</td>
</tr>
<tr>
<td></td>
<td>Ca1 O6</td>
<td>2.414(6)</td>
<td>2.41(2)</td>
<td>2.39(2)</td>
<td>O9 O6</td>
<td>2.400(6)</td>
<td>2.42(2)</td>
<td>2.38(2)</td>
<td>W1</td>
<td>2.49(8)</td>
<td>2.39(5)</td>
<td>2.44(2)</td>
<td>O6</td>
<td>2.495(6)</td>
<td>2.53(2)</td>
<td>2.44(2)</td>
<td>W3</td>
<td>2.44(6)</td>
<td>2.39(6)</td>
<td>2.44(2)</td>
<td>O6</td>
<td>2.556(6)</td>
<td>2.57(2)</td>
<td>2.57(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O4 O6</td>
<td>2.647(6)</td>
<td>2.61(2)</td>
<td>2.62(2)</td>
<td>O9 O6</td>
<td>2.520(5)</td>
<td>2.51(2)</td>
<td>2.54(2)</td>
<td>O9 h</td>
<td>2.520(5)</td>
<td>2.51(2)</td>
<td>2.54(2)</td>
<td>W6</td>
<td>2.511(7)</td>
<td>2.50(3)</td>
<td>2.59(2)</td>
<td>O1</td>
<td>2.87(3)</td>
<td>2.89(3)</td>
<td>2.89(3)</td>
<td>W6</td>
<td>2.555(6)</td>
<td>2.53(2)</td>
<td>2.53(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a = x + 1$, $y$, $z$; $^b = x$, $y + 1$, $z$; $^c = x - 1$, $y$, $z$; $^d = x - 1/2$, $y$, $-z + 1/2$; $^e = x + 1/2$, $y + 1$, $-z + 1/2$; $^f = x + 1/2$, $y$, $-z + 1/2$; $^g = x - 1/2$, $y + 1$, $-z + 1/2$; $^h = x$, $y + 1$, $z$; $^i = x$, $y - 1$, $z$.

only 4 Ca atoms p.f.u., the electron density maxima were attributed to three H$_2$O molecules, W1, W2, and W3, respectively. After introducing anisotropic displacement parameters for the atoms of the complex layers (Ca1, Ca3, Si1, Si2, Si3 and ten oxygen atoms), the $R$ index dropped to 0.051 for 1650 $F_{obs} > 4c(F_{obs})$. Atomic coordinates and displacement parameters are reported in Table 2, whereas the bond distances are listed in Table 3. The structure is sketched in Fig. 5.

Normal tobermorite from Urals. The refined cell parameters, obtained through least-square refinement of 20 reflections with $24^\circ < 2\theta < 32^\circ$, were $a' = 6.732(2)$, $b' = 7.368(1)$, $c' = 22.680(4)$ Å, $\gamma = 123.18(1)^\circ$. We applied a procedure similar to that used for anomalous tobermorite, introducing the same starting model for the atoms of the complex layers and looking for the ‘zeolitic’ atoms of the structural cavities through Fourier synthesis. Also in this case, the least-square refinement confirmed that the wollastonite-like chains are condensed along $c$ to form double chains with symmetry 2$mm$. On the contrary, the examination of the Fourier map indicated that a significant difference exists between the two structures as regards the structural cavities. Here, in fact, a calcium cation (Ca2) partially occupies the site at 0.56, 0.08, 0.04. The very short distance (~ 1 Å) occurring between two mirror-related Ca2 atoms implies that the maximum occupancy of this site is 1/2. On the other hand, the electron density calculated through Fourier synthesis, as well as the chemical data, pointed to the occurrence of only 0.25 Ca cations in this site. Three other maxima were found in the Fourier map, and were attributed to three H$_2$O molecules W1, W2, and W3, respectively. Short distances between Ca2
Table 4. Tobermorite 11Å, orthorhombic polytype MDO₁,
space group F2dd: atomic coordinates and isotropic
displacement parameters.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U₁iso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₁</td>
<td>0.2500(6)</td>
<td>0.2900(8)</td>
<td>0.0790(2)</td>
<td>0.006(1)</td>
</tr>
<tr>
<td>Si₂</td>
<td>0.1760(6)</td>
<td>-0.001(1)</td>
<td>0.1006(3)</td>
<td>0.003(3)</td>
</tr>
<tr>
<td>Si₃</td>
<td>0.2518(6)</td>
<td>0.7077(8)</td>
<td>0.0975(4)</td>
<td>0.007(3)</td>
</tr>
<tr>
<td>O₁</td>
<td>0.136(1)</td>
<td>0.263(2)</td>
<td>0.0975(2)</td>
<td>0.003(3)</td>
</tr>
<tr>
<td>O₁b</td>
<td>0.138(1)</td>
<td>0.757(3)</td>
<td>0.0975(4)</td>
<td>0.007(3)</td>
</tr>
<tr>
<td>O₂</td>
<td>0.620(2)</td>
<td>0.505(3)</td>
<td>0.1511(4)</td>
<td>0.011(3)</td>
</tr>
<tr>
<td>O₂b</td>
<td>0.620(1)</td>
<td>0.003(3)</td>
<td>0.1511(4)</td>
<td>0.007(3)</td>
</tr>
<tr>
<td>O₃</td>
<td>0.183(2)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.017(4)</td>
</tr>
<tr>
<td>O₅</td>
<td>0.251(2)</td>
<td>0.499(3)</td>
<td>0.0667(3)</td>
<td>0.010(2)</td>
</tr>
<tr>
<td>O₆</td>
<td>0.248(2)</td>
<td>0.179(3)</td>
<td>0.0475(6)</td>
<td>0.019(4)</td>
</tr>
<tr>
<td>O₆b</td>
<td>0.244(2)</td>
<td>0.824(3)</td>
<td>0.0476(5)</td>
<td>0.011(4)</td>
</tr>
<tr>
<td>O₇</td>
<td>0.034(2)</td>
<td>0.007(3)</td>
<td>0.0457(5)</td>
<td>0.024(4)</td>
</tr>
<tr>
<td>O₇b</td>
<td>0.996(3)</td>
<td>0.508(4)</td>
<td>0.0478(6)</td>
<td>0.044(6)</td>
</tr>
<tr>
<td>Ca₁</td>
<td>0.0048(3)</td>
<td>0.9977(8)</td>
<td>0.1034(5)</td>
<td>0.0078(9)</td>
</tr>
<tr>
<td>Ca₃</td>
<td>0.9984(3)</td>
<td>0.5009(8)</td>
<td>0.1026(1)</td>
<td>0.0074(9)</td>
</tr>
<tr>
<td>W₂</td>
<td>0.692(4)</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.06(1)</td>
</tr>
<tr>
<td>W₃</td>
<td>0.416(6)</td>
<td>0.298(8)</td>
<td>0.001(2)</td>
<td>0.06(2)</td>
</tr>
</tbody>
</table>

and the water molecules strongly suggest that an order-
ded distribution of such atoms and molecules oc-
curs; this ordering will be presented in the chapter
titled ‘Structure description and discussion’.

After introducing anisotropic displacement pa-
rameters for the Ca₁ and Ca₃ cations and for the sil-
icon atoms, the $R$ index was 0.089 for 793 reflec-
tions with $F_{\text{obs}} > 4\sigma(F_{\text{obs}})$. The structural refinement
performed with the synchrotron data converged to
$R = 0.110$ for 608 reflections with $F_{\text{obs}} > 4\sigma(F_{\text{obs}})$.
The positional and displacement parameters of normal
tobermorite are listed in Table 2, whereas the bond
distances are reported in Table 3. The struc-
ture is drawn in Fig. 6.

Orthorhombic polytype MDO₁

Anomalous tobermorite from Wessels mine. As al-
ready mentioned, the characteristic reflections of the MDO₁ appeared particularly weak and diffuse.
However, they could be measured and used to re-
fine the structural model obtained through the OD
procedure. The final $R$ was 0.128 for 1316 reflec-
tions with $F_{\text{obs}} > 4\sigma(F_{\text{obs}})$. The structure of the or-
thorhombic polytype is drawn in Fig. 7. The cell
parameters and the refinement data are given in Ta-
ble 1; atomic coordinates and isotropic displace-
ment parameters are given in Table 4.

The bond distances are not given as they merely
confirm, with lower precision, the structural fea-
tures obtained through the refinement of the mono-
clinic polytype.

The lists of the $F_\text{o}/F_\text{c}$ data are available from the authors upon request (or through the E.J.M. Editorial Office – Paris).

Structure description and discussion

Calcium polyhedral layer

A common feature of the structural arrangements
of all the minerals in the tobermorite group is the
layer built up by sevenfold coordinated calcium
cations. We have already described, in a detailed
way, this aspect in our paper on clinotobermorite
(Merlino et al., 2000). There we observed two dis-
tinct types of polyhedra, whereas in the present
Infinite silicate tetrahedral chains of the wollastonite-type run along \( \mathbf{b} \) on both sides of the calcium polyhedral layers. These chains may be described as built up by ‘paired’ \( \text{Si}_2\text{O}_7 \) tetrahedra (centred by \( \text{Si}_1 \) and \( \text{Si}_3 \) cations) connected by a ‘bridging’ tetrahedron (centred by \( \text{Si}_2 \)). Each chain is firmly linked to a column of calcium trigonal prisms, with the ‘paired’ tetrahedra grasped to it by sharing the oxygen atoms of the edges opposite to the capping ligands, while the bridging tetrahedron shares the capping O6 ligand of the adjacent column as shown in Fig. 8. It illustrates the complex layer built up by the calcium polyhedral layer and the tetrahedral module. Successive tetrahedral chains on one side of the layer are shifted by \( \mathbf{b}/2 \); the tetrahedral chains on the hidden side are similarly connected to the layer, with paired tetrahedra grasped to the alternate columns and shifted by \( \pm \mathbf{b}/4 \) relatively to those on the visible side.

As in clinotbermorite, the wollastonite-like chains grasped to successive calcium layers and facing each other are condensed through the bridging oxygen O5 lying on the symmetry plane normal to \( \mathbf{c} \), thus building double chains with symmetry [2\( \mathbf{m} \mathbf{m} \)], to compare with the [-2\( \mathbf{m} \)-] symmetry of the corresponding double chains in clinotbermorite.

**Structural cavities and their ‘zeolitic’ content**

Adjacent layers of calcium polyhedra are firmly connected through the double silicate chains, thus building a robust scaffolding presenting channels running along \( \mathbf{b} \), the direction in which the wollastonite-type chains develop.

The main differences between the two specimens of tobermorite 11Å, which are the object of the present study, have been found in the content of these cavities. The material distributed in the cavities has also an influence on the actual chemical nature of O6 ligands, which therefore will be discussed in the same context.

In anomalous tobermorite 11Å from Wessels mine only water molecules are located in the cavities of the structure (Fig. 9a). Weak connections among them and with oxygen atoms of the scaffolding are established through long hydrogen bonds (no O…O distance shorter than 2.92 Å has
The real structure of tobermorite 11Å

Fig. 9. Schematic drawing of the structural cavities, as seen along [010] in (a) anomalous tobermorite 11Å from Wessels mine; (b) normal tobermorite 11Å from Urals; (c) clinotobermorite from Wessels mine (Merlino et al., 2000). In (b) one of the two possible ordered arrangements of Ca2, W1, and W3 is reported.

been observed. The large number of weak connections involving the water molecules makes any hydrogen-bond scheme too speculative. In any case, due to their weakness, the possible hydrogen bonds cannot sensibly change the valence bond sums calculated (Brese & O’Keefe, 1991) for the various atoms of the scaffolding, indicating that all the oxygen atoms are O2- anions, apart from W6 and O6, which are water molecule (bond valence sum 0.23) and hydroxyl anion (bond valence sum 1.13), respectively. The crystal chemical formula of anomalous tobermorite 11Å from Wessels mine is therefore Ca₄Si₆O₁₅(OH)₂·5H₂O.

By looking at the results of the refinement process reported in Table 2 we realise that the cavities of tobermorite 11Å from the Urals contain ‘zeolitic’ calcium cations Ca2, in general position with occupancies ¼, W2 water molecules, with full occupancy and in position similar to that of the corresponding molecule in the specimen from Wessels mine, and W1, W3 water molecules, with occupancy ½. Moreover these last molecules are located in positions not too different from those occupied by the corresponding molecules in the specimen from Wessels mine, apart from a small, but significant (∼0.4 Å) displacement from the symmetry plane. The valence bond sums bring to the same conclusions as for the specimen from Wessels mine for all the oxygen atoms except O6. In fact short distances between O6 on one side and Ca2, W1 and W3 on the other side are observed. A bond valence sum of 1.45 v.u. was calculated for O6, including the contribution of the hydrogen bonding from W1 and W3 (Ferraris & Ivaldi, 1988) and taking into account the actual occupancy of Ca2, W1 and W3. These results may be rationalised as explained in the following.

a) Two distinct situations occur with the same probability; in one the ‘zeolitic’ calcium cation Ca2 is located on either side of the reflection plane (Fig. 9b); in the other case Ca2 is absent, just as it happens in the crystal structure of tobermorite 11Å from Wessels mine.

b) When Ca2 is located on the upper side, relatively to the reflection plane, W1 and W3 water molecules are located on the opposite side and form fairly strong bonds with Ca2 which is also firmly connected to W2, O2 and O6 and more loosely bonded to O1 and O7. This situation is illustrated in Fig. 9b, where the bond distances are given as averages calculated from the two sets of structural results listed in Table 3. W1 and W3 form strong hydrogen bonds with O6 on the lower side, relatively to the reflection plane. Thus both O6 atoms are O2- anions, the first being saturated by Si2, Ca1 and Ca2, the other being saturated by Si2, Ca1 and as acceptor of two strong hydrogen bonds from W1 and W3. This atomic configuration is closely similar to that realised in clinotobermorite and illustrated in Fig. 9c. Closely similar is also the hydrogen bonding system (Fig. 10) which interconnect the ‘zeolitic’ water molecules, the W6 water molecules, which are the apical ligands of the Ca1 polyhedra, and O6 atoms. Obviously a similar situation occurs when Ca2 cations are located on the lower side, relatively to the symmetry plane, with W1 and W3 now located on the upper side.

c) When Ca2 is absent, most probably W1 and W3 shift their positions towards the symmetry plane, as it happens in tobermorite 11Å from Wes-
sels mine (Fig. 9a), and O6 anions on both sides of that plane are far from W1 and W3; in fact it is just the presence of Ca2 cations which displaces W1 and W3 from the symmetry plane towards O6.

Therefore, considering Ca2 cations and O6 anions, we have two distinct situations, corresponding to the presence and absence of ‘zeolitic’ calcium cations:

1) Ca2+ + 2 O2–, exactly as in the case of clinotobermorite (Merlino et al., 2000);
2) ! +2 OH−, exactly as in the case of the anomalous tobermorite 11Å from Wessels mine.

As both situations occur with the same frequency, the average result corresponds to: 0.5 Ca2+ + 1 O2– + 1 OH−. Therefore the structural results point to the crystal chemical formula Ca4.5 Si6 O15.56 (OH)1.44 ·5H2O for tobermorite 11Å from Urals.

In the preceding discussion we have assumed that only silicon atoms occur in the tetrahedral chains. In case of partial substitution of silicon by aluminium, which mainly occurs in the bridging tetrahedron Si2 (Komarneni et al., 1985), general and local charge balance is restored through additional OH− for O2− substitutions in O6 site. These coupled substitutions may explain the results of the chemical analysis carried out to determine the cationic content of tobermorite 11Å from Urals. The analysis was performed with an ARL-SEMQ electron microprobe, at 15 kV and 10 nA. Because of the small size of the crystal, the diameter of the beam was reduced to 10 µm. The analytical data (average of 7 analysed points, recalculated on the basis of six tetrahedral cations, and assuming 5 H2O molecules p.f.u.) point to the crystal chemical formula Ca4.42K0.04Si5.68Al0.32O15.56(OH)1.44·5H2O.

Conclusions

Through the application of the OD procedures we succeeded in unravelling the real structure of tobermorite 11Å, defining the two main polytypes and indicating their structural arrangements and relationships. The structural investigations have been carried on two different specimens, a ‘normal’ one from Baškenov, Urals, Russia, and an ‘anomalous’ one from Wessels mine, Kalahari manganese field, South Africa. The two specimens differ in the behaviour upon heating at 300°C, at which temperature tobermorite 11Å loses most of its water molecules: in fact, whereas the specimen from Urals, as all the ‘normal’ tobermorites, shows a decrease in the characteristic basal spacing from 11.3 to 9.3 Å, the specimen from Wessels mine, as all the ‘anomalous’ tobermorites, keeps its characteristic spacing at 11.3 Å.

This distinct behaviour had been explained with the presence of ‘interlayer Si-O-Si linkages’ in ‘anomalous’ tobermorites and their absence in ‘normal’ tobermorites, an absence which would consent an approach of adjacent calcium polyhedral layers on dehydration, with corresponding decrease of the basal spacing. However the present structural investigation has definitely demonstrated that the wollastonite-like chains, grasped to both sides of the polyhedral layers, condense to form double chains (Dreierdoppelketten, as defined by Liebau, 1956), just as it has been already shown for clinotobermorite (Merlino et al., 2000). These double chains, different in symmetry and shape from those found in clinotobermorite, occur in both ‘normal’ and ‘anomalous’ specimens.

These results definitely rule out the explanation reported above for the different behaviour of the two types of tobermorite 11Å on heating, an explanation that had been already seriously questioned since we have demonstrated that clinotobermorite, which does shrink to a 9Å phase upon dehydration (Henmi & Kusachi, 1989, 1992) has tetrahedral double chains (Merlino et al., 1999; 2000). We had put forward an alternative explanation, which is fully confirmed by the present structural results and is here more precisely formulated.

In clinotobermorite, Ca5 Si6 O17·5H2O, ‘zeolitic’ calcium cations are placed in the cavities of the structure and form strong bonds with oxygen atoms of the complex layers and with the ‘zeolitic’ water...
molecules. Upon heating at 300°C these water molecules are lost and a general structural rearrangement is imposed by the requirement of properly completing the calcium coordination. As the missing ligands may be presented only by atoms of the complex layers, chain decondensation must occur so to consent the proper approach of adjacent polyhedral layers.

‘Zeolitic’ calcium cations occur, with partial occupancy, also in the cavities of the structure of tobermorite 11Å from Urals, with closely similar location and coordination as found in clinotbermorite. The loss of water upon heating at 300°C has the same consequences as we have previously discussed, with formation of tobermorite 9Å. On the contrary, no ‘zeolitic’ calcium cations occur in the cavities of tobermorite 11Å from Wessels mine, Ca₅Si₆O₁₆(OH)₂·8H₂O; consequently no requirement of proper calcium coordination is caused by dehydration, no severe structural rearrangement occurs, no chain decondensation takes place: the specimen exhibits ‘anomalous’ behaviour.

The structural results we have presented and discussed have been obtained with natural specimens, but we think that they not only give a sound basis for any future comprehensive crystal chemical study on natural tobermorite 11Å, but also for the interpretation and the rationalisation of the wide series of investigations performed on synthetic materials.

Some questions still remain unanswered; among them the most interesting are those related to the nature of tobermorite 11Å obtained by mildly heating tobermorite 14Å and to the nature and behaviour of ‘mixed’ tobermorite 11Å.

Tobermorite 14Å presents the same complex layers which appear in all the phases of the tobermorite group, as well as extra layers of ‘zeolitic’ calcium cations and water molecules, regularly alternating with the complex layers (Merlino et al., in prep.). Consequently tobermorite 14Å is characterised by single wollastonite-like chains and has the general crystal chemical formula Ca₅Si₆O₁₆(OH)₂·8H₂O. It has been maintained that tobermorite 11Å formed by heating tobermorite 14Å at temperature up to 105°C contains single chains. As regards the natural specimens, some evidence for that has been given through the molybdate method applied to tobermorite 11Å obtained by heating tobermorite 14Å from Crestmore (Wieker, 1968). Some objections may be raised to such chemical method for testing the degree of silicate condensation, due to possible chain rearrangements occurring during the dissolution in HCl 0.1N. However that evidence seems confirmed by 29Si NMR investigations carried on tobermorite 11Å produced by heating synthetic specimens of tobermorite 14Å at 100-105°C (Wieker et al., 1982; Cong & Kirkpatrick, 1996). It would be extremely useful to carry out structural studies by means of X-ray or electron diffraction on those materials to unravel the structural arrangement of the possible new form of tobermorite 11Å and to conclusively define its relationships with the forms described in the present paper.

It has been shown here that the absence of ‘zeolitic’ calcium cations is the determinant for anomalous behaviour, but we do not exactly know which is the amount of calcium which determines such behaviour. It is generally known that natural tobermorites with a low content of ‘zeolitic’ calcium cations (0.1 to 0.3 a.p.f.u.) display ‘mixed’ behaviour: upon heating at 300°C they partly transform to tobermorite 9Å, partly do not transform; the product displays both characteristic basal spacings of 9.3 and 11.3 Å. However, it is neither known whether a precise relationships exists between the transformed quantity and the calcium content of the parent phase, nor which is the actual mechanism of transformation. It may be guessed that the parent phase is inhomogeneous as regards the calcium distribution, or that inhomogeneity arises through calcium diffusion during the dehydration process, with consequent formation of domains of two types, one rich and another poor in ‘zeolitic’ calcium cations, domains which produce tobermorite 9Å and untransformed tobermorite 11Å, respectively. To understand these aspects a crystal chemical study of the known specimens of natural tobermorites, with attention to their thermal behaviour, will be undertaken.

Acknowledgements: This work was supported by MURST (Ministero dell’Università e della Ricerca Scientifica) through grants to the national projects ‘Relations between structure and properties in minerals: analysis and applications’ (MURST 97) and ‘Transformations, reactions, ordering in minerals’ (MURST 99). We thank Prof. H.F.W. Taylor for his suggestions and remarks. We are grateful to Prof. A. Zadov, who kindly provided us with the tobermorite crystals from Bašćenov, Urals, Russia; to Dr. S. Bigi, who performed the electron microprobe analysis on that sample, and to Prof. E. Makovicky, for his valuable comments.
References


Hamid, S.A. (1981): The crystal structure of the 11Å natural tobermorite Ca$_{2.25}$[Si$_3$O$_7$.(OH)$_1$.5]·1H$_2$O. *Z. Kristallogr.*, 154, 189-198.


Received 28 April 2000
Modified version received 1 December 2000
Accepted 8 December 2000