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

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Abstract: Specimens of tobermorite 11Å from Wessels mine, South Africa, an 'anomalous' tobermorite, and from Baščenov, 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 MDO_1 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 MDO_2 polytype [monoclinic, space group $B11m$, $a = 6.735(2)$, $b = 7.385(1)$, $c = 22.487(4)$ Å, $\gamma = 123.25(1)°$] converged to $R = 0.051$. Two refinements were carried out for the MDO_2 polytype of the specimen from the Urals [space group $B11m$, $a = 6.732(2)$, $b = 7.368(1)$, $c = 22.680(4)$ Å, $\gamma = 123.18(1)°$] 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 $[Si_6O_{15}(OH)_2]$ and $[Si_6O_{16}(OH)]$ 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, specially 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 dehydration 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 dehydration and are called 'anomalous' to distinguish them from those specimens that shrink on dehydration ('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 $C222_1$, 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 $\mathbf{c}^*$-axis in reciprocal space, indicating that the mineral is built of perfect structural slabs normal to $\mathbf{c}$ 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 $Immm$, $I222$, $I2_12_12_1$, 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 dehydration of tobermorite 11Å (McConnell, 1954) which is therefore of 'normal' type. The composition of tobermorite 11Å has been indirectly determined by following the cumulative dehydration curve of a mixture of '11Å' and '14Å' hydrates, thus obtaining the crystal chemical formulas $Ca_5Si_6O_{17} \cdot 5H_2O$ or $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$.

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 'pseudorhombic' 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 CaO_2 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' Si_2O_7 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 $Ca_4Si_6O_{18}$ 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: $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$. 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 $Imm2$ 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 $\mathbf{b}/2$. 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 $Ca_{4.5}[Si_6O_{15}(OH)_3] \cdot 2H_2O$. 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 λ-operations (symmetry operations of the single layer, namely one of the 80 layer groups) and the σ-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 ($a = 11.3$, $b = 7.33$ Å) and third basis vector (not a translation vector) c_0 ($c_0 = 11.3$ Å; cell parameters taken from McConnell, 1954). At difference from the corresponding layer in clinotobermorite, the double chain is obtained from the single
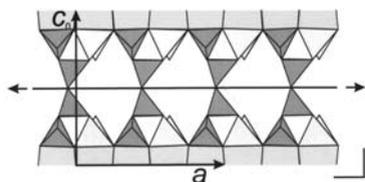
Fig. 1. Single layer in tobermorite 11Å, as seen along **b**.

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):

$$C \quad 2 \quad m \quad (m) \qquad C \quad 2 \quad m \quad (m) \\ \{n_{r,2} \quad 2_r \quad (2_2)\} \qquad \{2_s \quad n_{2,s} \quad (n_{s,r})\} \tag{1}$$

The second is the correct one. In fact, the λ- and σ-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 $r = s = ½$, 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 0.21**c**.

1 The symbols which describe the σ-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 r**b**/2+$\mathbf{c}_0$. The symbol 2_r in the second position indicates a screw parallel to **b** with translation component r**b**/2. The parentheses in the third position of each line indicate that $\mathbf{c}_0$, the third basis vector of the single layer, is not a translation vector.
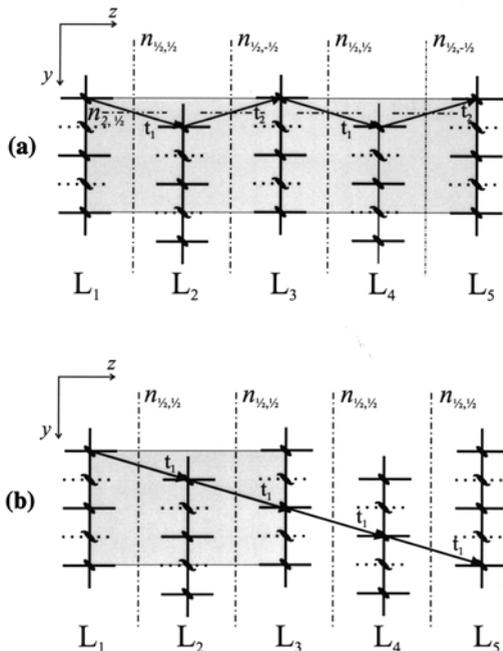

Fig. 2. Sequences of λ-operators (heavy marks) and σ-operators (light marks) in the orthorhombic MDO$_1$ (a) and monoclinic MDO$_2$ (b) structures of tobermorite 11Å, as seen along **a***. The unit cells and the sequences of the stacking vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ are outlined.

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

$$C \quad 2 \quad m \quad (m) \\ \{2_½ \quad n_{2,½} \quad (n_{½,½})\} \tag{2}$$

Layers with $C2mm$ symmetry may follow each other in the **c** direction, related by the operator $n_{½,½}$ ($\equiv n_{-½,-½}$ due to the C centring of the single layer) normal to **c** or by the operator $n_{½,-½}$ ($\equiv n_{-½,½}$). Pairs of layers related in both ways are geometrically equivalent. It is worth to note that layers related by the operators $n_{½,½}$ and $n_{½,-½}$ are translationally equivalent and stacked according to the vectors:

$$\mathbf{t}_1 = \mathbf{c}_0 + (\mathbf{a} + \mathbf{b})/4$$
$$\mathbf{t}_2 = \mathbf{c}_0 + (\mathbf{a} - \mathbf{b})/4$$

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 $n_{½,½}$ and $n_{½,-½}$ 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 operator $n_{1/2,1/2}$ 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 σ-operator $n_{2,1/2}$ 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 **a**/2 + **b**/2 is valid for all the layers and the operators $n_{1/2,1/2}$ and $n_{1/2,-1/2}$ become total [- - d] glides;

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

Therefore the whole structure has *F*2*dd* 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 $n_{1/2,1/2}$ corresponds to a translation $2c_0 + (a + b)/2$. As all the layers are *C* centred, the third layer is translated by **c** = $2c_0$ relatively to the first one; the λ-operator [- - m] is total operator, valid for the whole structure. The corresponding *C* cell with $a = 11.3$, $b = 7.33$, $c = 22.6$ Å, $\gamma = 90°$, presents additional lattice points at ¼, ¼, ½ and ¾, ¾, ½ (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 *B*11*m* and cell parameters: $a' = 6.73$, $b' = 7.33$, $c' = 22.6$ Å, $\gamma = 122.9°$. 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
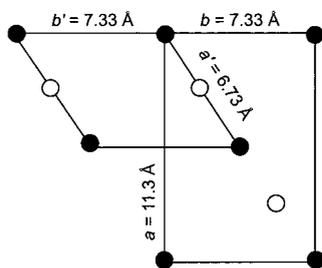

Fig. 4. Drawing of the diffraction pattern of tobermorite 11Å, as seen along the **b** axis. The reciprocal vectors **A*** and **C*** corresponding to the subcell are indicated. Large circles indicate family reflections. For sake of clarity, the characteristic reflections of only MDO$_1$ and MDO$_2$ polytypes are reported (small circles and crosses, respectively; differently oriented crosses correspond to different *k* values). The characteristic reflections of the twin MDO$_2$' polytype correspond to those of MDO$_2$, once the symbols + and × are inverted.

observe that reflections 00*l* 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 Mo*K*α 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, $\gamma = 90.00(1)°$, refined on the basis of 20 reflections with $24° < 2\theta < 32°$. The separation of the reflections pertaining to the different individuals was performed successively, applying the transformation matrices |-½ ½ 0, 0 1 0, 0 0 1 | and |½ ½ 0, 0 -1 0, 0 0 -1 |, respective-

Fig. 3. Relationships between the *C* centred cell, which presents additional lattice points at ¼, ¼, ½ (empty circles), and the *B* centred cell of the MDO$_2$ polytype of tobermorite 11Å.

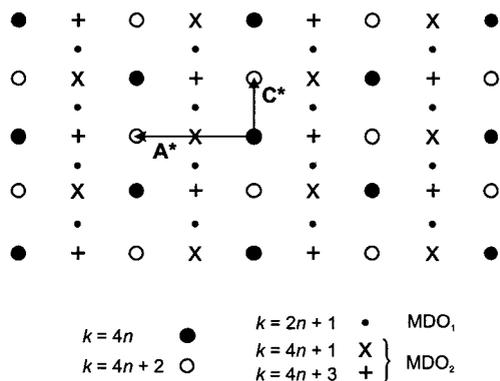S. Merlino, E. Bonaccorsi, T. Armbruster

Table 1. Unit cell, data collection and refinement parameters for the two MDO polytypes of anomalous tobermorite and for MDO_2 polytype of normal tobermorite.

	Anomalous tobermorite from Wessels mine		Normal tobermorite from Urals	
	MDO_1	MDO_2	MDO_2	
			(Conventional X-ray source)	(Synchrotron radiation source)
Crystal dimensions (mm)	$0.16 \times 0.26 \times 0.80$		$0.08 \times 0.08 \times 0.20$	
a (Å)	11.265(2)	6.735(2)	6.732(2)	
b (Å)	7.386(1)	7.385(1)	7.369(1)	
c (Å)	44.970(9)	22.487(4)	22.680(4)	
γ (°)		123.25(1)	123.18(1)	
Space group	$F2dd$	$B11m$	$B11m$	
2θ max	60°	60°	60°	41°
Unique reflections	1880	1722	1707	639
Observed reflections [with $F_{obs} > 4\sigma(F_{obs})$]	1314	1650	677	608
Absorption correction	psi-scan	–	–	–
R(obs.)	0.128	0.051	0.089	0.110
Equipment	P4 Siemens four-circle automatic diffractometer			345 mm Imaging plate from MarResearch®
Wavelength of radiation	0.71069 Å (graphite monochromatized Mo$K\alpha$)			1 Å
Scan mode	ω–2θ	ω –2θ	ω –2θ	*
Scan width	1° in ω			
Scan speed	4°/min	3°/min	3°/min	
Refinement	Full-matrix least squares against F^2 with SHELXL-97 (Sheldrick, 1997)			
Chemical formula ($Z = 2$)	$Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$		$Ca_{4.5}Si_6O_{16}(OH) \cdot 5H_2O$	

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

ly. In a second stage, we collected the reflections of the MDO_1 polytype, with space group $F2dd$ and refined cell parameters $a = 11.265(2)$, $b = 7.386(1)$, $c = 44.970(9)$ Å. The characteristic reflections of this polytype (with h, k, and l odd) were weaker and more diffuse than those of the MDO_2 polytype.

As regards tobermorite 11Å from Urals, we collected two sets of data from the same single crystal ($0.08 \times 0.08 \times 0.20$ mm^3), both of them concerning the MDO_2 polytype. The former set was obtained with a Siemens P4 automatic diffractometer, and graphite monochromatized Mo$K\alpha$ radiation. As the crystal was quite small and the superstructure reflections showed very low intensities, a second data collection was performed with an Imaging Plate from MarResearch® at the Elettra Synchrotron Light Source (with $\lambda = 1$ Å). The experimental conditions of both the data collections are reported in Table 1.

In all the structure refinements, the intensities of the family reflections were divided by an appropriate scale factor, to refer the data to the same crystal volume.

Monoclinic polytype MDO_2

Anomalous tobermorite from Wessels mine. The refined cell parameters were $a' = 6.735(2)$, $b' = 7.385(1)$, $c' = 22.487(4)$ Å, $\gamma = 123.25(1)°$. 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 11Å, monoclinic polytype MDO$_2$, space group $B11m$: atomic coordinates and isotropic or equivalent displacement parameters.

	Anomalous tobermorite from Wessels mine				Normal tobermorite from Urals conventional X-ray tube				synchrotron radiation			
	x	y	z	U_{eq} or U_{iso}	x	y	z	U_{eq} or U_{iso}	x	y	z	U_{eq} or U_{iso}
Si1	0.7581(4)	0.3862(3)	0.15738(7)	0.0054(4)	0.757(1)	0.3876(9)	0.1574(3)	0.007(1)*	0.771(2)	0.383(1)	0.1578(3)	0.031(3)
Si2	0.9087(4)	0.7531(3)	0.07117(7)	0.0086(3)	0.915(1)	0.756(1)	0.0710(3)	0.015(1)*	0.925(2)	0.750(1)	0.0721(3)	0.030(2)
Si3	0.7592(4)	0.9697(3)	0.15773(8)	0.0056(4)	0.758(1)	0.967(1)	0.1589(3)	0.007(1)*	0.772(1)	0.962(1)	0.1596(3)	0.027(3)
O1	0.771(1)	0.5059(8)	0.0942(2)	0.014(1)	0.754(3)	0.499(3)	0.0949(8)	0.018(4)	0.774(4)	0.495(3)	0.0932(7)	0.039(5)
O2	0.759(1)	0.178(1)	0.1327(2)	0.0127(8)	0.772(4)	0.185(3)	0.1328(5)	0.014(2)	0.762(3)	0.169(3)	0.1305(5)	0.019(4)
O3	0.985(1)	0.5369(9)	0.1982(2)	0.0091(9)	0.992(3)	0.537(3)	0.1971(8)	0.011(4)	0.002(4)	0.527(4)	0.2000(7)	0.032(5)
O4	0.519(1)	0.3063(8)	0.1942(2)	0.012(1)	0.523(3)	0.312(3)	0.1946(9)	0.015(4)	0.536(4)	0.304(4)	0.1926(8)	0.035(5)
O5	0.894(2)	0.746(1)	0.0	0.017(1)	0.898(4)	0.752(4)	0.0	0.017(4)	0.910(5)	0.747(5)	0.0	0.034(6)
O6	0.188(1)	0.893(1)	0.0940(2)	0.018(1)	0.197(3)	0.896(3)	0.0949(7)	0.018(4)	0.202(4)	0.887(4)	0.0942(9)	0.053(6)
W6	0.270(2)	0.434(2)	0.0939(3)	0.045(2)	0.237(6)	0.416(6)	0.097(1)	0.09(1)	0.289(5)	0.436(5)	0.094(1)	0.076(7)
O7	0.770(1)	0.8601(9)	0.0951(2)	0.015(1)	0.752(3)	0.853(3)	0.0972(8)	0.017(4)	0.769(3)	0.843(3)	0.0953(7)	0.027(5)
O8	0.523(1)	0.8110(8)	0.1950(2)	0.011(1)	0.524(3)	0.807(3)	0.1962(8)	0.008(4)	0.537(4)	0.798(4)	0.1968(8)	0.036(6)
O9	0.987(1)	0.0459(9)	0.1985(2)	0.010(1)	0.984(3)	0.045(3)	0.2002(8)	0.011(4)	0.004(4)	0.042(4)	0.2008(7)	0.034(6)
Ca1	0.2651(2)	0.4328(2)	0.20557(6)	0.0085(3)	0.2632(9)	0.4310(9)	0.2069(3)	0.011(1)	0.277(1)	0.4257(9)	0.2083(2)	0.024(2)
Ca3	0.7499(2)	0.9228(2)	0.29348(5)	0.0074(3)	0.7519(9)	0.9228(9)	0.2945(3)	0.009(1)	0.763(1)	0.916(1)	0.2951(2)	0.027(2)
W1*	0.427(5)	0.219(5)	0.0	0.14(1)	0.42(1)	0.26(1)	-0.020(3)	0.13(3)	0.433(9)	0.223(8)	-0.025(2)	0.072(1)
W2	0.879(3)	0.237(3)	0.0	0.060(4)	0.922(7)	0.250(7)	0.0	0.07(1)	0.949(7)	0.256(6)	0.0	0.08(1)
W3*	0.422(5)	0.800(5)	0.0	0.13(1)	0.40(1)	0.76(1)	-0.019(2)	0.10(2)	0.43(1)	0.77(1)	-0.022(2)	0.09(2)
Ca2*	–	–	–	–	0.559(4)	0.078(4)	0.044(1)	0.035(5)	0.562(4)	0.064(4)	0.045(1)	0.038(6)

* 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.

Si1					Si2					Si3				
Si1	O1	1.649(5)	1.64(2)	1.67(2)	Si2	O1	1.614(5)	1.67(2)	1.65(2)	Si3	O2[b]	1.639(6)	1.67(2)	1.69(2)
	O2	1.637(6)	1.64(2)	1.67(2)		O5	1.603(2)	1.614(6)	1.638(8)		O7	1.646(5)	1.62(2)	1.69(2)
	O3	1.599(6)	1.62(2)	1.63(2)		O6[a]	1.654(6)	1.68(2)	1.64(2)		O8	1.602(6)	1.60(2)	1.61(2)
	O4	1.609(7)	1.60(2)	1.57(2)		O7	1.612(6)	1.71(2)	1.62(2)		O9[b]	1.601(6)	1.60(2)	1.63(2)
Ca1	O4	2.368(6)	2.36(2)	2.38(2)	Ca3	O4[e]	2.398(5)	2.43(2)	2.42(2)	Ca2	O6[i]		2.35(3)	2.32(3)
	O8	2.356(5)	2.35(2)	2.32(2)		O8[f]	2.407(6)	2.42(2)	2.44(2)		O2		2.35(3)	2.24(3)
	O3[c]	2.399(6)	2.35(2)	2.35(2)		O3[d]	2.401(6)	2.40(2)	2.41(2)		W2		2.28(4)	2.41(4)
	O9[c]	2.414(6)	2.41(2)	2.39(2)		O9[g]	2.400(6)	2.42(2)	2.38(2)		W1		2.49(8)	2.39(5)
	O3[d]	2.495(6)	2.53(2)	2.44(2)		O8	2.556(6)	2.57(2)	2.57(2)		W3[i]		2.44(6)	2.39(6)
	O4[d]	2.647(6)	2.61(2)	2.62(2)		O9[h]	2.520(5)	2.51(2)	2.54(2)					
	W6	2.511(7)	2.50(3)	2.59(2)		O6[f]	2.555(6)	2.53(2)	2.53(2)		O1		2.87(3)	2.89(3)
											O7[i]		2.88(3)	2.89(3)

[a] = x + 1, y, z; [b] = x, y +1, z; [c] = x – 1, y, z; [d] = x – ½, y, -z + ½; [e] = x + ½, y + 1, -z + ½; [f] = x + ½, y, -z + ½; [g] = x – ½, y + 1, -z + ½; [h] = x, y + 1, z; [i] = x, y – 1, z.
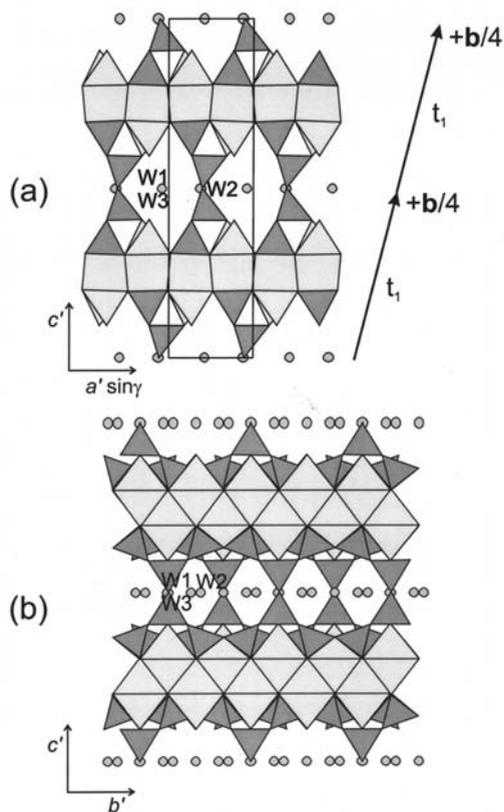

Fig. 5. Crystal structure of the monoclinic polytype MDO_2 of anomalous tobermorite 11Å, as seen along [010] (a) and down [210] (b). Silicate double chains (dark grey) are connected to layers of sevenfold coordinated calcium polyhedra (light grey). Grey circles indicate the 'zeolitic' water molecules W1, W2, and W3. The stacking vectors are drawn in (a), with the indication of their component along **b**.

only 4 Ca atoms p.f.u., the electron density maxima were attributed to three H_2O 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} > 4σ(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° < 2θ < 32°, were *a'* = 6.732(2), *b'* = 7.368(1), *c'* = 22.680(4) Å, γ = 123.18(1)°. 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 ½. 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_2O molecules W1, W2, and W3, respectively. Short distances between Ca2

Table 4. Tobermorite 11Å, orthorhombic polytype MDO$_1$, space group *F*2*dd*: atomic coordinates and isotropic displacement parameters.

	x	y	z	U_{iso}
Si1	0.2500(6)	0.2900(8)	0.0790(2)	0.006(1)
Si2	0.1760(6)	–0.001(1)	0.0356(1)	0.008(1)
Si3	0.2518(6)	0.7077(8)	0.0789(2)	0.004(1)
O1	0.136(1)	0.263(2)	0.1006(3)	0.003(3)
O1b	0.138(1)	0.757(3)	0.0975(4)	0.007(3)
O2	0.620(2)	0.505(3)	0.1511(4)	0.011(3)
O2b	0.620(1)	0.003(3)	0.1541(4)	0.007(3)
O3	0.183(2)	0.0	0.0	0.017(4)
O5	0.251(2)	0.499(3)	0.0667(3)	0.010(2)
O6	0.248(2)	0.179(3)	0.0475(6)	0.019(4)
O6b	0.244(2)	0.824(3)	0.0476(5)	0.011(4)
O7	0.034(2)	0.007(3)	0.0457(5)	0.024(4)
O7b	0.996(3)	0.508(4)	0.0478(6)	0.044(6)
Ca1	0.0048(3)	0.9977(8)	0.1034(1)	0.0078(9)
Ca3	0.9984(3)	0.5009(8)	0.1026(1)	0.0074(9)
W2	0.692(4)	0.000000	0.000000	0.06(1)
W3	0.416(6)	0.298(8)	0.001(2)	0.06(2)

and the water molecules strongly suggest that an ordered distribution of such atoms and molecules occurs; this ordering will be presented in the chapter titled 'Structure description and discussion'.

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

Orthorhombic polytype MDO$_1$

Anomalous tobermorite from Wessels mine. As already mentioned, the characteristic reflections of the MDO$_1$ appeared particularly weak and diffuse. However, they could be measured and used to refine the structural model obtained through the OD procedure. The final *R* was 0.128 for 1316 reflections with $F_{obs} > 4\sigma(F_{obs})$. The structure of the orthorhombic polytype is drawn in Fig. 7. The cell parameters and the refinement data are given in Table 1; atomic coordinates and isotropic displacement parameters are given in Table 4.

The bond distances are not given as they merely confirm, with lower precision, the structural fea-
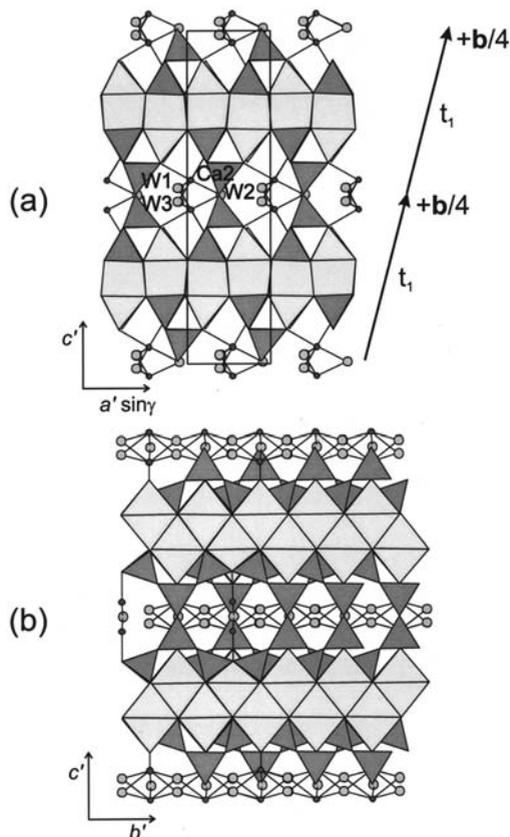

Fig. 6. Crystal structure of the monoclinic polytype MDO$_2$ of normal tobermorite 11Å, as seen along [010] (a) and down [210] (b). Symbols are as in Fig. 5. Dark grey dots indicate additional calcium cations Ca2.

tures obtained through the refinement of the monoclinic polytype.

The lists of the F_o/F_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 distinct types of polyhedra, whereas in the present
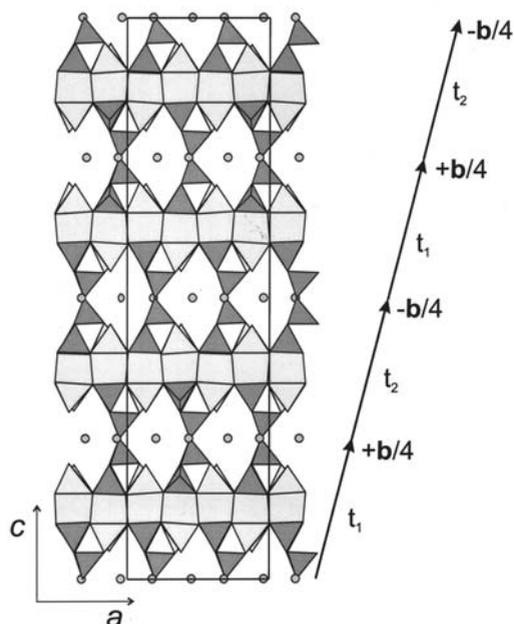
Fig. 7. Crystal structure of the orthorhombic polytype MDO₁ of tobermorite 11Å, as seen along [010]. Symbols are as in Fig. 5.

Fig. 8. Connection of silicate chains (dark grey) to the layer of calcium polyhedra (light grey), as seen along [001].

case the polyhedra are of one kind, which we have defined as mono-capped trigonal prism and illustrated in Fig. 4b of the cited paper (Merlino *et al*., 2000). Columns of mono-capped trigonal prisms run along **b**; adjacent columns in each layer present the capping ligands on its opposite surfaces. In both types of tobermorite 11Å very similar Ca-O distances occur (Table 3) and the capping ligands are W6 (water molecule) and O6 (its chemical nature will be discussed later on).

Silicate tetrahedral chains

Infinite silicate tetrahedral chains of the wollastonite-type run along **b** on both sides of the calcium polyhedral layers. These chains may be described as built up by 'paired' Si_2O_7 tetrahedra (centred by Si1 and Si3 cations) connected by a 'bridging' tetrahedron (centred by Si2). 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
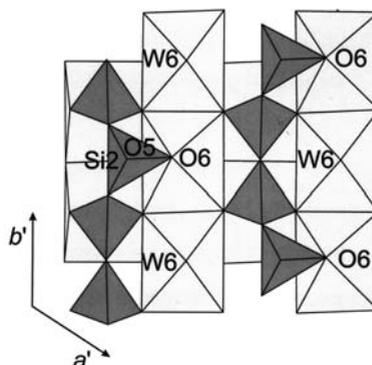
the calcium polyhedral layer and the tetrahedral module. Successive tetrahedral chains on one side of the layer are shifted by **b**/2; the tetrahedral chains on the hidden side are similarly connected to the layer, with paired tetrahedra grasped to the alternate columns and shifted by ±**b**/4 relatively to those on the visible side.

As in clinotobermorite, 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 **c**, thus building double chains with symmetry [2*mm*], to compare with the [- 2/*m* -] symmetry of the corresponding double chains in clinotobermorite.

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 **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
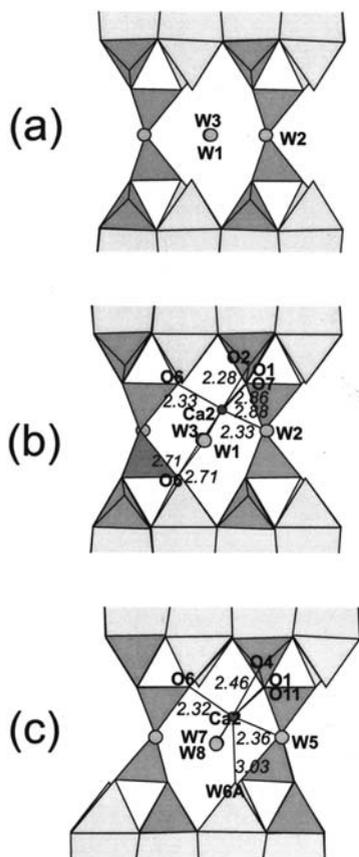
Fig. 9. Schematic drawing of the structural cavities, as seen along [010] in (a) anomalous tobermorite 11Å from Wessels mine; (b) normal tobermorite 11Å from Urals; (c) clinotobermorite from Wessels mine (Merlino *et al.*, 2000). In (b) one of the two possible ordered arrangements of Ca2, W1, and W3 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 O^{2-} 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 $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$.

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 'zeolit-

ic' 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 ($\approx$ 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 O^{2-} 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-
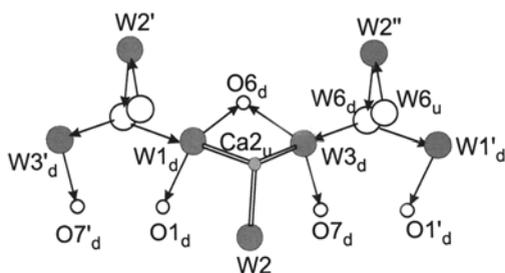
Fig. 10. Hydrogen bond system in normal tobermorite from Urals, whenever Ca2 is present. The atoms are seen approximately along [001]; the letters 'u' and 'd' mean 'up' and 'down' with respect to the plane at $z = ½$. Large empty circles represent H_2O molecules belonging to the scaffolding (W6), whereas large grey circles represent 'zeolitic' H_2O molecules (W1, W2, W3). Small empty circles indicate oxygen atoms. The Ca2 cation is indicated with a small grey circle.

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) $Ca^{2+} + 2 O^{2-}$, exactly as in the case of clinotobermorite (Merlino *et al*., 2000);

2) $\square + 2 OH^-$, 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: $0.5\ Ca^{2+} + 1\ O^{2-} + 1\ OH^-$. Therefore the structural results point to the crystal chemical formula $Ca_{4.5}Si_6O_{16}(OH) \cdot 5H_2O$ 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 O^{2-} 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

H_2O molecules p.f.u.) point to the crystal chemical formula $Ca_{4.42}K_{0.04}Si_{5.68}Al_{0.32}O_{15.56}(OH)_{1.44} \cdot 5H_2O$.

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 Bašcenov, 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, $Ca_5Si_6O_{17} \cdot 5H_2O$, '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 clinotobermorite. 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, $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$; 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 $Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O$. 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 ^{29}Si 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.

References

Brese, N.E. & O'Keefe, M. (1991): Bond-valence parameters for solids. *Acta Cryst.*, **B47,** 192-197.

Cong, X. & Kirkpatrick, R.J. (1996): ^{29}Si and ^{17}O NMR investigations of the structure of some crystalline calcium silicate hydrates. *Advn. Cem. Bas. Mater.*, **3**, 133-143.

Dornberger-Schiff, K. (1956): On the order-disorder (OD-) structures). *Acta Cryst.*, **9**, 593.

– (1964): Grundzüge einer Theorie von OD-Strukturen aus Schichten. *Abhandl. d. Deutsch. Akad. d. Wiss. zu Berlin. Klasse f. Chemie, Geol. u. Biol.*, **3**, 1-107.

– (1966): Lehrgang über OD-Strukturen, Akademie-Verlag, Berlin, 135 p.

Dornberger-Schiff, K. & Fichtner, K. (1972): On the symmetry of OD-structures consisting of equivalent layers. *Kristall und Technik*, **7,** 1035-1056.

Ferraris, G. & Ivaldi, G. (1988): Bond valence *vs.* bond length in O...O hydrogen bonds. *Acta Cryst.*, **B44**, 341-344.

Hamid, S.A. (1981): The crystal structure of the 11Å natural tobermorite $Ca_{2.25}[Si_3O_{7.5}(OH)_{1.5}]\cdot1H_2O$. *Z. Kristallogr.*, **154**, 189-198.

Heddle, M.F. (1880): Preliminary notice of substances which may prove to be new minerals. *Mineral. Mag.*, **4**, 119-123.

Henmi, C. & Kusachi, I. (1989): Monoclinic tobermorite from Fuka, Bitchu-cho, Okayama Prefecture, Japan. *J. Min. Petr. Econ. Geol.*, **84**, 374-379 (in Japanese).

–,– (1992): Clinotobermorite, $Ca_5Si_6(O,OH)_{18}\cdot5H_2O$, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineral. Mag.*, **56**, 353-358.

Hoffmann, C. & Armbruster, T. (1997): Clinotobermorite, $Ca_5[Si_3O_8(OH)]_2\cdot4H_2O - Ca_5[Si_6O_{17}].5H_2O$, a natural C-S-H(I) type cement mineral: determination of the substructure. *Z. Kristallogr.*, **212**, 864-873.

Komarneni, S., Roy, R., Roy, D.M., Fyfe, C.A., Kennedy, G.J., Bothner-By, A.A., Dadok, J., Chesnick, A.S. (1985): ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy of Al-substituted tobermorites. *J. Mater. Sci.*, **20**, 4209-4214.

Liebau, F. (1956): Bemerkungen zur Systematik der Kristallstrukturen von Silikaten mit hochkondensierten Anionen. *Physikal. Chem.,* **206**, 73-92.

McConnell, J.D.C. (1954): The hydrated calcium silicates riversideite, tobermorite, and plombierite. *Mineral. Mag.*, **30,** 293-305.

Megaw, H.D. & Kelsey, C.H. (1956): Crystal structure of tobermorite. *Nature*, **177**, 390-391.

Merlino, S. (1997): OD approach in minerals: examples and applications. *in* 'Modular aspects of minerals - EMU Notes in Mineralogy, Vol. **1'**, S. Merlino, Ed., Eötvös University Press, Budapest, 29-54.

Merlino, S., Bonaccorsi, E., Armbruster, T. (1999): Tobermorites: their real structure and OD character. *Amer. Mineral.*, **84**, 1613-1621.

–,–,– (2000): The real structures of clinotobermorites and tobermorite 9Å: OD character, polytypes, and structural relationships. *Eur. J. Mineral.,* **12**, 411-429.

Mitsuda, T. & Taylor, H.F.W. (1978): Normal and anomalous tobermorites. *Mineral. Mag.*, **42,** 229-235.

Sheldrick, G.M. (1997): SHELX-97. Programs for crystal structure determination and refinement. Institut für Anorg. Chemie, Univ. of Göttingen, Germany.

Taylor, H.F.W. (1964): The calcium silicate hydrates. *in* 'The Chemistry of Cements' H.F.W. Taylor, Ed., Academic Press, London, 167-232.

– (1992): Tobermorite, jennite, and cement gel. *Z. Kristallogr.*, **202**, 41-50.

– (1997): Cement Chemistry, 2nd edition. Thomas Telford Publishing, London.

Wieker W. (1968): Silikatanionenstruktur des 14Å Tobermorits von Crestmore und seiner Entwässerungsprodukte. *Zeit. Anorg. Allg. Chemie*, **360**, 307-316.

Wieker, W., Grimmer, A.-R., Winkler, A., Mägi, M., Tarmak, M., Lippmaa, E. (1982): Solid state high-resolution ^{29}Si NMR spectroscopy of synthetic 14Å, 11Å and 9Å tobermorites. *Cem. Concr. Res.*, **12**, 333-339.