

The real structures of clinotobermorite and tobermorite 9 Å: OD character, polytypes, and structural relationships

STEFANO MERLINO^(1,*), ELENA BONACCORSI⁽¹⁾ and THOMAS ARMBRUSTER⁽²⁾

⁽¹⁾ Università di Pisa, Dipartimento di Scienze della Terra,
Via S. Maria 53, I-56126 Pisa, Italy

⁽²⁾ Universität Bern, Laboratorium für chemische und mineralogische Kristallographie,
Freiestrasse 3, CH-3012 Bern, Switzerland

Abstract: Clinotobermorite, $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5\text{H}_2\text{O}$, is a rare mineral, structurally related to tobermorite 11 Å. It is characterized by the presence of structural disorder (evidenced by the diffuseness of the reflections with k odd) which, until now, prevented the determination of its real structure. In this paper, a model for the real structure of clinotobermorite is proposed on the basis of OD theory, through examination of the X-ray diffraction pattern of a sample coming from the Wessels mine (South Africa). The proposed model, which assumes the presence of silicate double chains of wollastonite-type, is confirmed by structural refinements carried out for the two polytypes with maximum degree of order (MDO). The MDO_1 polytype of clinotobermorite (monoclinic, space group Cc , $a = 11.276(2)$, $b = 7.3427(8)$, $c = 22.642(4)$ Å, $\beta = 97.28(1)^\circ$) was refined up to $R = 0.15$, whereas the two refinements performed on the MDO_2 polytype (triclinic, space group $C1$, $a = 11.274(2)$, $b = 7.3439(7)$, $c = 11.468(2)$ Å, $\alpha = 99.18(1)$, $\beta = 97.19(1)$, $\gamma = 90.09(1)^\circ$) converged to $R = 0.12$ and $R = 0.10$, respectively. In clinotobermorite infinite calcium polyhedral layers parallel to (001) are connected through double silicate chains $[\text{Si}_6\text{O}_{17}]^{10-}$ running along b ; additional calcium cations and H_2O molecules are placed in the channels of the resulting framework.

By dehydration at 225°C, clinotobermorite transforms topotactically into a new phase, which also displays an OD character. The results of the structural refinement carried out for its triclinic MDO_2 polytype (space group $C1$, $a = 11.156(5)$, $b = 7.303(3)$, $c = 9.566(5)$ Å, $\alpha = 101.08(4)$, $\beta = 92.83(5)$, $\gamma = 89.98(4)^\circ$) indicate that this phase, with crystal chemical formula $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$, exhibits single chains of wollastonite-type, resulting from decondensation of the double chains.

On the basis of the new detailed structural information a possible explanation for the enigmatic thermal behaviour of tobermorite 11 Å has been proposed.

Key-words: clinotobermorite, crystal structure, OD theory, polytypism, tobermorite 11 Å, tobermorite 9 Å.

Introduction

Many of the structural features of the calcium silicate hydrates (one-dimensional disorder, polytypism, twinning) are dependent on their peculiar

crystal chemistry, in particular on the metrical relationships between the calcium polyhedral module, with the typical repeat of 3.65 Å, and the tetrahedral wollastonite-like chains with their typical repeat of 7.3 Å. These phases (foshagite,

*E-mail: merlino@dst.unipi.it

xonotlite, hillebrandite, tobermorite, clinotobermorite, ...), which occur in nature as alteration products of calcium carbonate rocks and as vesicle fillings in basaltic rocks, are also known to form when Portland cement reacts with water during the process of cement binding and are designated as C-S-H compounds in cement chemistry. All of them display some kind of structural disorder and for most of them the 'real' structural arrangements have not been fully recognised, although the 'average' structure is known.

Clinotobermorite was first found as a new natural phase at Fuka, Okayama Prefecture, Japan, by Henmi & Kusachi (1989) who studied its chemical and crystallographic properties and indicated the composition $\text{Ca}_5\text{Si}_6(\text{O}, \text{OH})_{18} \cdot 5\text{H}_2\text{O}$. The symmetry of the diffraction patterns and the systematic absences pointed to Cc or $C2/c$ as possible space groups; the unit cell parameters obtained by X-ray powder diffraction were $a = 11.331(9)$, $b = 7.353(7)$, $c = 22.67(2)$ Å, $\beta = 96.59(7)^\circ$, thus showing the 7.3 Å translation, which is typical of the wollastonite-like silicate chains displayed by several C-S-H minerals ['Dreierketten' according to the terminology of Liebau (1956)]. Although the reflections with $k = 2n$ were always sharp, continuous streaks parallel to c^* , or diffuse maxima on rows parallel to c^* , were found for $k = 2n + 1$ (Henmi & Kusachi, 1989, 1992). The relationship between the unit cells of clinotobermorite and tobermorite 11 Å (McConnell, 1954) suggested that their crystal structures are closely related, although their X-ray powder patterns are appreciably different from each other.

A second occurrence of clinotobermorite was recently described by Hoffmann & Armbruster (1997) from the Wessels mine, Kalahari manganese field, South Africa; the unit cell parameters¹, determined from single-crystal X-ray data, were the following: $a = 11.276(4)$, $b = 7.343(1)$, $c = 22.629(4)$ Å, $\beta = 97.03(1)^\circ$. The authors observed diffuse and weak reflections of the type hkl with $h, k = 2n + 1$. Neglecting these reflections, they determined the family structure of clinotobermorite in the space group $I2/m$, with $A_s = a/2 = 5.638$, $B_s = b/2 = 3.672$, $C_s = c = 22.629$ Å, $\beta_s = 97.03^\circ$. The structure is composed of layers, parallel to (001), formed by seven-fold coordinated calcium polyhedra. 'Dreierketten' with periodicity 7.3 Å are attached to both sides of the Ca polyhe-

dra layers. These sandwich-like layers are stacked along c ; the cavities of the resulting structure are occupied by H_2O molecules and additional calcium cations. The refinement of the family structure corresponding to halved a and b parameters (Hoffmann & Armbruster, 1997) did not allow to determine definitely whether single or double chains of silicate tetrahedra actually occur in clinotobermorite. In fact, the observed maxima of electron density corresponding to half-occupied $[\text{Si}_3\text{O}_9]$ chains may result from the stacking along c of two single chains shifted by $b/2$, as well as from the stacking of a double chain. Moreover, knowledge of the family structure did not permit a precise positioning of the additional calcium cations and H_2O molecules in the cavities of the structure.

Some features of the diffraction patterns of clinotobermorite (presence of sharp spots and diffuse streaks; non-space-group absences, evidences for twinning...) suggest that this mineral displays OD character [Dornberger-Schiff, 1956, 1964, 1966; an introduction to the OD theory and to its mineralogical applications may be found in Āurovič (1997) and Merlino (1997), respectively].

These features are displayed also by the other members of the tobermorite group. Just on the basis of an OD approach we were able to determine their real structures, which have been presented in a comprehensive paper (Merlino *et al.*, 1999) dealing with the main structural aspects of various members of this family.

The aim of the present paper is to give, together with a short description of the OD character and polytypic modifications in clinotobermorite and its dehydration product tobermorite 9 Å, a detailed description and discussion of their structural arrangements. The same aspects in tobermorite 11 Å will be presented in a successive paper.

OD character of the structural family of clinotobermorite

A family of OD structures is defined as the set of structures consisting of the same kinds (one or more) of layers and the same kinds of layer pairs. A full appreciation of the symmetry properties of the whole OD family of possible structures

¹ These parameters, as well as those of the family cell, are slightly different from those published by Hoffmann & Armbruster (1997), and quoted in Merlino (1997), that appear to be suffering from some systematic error.

requires the knowledge of the symmetry of the building structural layers, λ partial operators, as well as the symmetry operations of the layer pairs, σ partial operators. In the particular case of clinotobermorite, and also in the case of the other phases in the tobermorite group, only one kind of layer and one kind of layer pair occur. These symmetries, which are described by the so called OD groupoid family, can be derived, in favourable cases, through a careful examination of the diffraction patterns with attention to the systematic absences in the substructure reflections ('family reflections' in OD theory) and in the whole diffraction pattern. In the present case it was observed:

- a) the C centring condition, valid for all the reflections, namely $h + k = 2n$ (Henmi & Kusachi, 1992; Hoffmann & Armbruster, 1997);
- b) a condition valid for reflections with even k value (and therefore even h value), which are present only for $h + k + 2l = 4n$ (Hoffmann & Armbruster, 1997).

Rule b) becomes an ordinary rule for reflections with $k = 2K$ (and thus $h = 2H$). These reflections correspond to a reciprocal lattice with vectors $A^* B^* C^*$ related to the vectors $a^* b^* c^*$ in the way $A^* = 2a^*, B^* = 2b^*, C^* = c^*$. For these reflections (which are the family reflections) the rule b) becomes: reflections HKL are present for $H + K + L = 2n$, which corresponds to the I centring of the lattice of the 'family' structure (Hoffmann & Armbruster, 1997). In the following we shall refer to a different family cell, with $A = 5.638, B = 3.671, C = 22.642$ Å, $\beta = 97.28^\circ$, space group $A2/m$. Such a family cell, which is the more convenient for the OD approach, may be obtained from the family cell described by Hoffmann & Armbruster (1997) in the space group $I2/m$ by the transformation matrix $100 / 010 / 101$.

On the basis of the symmetry information and of the family structure refinement (Hoffmann & Armbruster, 1997), the structure of clinotobermorite may be described as an OD structure built from layers of one kind. Such layers have symmetry $C2/m$ [more precisely $C12/m(1)$], assuming axes oriented as in the family cell with space group $A2/m$. The layers have translation vectors a and b ($a = 11.276, b = 7.343$ Å) and a third basis vector c_0 (not a translation vector; width of the layer $c_0 \sin \beta = 11.230$ Å).

For layer symmetry $C12/m(1)$ there is only one OD groupoid family (Dornberger-Schiff & Fichtner, 1972)

$$\begin{array}{ccc} C1 & 2/m & (1) \\ \{1 & 2_{1/2}/c_2 & (1)\} \end{array} \quad (1)$$

which presents operators compatible with those of the space group of the family structure. The symbol in (1) represents the symmetry of the single layer (λ operations), in the first line, and, in the second line, the σ operations. The parentheses in the third position of each line indicate the direction of missing (or variable) periodicity. According to (1), layers with $C2/m$ symmetry may follow each other in the c direction, related by the operator $2_{1/2}$ (twofold screw axis with translational component $b/4$) or by the operator $2_{-1/2}$ (twofold screw axis with translational component $-b/4$). Pairs of layers related in one or in the other way are geometrically equivalent: infinite ordered or disordered sequences of layers may occur, corresponding to the infinite possible sequences of the operators $2_{1/2}$ and $2_{-1/2}$. For all the possible sequences it may be shown that, as usual in OD structures, the family reflections, namely those with $h, k = 2n$, are sharp and have the same intensities. The reflections with $h, k = 2n + 1$ vary (in position, shape and intensity) depending on the sequence, giving rise to continuous streaks along c^* for fully disordered sequences. Among the infinite possible ordered sequences (polytypes), OD approach singles out those in which not only pairs, but also triples, quadruples, ..., n -tuples of adjacent layers are geometrically equivalent. They are called MDO polytypes (sequences of maximum degree of order). Two MDO polytypes are possible in this family:

(1) MDO₁ corresponds to the sequence in which the operators regularly alternate: $2_{-1/2} / 2_{1/2} / 2_{-1/2} / 2_{1/2} / \dots$. It has symmetry $C2/c$, with cell parameters: $a = 11.276, b = 7.343, c = 22.642$ Å, $\beta = 97.28^\circ$ (Merlino *et al.*, 1999);

(2) MDO₂ corresponds to the sequence in which only one operator is constantly active: $2_{-1/2} / 2_{-1/2} / 2_{-1/2} / 2_{-1/2} / \dots$ (the sequence $2_{1/2} / 2_{1/2} / 2_{1/2} / 2_{1/2} / \dots$ corresponds to the twin structure). It has $C1$ symmetry, with cell parameters: $a = 11.276, b = 7.343, c = 11.469$ Å, $\alpha = 99.21, \beta = 97.19, \gamma = 90.0^\circ$.

The relation between the two MDO structures, and more generally, among the various polytypes in the family, may be easily estimated by observing that layers related by the operators $2_{-1/2}$ and $2_{1/2}$ are translationally equivalent and stacked according to the vectors:

$$\begin{aligned} t_1 &= c/2 - b/4 \\ t_2 &= c/2 + b/4 \end{aligned}$$

respectively. In the monoclinic polytype the two stacking vectors regularly alternate, whereas in the triclinic polytype the vector t_1 is constantly applied (the constant application of vector t_2 gives

rise to the twin structure). A partial drawing of the reciprocal lattice of clinotobermorite, with the positions of the family reflections and of the reflections corresponding to the MDO polytypes, is illustrated in Fig. 1.

Experimental

The intensity data collections were performed with the same single crystal used by Hoffmann & Armbruster (1997) for determining and refining the family structure of clinotobermorite. We compared their precession and Weissenberg photographs with the model of reciprocal lattice sketched in Fig. 1 and deduced that both MDO polytypes of clinotobermorite were present within the examined crystal; moreover, both the twin-related orientations of the triclinic polytype MDO₂ were found. The reflections with odd h and k were very diffuse, giving rise to almost continue streaks along c^* , and indicating a high degree of structural disorder within the crystal. Nevertheless, the individual Bragg reflections corresponding to the different polytypes could be detected over the diffuse background. X-ray data collections were initially performed with a CCD Imaging Plate system at the University of Bern, as regards the twinned triclinic polytypes. Subsequently, new intensity data collections, respectively for the monoclinic MDO₁ and the triclinic MDO₂ polytypes, were obtained at the University of Pisa with a SIEMENS P4 single-crystal automatic diffractometer using graphite monochromatized MoK α radiation. Miscellaneous data concerning the intensity collections and the structure refinements are reported in Table 1.

In each collection, we measured both the family reflections, common to all the polytypes, and the reflections representative of a given polytype (hereafter called 'characteristic reflections'); the intensity of the family reflections was subsequently divided by the appropriate scale factor (corresponding to the minimum value of the reliability index), to refer the data to the same crystal volume. Whenever it is possible, the same atomic labels used in the refinement of the clinotobermorite family structure (Hoffmann & Armbruster, 1997) will be used here.

Triclinic polytype MDO₂

Firstly we shall describe the structure determination and refinement of the triclinic polytype performed by using the data collected at Pisa. The

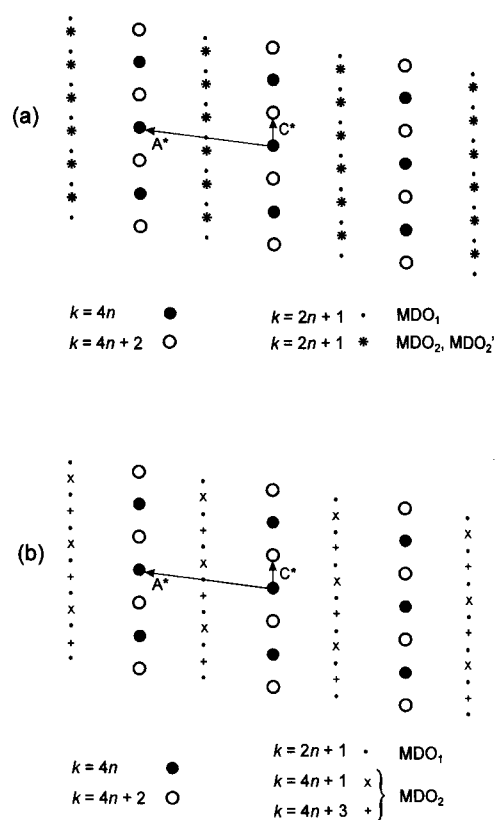


Fig. 1. Drawing of the diffraction patterns of clinotobermorite, as seen along the **B** axis of the family cell. The reciprocal vectors A^* and C^* corresponding to the family cell are indicated. In (a) the observed diffraction pattern is reported, with the dots indicating characteristic reflections of the monoclinic MDO₁ polytype, whereas the stars indicate superimposed characteristic reflections of both the twinned polytypes MDO₂ and MDO₂'. For sake of clarity, in (b) only the MDO₁ and MDO₂ polytype reflections are reported.

cell parameters $a = 11.274(2)$, $b = 7.3439(7)$, $c = 11.468(2)$ Å, $\alpha = 99.18(1)$, $\beta = 97.19(1)$, $\gamma = 90.09(1)^\circ$ were obtained from least-square refinement using 20 reflections with $22^\circ < 2\theta < 36^\circ$. The structure determination was carried out by means of the direct methods (SHELXS-97 program; Sheldrick, 1997) in space group $C1$, in accordance with the symmetry of the model provided by OD theory. The positions of Ca1 and Ca3 (calcium cations building up the characteristic layers of seven-fold coordinated calcium polyhedra), and Si1, Si2, and Si3 were found, together with the coordinates of several oxygen atoms. The remain-

Table 1. Cell parameters, data collection and refinement parameters for the clinotobermorite polytypes.

	MDO ₁ (data collected at Pisa)	MDO ₂ (data collected at Bern; refinements performed at Pisa)	MDO ₂ (data collected at Bern; refinements performed at Pisa)	MDO ₂ ' (data collected at Bern; refinements performed at Pisa)
crystal dimensions (mm)	0.17 x 0.1 x 0.04			
<i>a</i> (Å)	11.276(2)	11.274(2)	11.273(1)	11.273(2)
<i>b</i> (Å)	7.343(1)	7.344(1)	7.350(2)	7.350(1)
<i>c</i> (Å)	22.642(4)	11.468(2)	11.498(2)	11.498(2)
α (°)		99.18(1)	99.17(1)	99.17(3)
β (°)	97.28(3)	97.19(1)	97.19(1)	97.19(3)
γ (°)		90.02(1)	89.97(2)	89.97(3)
space group	<i>Cc</i>	<i>C1</i>	<i>C1</i>	<i>C1</i>
unique reflections	2776	3085	1585	1584
refl. obs. [F ₀ >4σ(F ₀)]	1930	2673	1542	1538
absorption correction	psi-scan	--		
<i>R</i> (obs.)	0.150	0.120	0.099	0.115
diffractometer	P4 Siemens		Siemens SMART 3-circle CCD system*	
radiation	graphite monochromatized MoKα			
scan mode	ω-2θ		ω	
scan width	1° in ω			
scan speed	3°/min	4°/min		
refinement	Full-matrix least squares against F ² with SHELXL-97			
Chemical formula (<i>Z</i> = 2)	Ca ₅ Si ₆ O ₁₇ ·5H ₂ O			

* 2047 frames of 512x512 pixels were collected, each after 0.3° of rotation in ω. Exposure time was 10 s.

* 2047 frames of 512x512 pixels were collected, each after 0.3° of rotation in ω . Exposure time was 10 s.

ing oxygen atoms, as well as the half-occupied Ca2 in the cavities of the structure, were localized through difference-Fourier maps. In the cavities we found two additional electron density peaks corresponding to two H₂O molecules, W7 and W8, with half occupancy. Another H₂O molecule W5 was placed on the inversion centre at 0, 1/2, 0, so that along [010], H₂O molecules W5 alternate with the oxygen atoms O5 which connect two tetrahedral chains.

The half occupancies and the unreliably short cation- H₂O and H₂O - H₂O distances involving the calcium cation Ca2 and the H₂O molecules W5, W7 and W8 placed in the cavities, strongly pointed to a symmetry reduction and to an actual ordered distribution, obtained by releasing the inversion centre with decrease of the space group symmetry to *C1*. A reliable ordered distribution, with full occupancies of the sites, was quickly refined: reasonable H₂O - H₂O distances and Ca2-H₂O distances not shorter than 2.3 Å were obtained; moreover, the release of the inversion centre allowed displacements of O5 and W5 from their fixed positions, giving rise to more reliable Ca-W5 distances and a more favourable T-O-T angle. Without any refinement and only by ordering Ca2, W7 and W8 in the acentric space group, the *R* value dropped significantly. Finally, several cycles of least-squares refinement were performed

in the space group *C1*; to avoid correlations among parameters, the isotropic displacement parameters for the atoms related by the pseudo-symmetry centre were constrained to be equal. The final *R* index was 0.12 for 2673 reflections with $F_o > 4\sigma(F_o)$. The same structural model gave a reliability index of 0.09 for 1368 family reflections with $F_o > 4\sigma(F_o)$.

We then carried out a parallel structure refinement with the data collected at Bern (CCD Imaging Plate system), following the same steps just described. The final *R* value was 0.10 for 1542 reflections with $F_o > 4\sigma(F_o)$ (a slightly higher *R* value has been obtained in the refinement of the twin counterpart, in accordance with its smaller volume). The *R* value for the 782 family reflections with $F_o > 4\sigma(F_o)$ was 0.07.

It is proper to stress that the final *R* values obtained with the data collected at Pisa and with those collected at Bern are highly satisfactory, considering the quality of the crystal, characterized by disorder, simultaneous presence of polytypes and twinning.

The refined atomic positions and isotropic displacement parameters, obtained with both sets of data, are reported in Table 2, whereas selected bond distances are listed in Table 3. Two projections of the crystal structure of the triclinic polytype are plotted in Fig. 2.

Table 2. Clinotobermorite, triclinic polytype MDO₂, space group C1: atomic coordinates and isotropic displacement parameters.

Atom	x		y		z		<i>U</i> _{iso}	
Si1	0.8931(5)	0.8933(5)	0.2046(7)	0.2067(9)	0.1839(4)	0.1829(5)	0.0014(5)	0.0016(8)
Si1A	-0.8941(5)	-0.8926(6)	-0.2096(7)	-0.2073(9)	-0.1841(4)	-0.1841(5)	0.0014(5)	0.0016(8)
Si2	0.9963(6)	0.9969(6)	-0.0362(8)	-0.0381(9)	0.3553(5)	0.3577(6)	0.0056(5)	0.0066(9)
Si2A	-0.9950(6)	-0.9938(6)	0.0383(8)	0.0376(9)	-0.3608(5)	-0.3586(6)	0.0056(5)	0.0066(9)
Si3	0.8949(5)	0.8949(6)	-0.3726(7)	-0.3723(9)	0.1869(4)	0.1877(6)	0.0018(5)	0.0051(9)
Si3A	-0.8946(5)	-0.8962(6)	0.3688(7)	0.3702(9)	-0.1859(4)	-0.1872(5)	0.0018(5)	0.0051(9)
O1	0.913(2)	0.913(2)	0.124(2)	0.125(3)	0.310(1)	0.311(2)	0.013(1)	0.009(2)
O1A	-0.916(2)	-0.914(2)	-0.128(2)	-0.122(3)	-0.309(1)	-0.306(2)	0.013(1)	0.009(2)
O11	0.919(1)	0.914(2)	-0.229(2)	-0.221(3)	0.316(1)	0.314(2)	0.010(1)	0.012(2)
O11A	-0.912(1)	-0.916(2)	0.227(2)	0.230(3)	-0.309(1)	-0.312(2)	0.010(1)	0.012(2)
O2	0.771(1)	0.770(1)	-0.343(2)	-0.349(2)	0.115(1)	0.110(1)	0.004(1)	0.004(2)
O2A	-0.767(1)	-0.769(1)	0.349(2)	0.346(2)	-0.108(1)	-0.114(1)	0.004(1)	0.004(2)
O21	0.765(2)	0.764(1)	0.149(2)	0.153(2)	0.106(1)	0.110(1)	0.008(1)	0.007(2)
O21A	-0.767(2)	-0.769(1)	-0.151(2)	-0.148(2)	-0.111(1)	-0.105(1)	0.008(1)	0.007(2)
O3	0.005(1)	0.003(1)	-0.355(2)	-0.351(2)	0.111(1)	0.113(1)	0.005(1)	0.005(2)
O3A	0.003(1)	0.001(1)	0.357(2)	0.358(2)	-0.106(1)	-0.106(1)	0.005(1)	0.005(2)
O31	0.002(1)	0.002(1)	0.155(2)	0.154(2)	0.099(1)	0.099(1)	0.004(1)	0.005(2)
O31A	0.005(1)	0.004(1)	-0.161(2)	-0.161(2)	-0.105(1)	-0.104(1)	0.004(1)	0.005(2)
O4	0.891(1)	0.891(2)	0.431(2)	0.429(2)	0.237(1)	0.236(1)	0.009(1)	0.008(2)
O4A	-0.895(1)	-0.895(2)	-0.432(2)	-0.432(2)	-0.238(1)	-0.237(1)	0.009(1)	0.008(2)
O5	0.009(2)	0.009(2)	-0.002(3)	-0.005(3)	0.497(2)	0.498(2)	0.014(2)	0.017(3)
W5	0.514(2)	0.508(2)	0.009(3)	0.009(3)	0.511(2)	0.508(2)	0.023(3)	0.026(4)
O6	0.127(1)	0.122(2)	-0.041(2)	-0.041(2)	0.311(1)	0.310(2)	0.014(2)	0.010(2)
O6A	-0.124(1)	-0.128(2)	0.053(2)	0.046(2)	-0.319(1)	-0.320(2)	0.014(2)	0.010(2)
W6	-0.335(4)	-0.335(3)	-0.051(5)	-0.063(5)	-0.683(4)	-0.691(3)	0.092(7)	0.072(5)
W6A	0.342(4)	0.335(3)	0.043(5)	0.041(5)	0.699(4)	0.695(3)	0.092(7)	0.072(5)
Ca1	0.3640(3)	0.3617(4)	0.1072(4)	0.1076(6)	0.9228(3)	0.9233(4)	0.0023(4)	0.0029(7)
Ca1A	-0.3634(3)	-0.3643(4)	-0.1042(4)	-0.1044(6)	-0.9134(3)	-0.9149(4)	0.0023(4)	0.0029(7)
Ca3	0.8679(3)	0.8709(4)	0.0998(4)	0.0988(6)	0.8981(3)	0.8976(4)	0.0024(4)	0.0025(7)
Ca3A	-0.8711(3)	-0.8694(4)	-0.1001(4)	-0.1010(6)	-0.9069(3)	-0.9056(4)	0.0024(4)	0.0025(7)
Ca2	0.3113(5)	0.3118(5)	-0.0177(7)	-0.0190(8)	0.4289(5)	0.4273(6)	0.025(1)	0.026(1)
W7	0.260(3)	0.258(2)	-0.238(4)	-0.231(3)	0.537(2)	0.542(2)	0.054(6)	0.045(6)
W8	0.260(2)	0.262(2)	0.257(4)	0.250(4)	0.535(2)	0.532(2)	0.057(7)	0.057(7)

The former values refer to the data collected at Pisa, whereas the latter refer to the data collected at Bern. The atoms related by the pseudo-centre of inversion are differentiated by the letter A (for example, Si1 and Si1A).

Monoclinic polytype MDO₁

The model derived through OD theory pointed to *C2/c* symmetry for the MDO₁ polytype. A first problem, in the structural study of the MDO₁ polytype, was the presence of several reflections *h0l* with $l = 2n + 1$, which violate the *c* glide symmetry, as well as the presence of reflections *hkl*, with $h, k = 2n$ (family reflections) and with $l = 2n + 1$, which are in contrast to the *A*-centring condition for the family cell. These reflections, which were

observed also by Hoffmann & Armbruster (1997) on precession photographs, are easily explained by assuming that the crystal is affected by (001) twinning, as will be discussed in another paragraph.

Therefore, the extra reflections which violate the extinction rules were preliminarily neglected, and the refinement started in space group *C2/c*, by using the atomic coordinates calculated on the basis of the structural model. The characteristic reflections of this polytype are, on average, weaker and more diffuse than the characteristic reflec-

Table 3. Selected bond distances (in Å) in triclinic MDO₂ clinotobermorite, as obtained from data collected at Pisa (first columns) and Bern (second columns). e.s.d. are reported in parentheses.

Si1	O1	1.64(2)	1.67(2)	Si2	O1	1.61(2)	1.64(2)	Si3	O11	1.67(2)	1.67(2)
	O21	1.61(2)	1.60(2)		O11	1.63(2)	1.62(2)		O2	1.57(2)	1.60(2)
	O31 ^a	1.66(1)	1.66(2)		O5 ^a	1.59(2)	1.58(2)		O3 ^a	1.61(2)	1.60(2)
	O4	1.68(2)	1.65(2)		O6 ^a	1.62(2)	1.57(2)		O4 ^b	1.63(2)	1.65(2)
Si1A	O1A	1.63(2)	1.61(2)	Si2A	O1A	1.66(2)	1.63(2)	Si3A	O11A	1.61(2)	1.62(2)
	O21A	1.60(2)	1.59(2)		O11A	1.66(2)	1.64(2)		O2A	1.62(2)	1.60(2)
	O31A ^c	1.55(2)	1.58(2)		O5 ^d	1.62(2)	1.64(2)		O3A ^c	1.57(2)	1.59(2)
	O4A	1.65(2)	1.66(2)		O6A ^c	1.59(2)	1.63(2)		O4A ^c	1.67(2)	1.65(2)
Ca1	O2 ^f	2.53(1)	2.47(2)	Ca3	O2A ^j	2.38(1)	2.42(2)	Ca2	O4 ^m	2.46(2)	2.45(2)
	O2A ^g	2.35(1)	2.34(2)		O21 ^k	2.75(2)	2.82(2)		O6	2.32(2)	2.37(2)
	O21A ^g	2.35(2)	2.34(2)		O21A ^l	2.38(2)	2.44(2)		W5	2.36(2)	2.28(2)
	O3 ^h	2.49(1)	2.52(2)		O3A ^g	2.43(1)	2.41(2)		W7	2.31(3)	2.32(2)
	O3A ⁱ	2.42(1)	2.42(2)		O31 ^g	2.57(1)	2.56(2)		W8	2.30(2)	2.26(3)
	O31A ^h	2.41(1)	2.42(2)		O31A ^g	2.46(1)	2.43(2)				
	W6A	2.52(4)	2.57(4)		O6A ^g	2.47(2)	2.48(2)		O1 ^m	3.06(2)	3.03(2)
Ca1A	O2 ^d	2.35(1)	2.38(2)	Ca3A	O2 ^r	2.44(1)	2.40(2)		O11 ⁿ	2.98(2)	3.02(2)
	O2A ^o	2.57(1)	2.62(2)		O21 ^s	2.41(2)	2.37(2)		W6A	3.03(4)	3.02(4)
	O21 ^d	2.33(2)	2.35(2)		O21A ^t	2.72(2)	2.66(2)				
	O3 ^p	2.36(1)	2.39(2)		O3 ^d	2.39(1)	2.38(2)				
	O3A ^q	2.49(1)	2.48(2)		O31 ^d	2.35(1)	2.36(2)				
	O31 ^q	2.36(1)	2.37(2)		O31A ^d	2.49(1)	2.51(2)				
	W6	2.58(4)	2.52(4)		O6 ^d	2.46(2)	2.47(2)				
SYMMETRY CODES											
a) $x + 1, y, z$				h) $x + 1/2, y + 1/2, z + 1$				o) $x + 1/2, y - 1/2, z - 1$			
b) $x, y - 1, z$				i) $x + 1/2, y - 1/2, z + 1$				p) $x - 1/2, y + 1/2, z - 1$			
c) $x - 1, y, z$				j) $x + 3/2, y - 1/2, z + 1$				q) $x - 1/2, y - 1/2, z - 1$			
d) $x - 1, y, z - 1$				k) $x, y, z + 1$				r) $x - 3/2, y + 1/2, z - 1$			
e) $x, y + 1, z$				l) $x + 3/2, y + 1/2, z + 1$				s) $x - 3/2, y - 1/2, z - 1$			
f) $x - 1/2, y + 1/2, z + 1$				m) $x - 1/2, y - 1/2, z$				t) $x, y, z - 1$			
g) $x + 1, y, z + 1$				n) $x - 1/2, y + 1/2, z$							

tions of the triclinic polytypes MDO₂ and MDO₂'. In spite of that and of the (001) twinning which affects some classes of reflections, the centrosymmetrical model was refined to $R = 0.167$, with relatively good T-O distances and reasonable displacement parameters. Even in this case, some short Ca-O distances occur between the calcium cations in the half-occupied site Ca2 and the H₂O molecules located in the interlayer space. An ordered model of these atoms is possible in space group Cc , assuming that the calcium cations Ca2, as well as the W7 and W8 H₂O molecules, occupy only one of the two positions related by the inversion centre. The R index dropped to 0.156 only by ordering Ca2, W7 and W8 and keeping all the atomic coordinates fixed; after several cycles of

least-square refinement of positional and displacement parameters the R index became 0.150, which is satisfactory, taking into account the quality of the crystal.

The structure of the monoclinic polytype MDO₁ is drawn in Fig. 3. The refined cell parameters, as well as the refinement data, are reported in Table 1; the atomic coordinates and isotropic displacement parameters are listed in Table 4. The bond distances will not be reported, as they merely confirm, though with minor precision, the structural features obtained by the refinements of the triclinic polytype.

The list of the F_o/F_c data is available from the authors upon request (or through the E.J.M. Editorial Office-Paris).

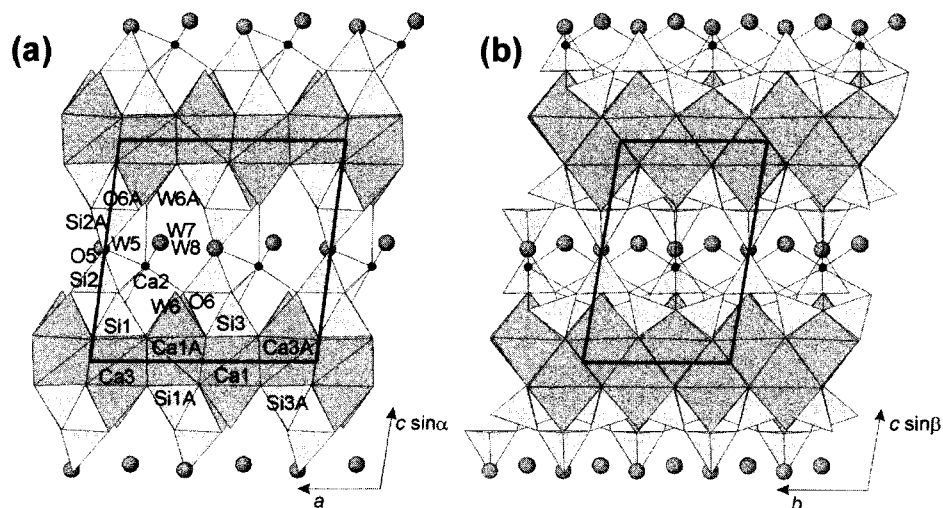


Fig. 2. Schematic drawing of the crystal structure of the triclinic polytype MDO_2 of clinotobermorite, as seen along the b axis (a) and down the a axis (b). Double chains of silicon tetrahedra (light grey) are attached to layers of sevenfold coordinated calcium polyhedra (dark grey).

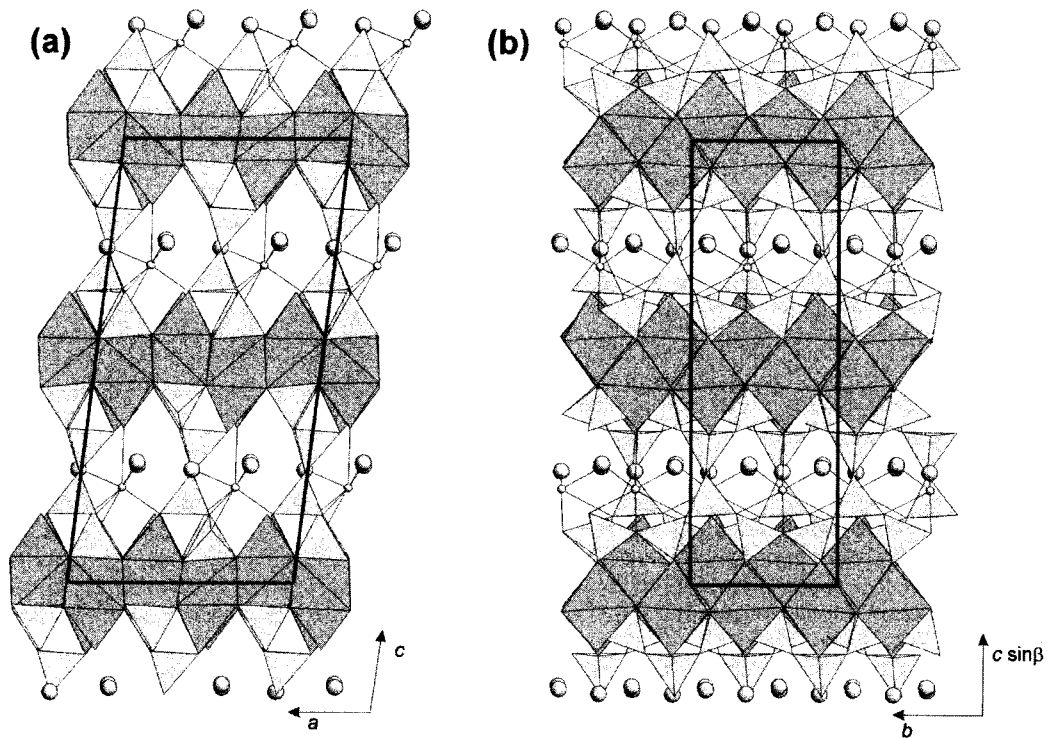


Fig. 3. Schematic drawing of the crystal structure of the monoclinic polytype MDO_1 of clinotobermorite, as seen along the b axis (a) and down the a axis (b).

Table 4. Clinotobermorite, monoclinic polytype MDO₁, space group *Cc*: atomic coordinates and isotropic displacement parameters.

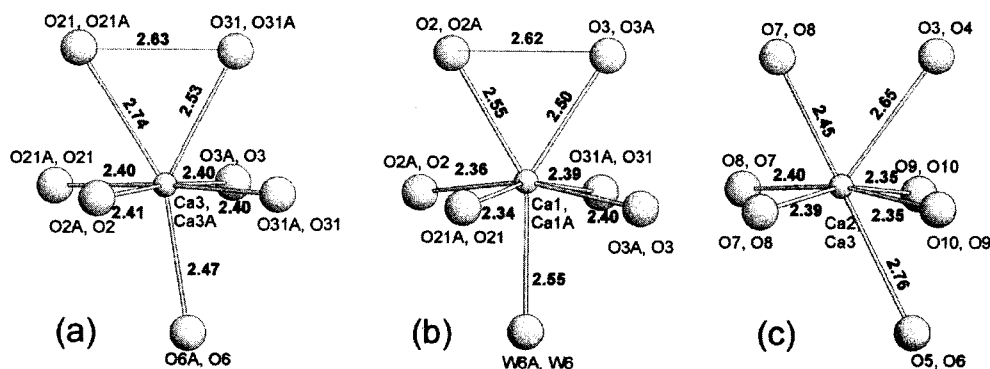
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
Si1	0.8908(8)	0.841(1)	0.5914(4)	0.001(1)
Si1A	0.1048(8)	0.833(1)	0.9105(4)	0.001(1)
Si2	0.9982(9)	0.123(2)	0.6779(4)	0.010(1)
Si2A	0.0067(9)	0.129(1)	0.8199(5)	0.010(1)
Si3	0.8972(8)	0.421(1)	0.5955(4)	0.003(1)
Si3A	0.1057(8)	0.410(1)	0.9055(4)	0.003(1)
O1	0.909(2)	0.970(3)	0.653(1)	0.004(3)
O1A	0.081(2)	0.935(3)	0.846(1)	0.004(3)
O11	0.925(2)	0.311(3)	0.661(1)	0.010(3)
O11A	0.091(2)	0.302(4)	0.845(1)	0.010(3)
O2	0.769(2)	0.371(4)	0.551(1)	0.005(2)
O2A	0.230(2)	0.376(4)	0.938(1)	0.005(2)
O21	0.766(2)	0.889(3)	0.557(1)	0.004(2)
O21A	0.234(2)	0.864(4)	0.951(1)	0.004(2)
O3	0.006(2)	0.382(4)	0.558(1)	0.009(2)
O3A	0.004(2)	0.370(4)	0.950(1)	0.009(2)
O31	-0.001(2)	0.866(3)	0.548(1)	0.001(2)
O31A	-0.002(2)	0.854(3)	0.943(1)	0.001(2)
O4	0.893(2)	0.631(4)	0.618(1)	0.013(2)
O4A	0.108(2)	0.626(4)	0.882(1)	0.013(2)
O5	0.009(2)	0.102(3)	0.749(1)	0.010(4)
W5	0.015(3)	0.380(5)	0.255(2)	0.027(6)
O6	0.130(2)	0.143(4)	0.655(1)	0.015(3)
O6A	0.878(2)	0.124(4)	0.839(1)	0.015(3)
W6	0.155(5)	0.682(7)	0.655(2)	0.062(8)
W6A	0.838(5)	0.634(7)	0.849(2)	0.062(8)
Ca1	0.8651(5)	0.380(1)	0.4620(3)	0.0061(7)
Ca1A	0.1370(5)	0.368(1)	0.0427(3)	0.0061(7)
Ca3	0.8671(5)	0.881(1)	0.4482(3)	0.0054(7)
Ca3A	0.1288(5)	0.870(1)	0.0469(3)	0.0054(7)
Ca2	0.8120(8)	0.377(1)	0.2147(4)	0.028(2)
W7	0.756(4)	0.108(6)	0.265(2)	0.04(1)
W8	0.760(4)	0.604(7)	0.272(2)	0.06(1)

Structure description and discussion

Calcium polyhedral layer

A characteristic feature of the structural arrangement of clinotobermorite is the layer built up by sevenfold coordinated calcium cations. The coordination of calcium in these layers has been described by Hoffmann & Armbruster (1997) in their paper on the family structure, as consisting of 'a pyramidal part on one side and a dome part on the other side joining the equatorial oxygen atoms'. Actually in the real structure there are four crystallographically independent polyhedra, centred by Ca1, Ca3, Ca1A and Ca3A. Two of them, *i.e.* those centred by Ca3 and Ca3A, closely conform to the description of Hoffmann & Armbruster (1997): the calcium cations lie in the centre of the basal plane of the pyramid; the pyramidal apical site is occupied by an oxygen atom (O6 and O6A) and the corresponding Ca-O bond is significantly displaced from the normal position (Fig. 4a), a displacement which will be soon explained, when we shall discuss the connection between calcium layer and tetrahedral chains. Average values of Ca-O distances for the equatorial oxygen atoms, for the oxygen atoms at dome apices and for that

Fig. 4. Coordination of Ca in the polyhedral layers of clinotobermorite, projected approximately along **b**. (a) The coordination of Ca3 and Ca3A consists of a distorted pyramidal part on one side and a dome part on the other side, whereas (b) the coordination of Ca1 and Ca1A may be better described as a monocapped trigonal prism, with a H₂O molecule as 'capping' ligand. For comparison, the coordination of Ca in xonotlite is shown in (c). The average Ca-O distances (in Å), as well as the short O-O distance of the dome edge, are indicated in bold letters.



placed at the opposite pyramidal apex are given in Fig. 4a, the averages being calculated over the two different Ca3 and Ca3A polyhedra and over the two sets of structural results listed in Table 3.

In contrast, the polyhedra centred by Ca1 and Ca1A (Fig. 4b) are better described as mono-capped trigonal prisms: in fact calcium cations do not lie in the basal plane of the 'pyramid' but are displaced towards the centre of the trigonal prisms; the 'capping' ligand is a H₂O molecule, W6 or W6A, with the corresponding Ca-O bond perpendicular to the 'pyramidal' basis. Average values of Ca-O distances were calculated as in the previous case and are presented in Fig. 4b. This kind of polyhedron - 'monocapped' trigonal prism - is present also in the structure of xonotlite $\text{Ca}_6[\text{Si}_6\text{O}_{17}](\text{OH})_2$, and is depicted for comparison in Fig. 4c, with the average bond distances for the various Ca-O bonds, the averages being calculated over the two crystallographically distinct Ca2 and Ca3 polyhedra, using the structural results of Kudoh & Takeuchi (1979).

The data presented in Fig. 4 indicate that in both types of calcium polyhedra the dome edge is substantially shorter than the two edges of the 'pyramidal' basis which are parallel to it. This geometrical feature is related to the connection of calcium layer and silicate chains, as explained later on.

Both kinds of polyhedral description may be usefully applied and in the following we shall use one or the other according to its capability to clearly describe the various structural features. Ca1 and Ca3 polyhedra, as well as Ca1A and Ca3A polyhedra, alternate along *b*, thus forming columns of edge-sharing polyhedra presenting coplanar 'pyramidal' bases. In a similar way H₂O molecules (W6 or W6A) and oxygen atoms (O6 or O6A respectively) regularly alternate as pyramidal apices (or 'capping' ligands). Such infinite columns adjoin each other, through edge sharing, along *a*, thus forming the infinite layers which are a fundamental structural module not only in clinotobermorite but also in the whole tobermorite family.

The peculiar way in which those calcium polyhedral layers are built up is described in Fig. 5, where, for the sake of simplicity, polyhedra are described as simple trigonal prisms, completed by the 'capping' ligands. Important consequences of this kind of connection are that adjacent columns present the 'capping' ligands on opposite sides of the layer and that, similarly, the short 'dome' edges are placed on opposite sides in adjacent columns, with a displacement of *b*/4.

Silicate tetrahedral chains

Infinite silicate tetrahedral chains of the wollastonite-type, *i.e.* with repeat every fourth tetrahedron ('Dreierketten'), run along *b* on both sides of the calcium polyhedral layers. These chains may be described, following the nomenclature common in cement chemistry, as built up by 'paired' tetrahedra (Si1 and Si3) connected by a 'bridging' tetrahedron (Si2). The chains are firmly linked to the calcium polyhedral layer, with the 'paired' tetrahedra attached to it by sharing the oxygen atoms of 'dome' edges and the 'bridging' tetrahedron sharing the pyramidal apices O6 or O6A. This kind of connection explains well not only the shortness of the 'dome' edges, which must conform to the length of a SiO₄ tetrahedral edge, but also the deviation from the normal position of the Ca-O bond involving the 'capping' oxygen atoms O6 and O6A. This deviation is necessary to form Si2-O6 and Si2A-O6A bonds of proper distance.

Our structural results definitely solve the problem of the multiplicity of the 'Dreierketten' discussed by Hoffmann & Armbruster (1997), and clearly show that the wollastonite chains attached to successive calcium layers and facing each other are condensed through the bridging oxygen O5, thus giving rise to double chains of $[\text{Si}_6\text{O}_{17}]^{10-}$ composition.

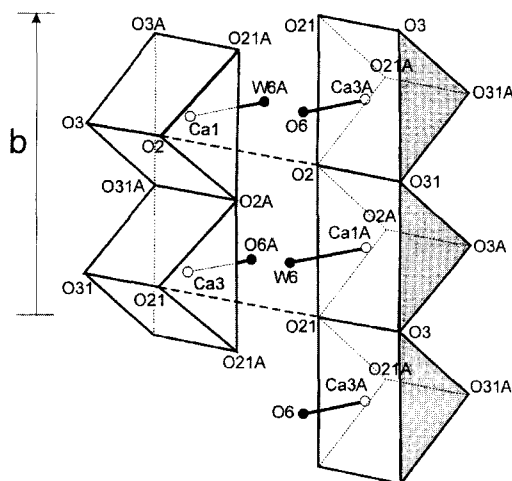


Fig. 5. Columns of CaO₇ polyhedra, schematically represented as trigonal prisms completed by the 'capping' ligands. To clearly display the polyhedral connection, two adjacent columns are drawn displaced along the dashed lines.

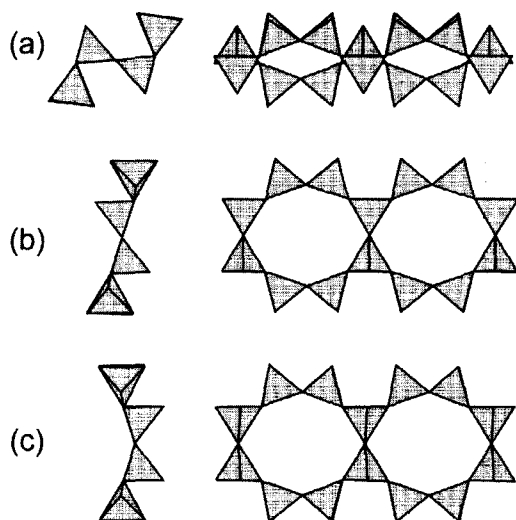


Fig. 6. Silicate double chains in (a) xonotlite (Kudo & Takeuchi, 1979), (b) clinotobermorite, and (c) tobermorite 11 Å (Merlino *et al.*, 1999). The double chains are projected along the chain direction and perpendicular to it, respectively.

'Dreierdoppelketten' (Liebau, 1956) of such composition were already found in xonotlite, $\text{Ca}_6[\text{Si}_6\text{O}_{17}](\text{OH})_2$ (Mamedov & Belov, 1955;

Kudoh & Takeuchi, 1979; Eberhard *et al.*, 1981). The chains in xonotlite are squeezed between two successive calcium polyhedral layers 7 Å apart, whereas in clinotobermorite the double chains present a larger width, connecting calcium polyhedral layers more than 11 Å apart. Very similar chains have been found also in the structure of tobermorite 11 Å, and Fig. 6 compares the three kinds of double chains: in xonotlite, with contraction in *c* direction and symmetry $[\cdot 2/m]$; in clinotobermorite, with extension in *c* direction and symmetry $[\cdot 2/m]$; in tobermorite 11 Å, with extension in *c* direction and symmetry $[2mm]$. A common feature of the three structures is the way by which the 'paired' tetrahedra are attached to the calcium layers: the paired tetrahedra are bonded to the oxygens of the 'dome' edges, on both sides of the layers with a relative displacements of $b/4$.

Structural cavities and hydrogen bond system

Adjacent calcium layers are firmly held together by the $[\text{Si}_6\text{O}_{17}]^{10-}$ double chains, thus building a strong scaffolding which hosts in its cavities Ca2 and H_2O molecules W5, W7 and W8. W5 is placed in the centre of the eight-membered rings of the silicate chains, whereas Ca2, W7, and W8 are placed in the central zone of the channels running along *b* and limited by adjacent tetrahe-

Table 5. Bond-valence sums (v.u.) for anions and cations in clinotobermorite.

	Si1	Si1A	Si2	Si2A	Si3	Si3A	Ca1	Ca1A	Ca3	Ca3A	Ca2	Σ_-	Σ_+^*
O1	0.92		1.00								0.05	1.97	
O1A		1.01		0.94								1.95	2.12
O11			1.00		0.88						0.06	1.94	
O11A				0.93		1.02						1.95	2.12
O2					1.11		0.24	0.34		0.29		1.98	
O2A						1.04	0.36	0.18	0.31			1.89	
O21	1.07							0.36	0.11	0.32		1.86	
O21A		1.08					0.36		0.30	0.14		1.88	
O3					1.05		0.23	0.33		0.32		1.93	
O3A						1.13	0.29	0.25	0.29			1.96	
O31	0.91							0.34	0.20	0.35		1.80	
O31A		1.17					0.30		0.27	0.24		1.98	
O4	0.90				0.96						0.27	2.13	
O4A		0.92				0.91						1.83	1.98
O5			1.11	0.98								2.09	
O6			1.08							0.26	0.36	1.70	
O6A				1.04					0.25			1.29	1.74
W5											0.39	0.39	0.25
W6								0.21				0.21	0.08
W6A							0.21				0.06	0.27	-0.16
W7											0.39	0.39	0.29
W8											0.43	0.43	0.29
Σ_+	3.80	4.18	4.19	3.89	4.00	4.10	1.99	2.01	1.73	1.92	2.01		

The average distances of the two sets of data for the triclinic polytype (Table 3) were used for the calculations. In the last column the values corrected for hydrogen bond contributions are reported, according to the scheme of Fig. 7a.

dral chains. These 'zeolitic' components play an important role for the stability of the whole structure and their positions and interactions are crucial also in understanding the actual composition of the scaffolding.

If we look at the bond-valence sums for the various oxygen atoms of the scaffolding (namely calcium polyhedra layers + silicate chains), calculated according to the parameters proposed by Brese & O'Keefe (1991) and excluding bonds and interactions with the 'zeolitic' components, we obtain bond-valence sums largely different from 2 v.u. (valence units) only for W6 and W6A, which present values of 0.2-0.3 v.u., corresponding to H₂O molecules, and for O6 and O6A, with valence sums of 1.34, and 1.29 v.u., respectively (Table 5). The undersaturation of O6 is removed by its linkage to Ca2, which is not only strongly bonded to the three 'zeolitic' H₂O molecules W5, W7, W8 but also to O6 and O4 atoms of the scaffolding (Table 3). The chemical role of O6A may be understood by looking at the system of hydrogen bonds connecting the 'zeolitic' H₂O molecules among them and to oxygen atoms of the scaffolding.

Fig. 7 presents the H₂O - H₂O and H₂O -oxygen connections corresponding to O...O distances shorter than 3.07 Å and shows a hydrogen bond system (Fig. 7a) which is in agreement with other structural evidences, as will be explained in the following.

O6A is acceptor in two relatively strong hydrogen bonds with W7 and W8: applying the equation proposed by Ferraris & Ivaldi (1988) to correlate bond valence *vs.* O...O distance, an additional contribution of 0.45 v.u. to O6A may be calculated, indicating that O6A is an oxygen anion. On this basis the composition of the scaffolding may be expressed as [Ca₄(Si₆O₁₇)·2H₂O]²⁻, the negative charge being compensated by the corresponding positive charge of the 'zeolitic' part [Ca·3H₂O]²⁺. The crystal chemical formula of clinotobermorite is therefore Ca₅Si₆O₁₇·5H₂O.

Assuming that O6A is a hydroxyl anion, an alternative hydrogen bonding scheme, presented in Fig. 7b, may be suggested. In this case O6A would behave as a donor in one of the two hydrogen bonds in which it is involved (O6A...W7 or O6A...W8). As the corresponding bond valences, 0.24 and 0.21 v.u., respectively, are very similar, the sum of bond valences of O6A would remain significantly higher than 1 v.u.. Moreover a second OH⁻ anion is necessary to keep neutrality and the only possible candidate is W6A, which could rise its bond-valence sum by inverting the donor-acceptor role in either W8...W6A or W7...W6A

hydrogen bonds. The bond-valence sums of the various oxygen atoms, calculated taking into account both the Ca-O bond as well as the hydrogen bond strengths, are indicated in Fig. 7 for both schemes. A good indicator for the correct choice is given by the deviation of the calculated bond-valence sums *v* from the ideal values 0, 1, 2 v.u. for H₂O molecule, hydroxyl anion and oxygen anion respectively. $\sum_i(\Delta v_i)^2$ is 0.18 v.u. for the scheme in Fig. 7a and 0.38 v.u. for the scheme in Fig. 7b, the sum being calculated over the three oxygen atoms W6A, W7, and O6A, which yield different bond-valence sums in the two cases.

It seems proper to remark that, assuming the scheme given in Fig. 7a as the correct one, we may easily explain the geometry of Ca3 and Ca3A polyhedra, which present the calcium cations in the centre of the basal pyramidal plane (Fig. 4a). In this position both Ca3 and Ca3A form relative-

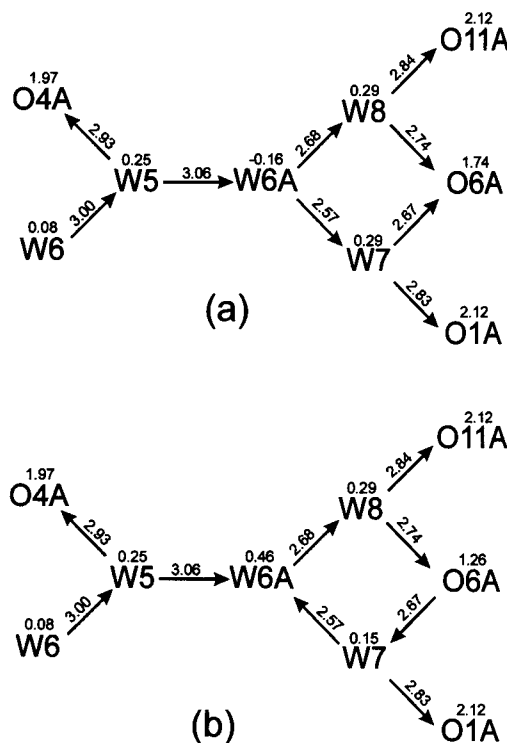


Fig. 7. Two possible hydrogen bond systems in clinotobermorite. O...O distances less than 3.07 Å are indicated. The bond valence sums (v.u.), corrected for hydrogen bond contributions, are reported above the oxygen labels. In (a) W6A is a H₂O molecule and O6A is an oxygen atom whereas in (b) W6A and O6A are OH groups.

ly short bonds with the undersaturated oxygen atoms O6A and O6, respectively. If O6A would be an oversaturated hydroxyl anion, as suggested by the scheme given in Fig. 7b, longer Ca3-O6A distances would be preferred, with the calcium cation displaced from the basal plane towards the centre of the trigonal prisms, as it is actually observed for Ca1 and Ca1A polyhedra (Fig. 4b). Moreover, according to the scheme of Fig. 7b, W6A would be an undersaturated hydroxyl anion, which is not in agreement with the shape of the Ca1 polyhedron, with Ca1 shifted from the pyramidal base and making a relatively long Ca1-W6A bond. In conclusion, both the analysis of the possible hydrogen bond schemes and the actual geometry of the calcium polyhedra point to the crystal chemical formula $\text{Ca}_5[\text{Si}_6\text{O}_{17}]\cdot 5\text{H}_2\text{O}$, which is also in good agreement with the known chemical analyses of clinotobermorite (Henmi & Kusachi, 1992; Hoffmann & Armbruster, 1997). To definitely rule out the presence of Si-OH groups, IR or ^{29}Si CPMAS NMR studies would be useful.

Twinning in clinotobermorite

As it was previously mentioned, violations of the c glide absences were observed during the collection of intensity data of the monoclinic polytype. Moreover, Hoffmann & Armbruster (1997) pointed to violations of A centring absences as regards the family reflections. A careful examination of these violations showed that they actually occur for $h = 4n + 2$ for the monoclinic polytype, *i.e.* for $H = 2n + 1$ for the family reflections. These observations suggested the occurrence of a twin with (001) as twin plane, a twinning additional to that relating MDO_2 and MDO_2' triclinic polytypes.

This additional twinning is illustrated in Fig. 8, which presents a schematic drawing of the superimposed $h0l$ reciprocal planes of both twin individuals of the monoclinic polytype MDO_1 . Due to the metrics of the lattice, $\mathbf{a}_m^* - \mathbf{a}_{mT}^* = \mathbf{c}^*/2$, reflections corresponding to the twin individuals coincide for $h = 4n$, whereas reflections of both individuals regularly alternate along $\mathbf{c}^*$ for $h = 4n + 2$, thus simulating a violation of the c glide absences.

These coincidences and regular alternations, illustrated in Fig. 8 for the $h0l$ plane, generally occur in the whole reciprocal space for $h = 2n$ (and therefore $k = 2n$), *i.e.* for reflections HKL corresponding to the family structure. This causes the apparent violation of the A centring for $H = 2n + 1$

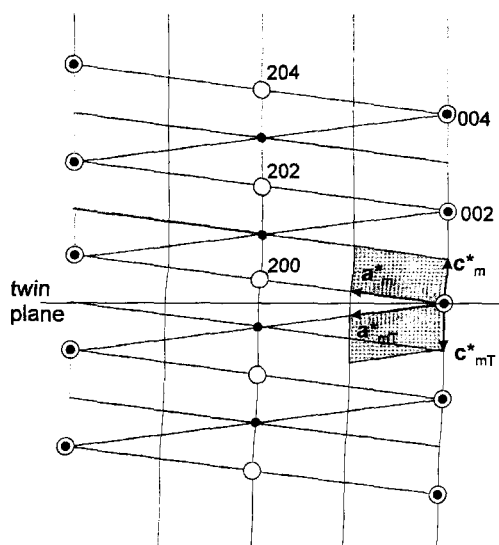


Fig. 8. Schematic drawing of the superimposed $h0l$ reciprocal planes of both twin individuals of the monoclinic clinotobermorite MDO_1 (white and black circles, respectively). The two reciprocal cells, with (001) as twin plane, are outlined.

and the coincidence of the reflections of the twin individuals for $H = 2n$.

In the triclinic polytype, the occurrence of (001) twinning causes the presence of two additional individuals besides the two individuals related by (010) [indices refer to the monoclinic cell; (041) with reference to the triclinic cell], previously denoted as MDO_2 and MDO_2' . Their spatial relationships are illustrated in Fig. 9, where the

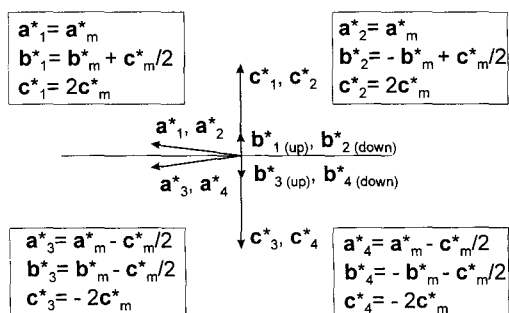


Fig. 9. Spatial relationships among the triclinic individuals in clinotobermorite. The indices 1 and 2 refer to the MDO_2 and MDO_2' twins, whereas the indices 3 and 4 refer to the individuals related to the previous pair through (001) twinning.

vectors with indices 1 and 2 refer to the already known MDO₂ and MDO₂' twins, whereas the vectors with indices 3 and 4 refer to the individuals related to the previous pair by (001) twinning.

We have checked the data collected for the monoclinic polytype and we found a constant ratio of 0.05 between the intensities of corresponding reflections in the two twinned individuals. Such a value is quite small, and no correction of the intensities of superimposed reflections was considered.

Heating experiments: the 9 Å phase

It was observed by Henmi & Kusachi (1992) that clinotobermorite from Fuka loses molecular water on heating to 300°C in air, resulting in shrinkage of d_{002} from 11.3 to 9.3 Å. Similar shrinkage occurs in 'normal' tobermorites, when dehydrated at nearly 300°C, whereas 'anomalous' tobermorites do not shrink when dehydrated (Mitsuda & Taylor, 1978). This peculiar behaviour stimulated extensive research with different approaches. The presently accepted knowledge is that the 'so called anomalous 1.1 nm tobermorite differs from the normal variety in containing inter-layer Si-O-Si links' (Taylor, 1992), the typical links of silicate double chains. We have just seen that silicate double chains are present in clinotobermorite; therefore it seemed interesting to investigate the thermal behaviour of clinotobermorite from the Wessels mine, to check the observations of Henmi & Kusachi (1992) on Fuka specimens and to define more precisely the temperature of transformation.

A crystal was heated, step by step, with a high-temperature device connected to the Siemens P4 four-circle diffractometer, and it was studied *in situ* before, during, and after the dehydration process. A preliminary examination of the starting crystal by Weissenberg photographs showed sharp family reflections and visible, even if diffuse, characteristic reflections. No other phase was detected.

After the family cell of clinotobermorite was obtained by centring some strong family reflections, we checked the presence of the triclinic polytype in the crystal by measuring the intensity of known reflections. The same procedure was repeated for its twin counterpart and for the monoclinic polytype; the results confirmed the coexistence of the three kinds of domain within the starting crystal, as already observed in the crystal used for structure refinements.

The temperature was subsequently increased

in steps of 25°C. During the heating process, a progressive increase in the width of the reflections was observed; however, a sufficient number of reflections could be observed and centred to obtain the clinotobermorite family cell, until the temperature reached 200°C. At 225°C a Polaroid film was exposed to look for possible new reflections to centre. The film showed several additional spots, whereas some others had disappeared. Through the auto-indexing routine, we obtained a new cell with parameters: $a = 5.580(3)$, $b = 3.651(2)$, $c = 18.771(8)$ Å, $\alpha = 90.19(6)$, $\beta = 92.89(4)$, $\gamma = 90.03(5)^\circ$. These parameters correspond to those presented by Taylor (1959) for the 'pseudo-cell' of tobermorite 9 Å, the phase obtained by heating 'normal' tobermorite 11 Å at 300°C (McConnell, 1954; Mitsuda & Taylor, 1978). In the following we will provisionally use the name tobermorite 9 Å also for the product obtained by heating clinotobermorite, although some cautionary remarks seem appropriate. In fact, whereas a Gandolfi diffraction pattern collected from the dehydrated crystal, obtained in the present work, was similar to the powder pattern reported for tobermorite 9 Å (Taylor, 1959), some details in the two powder patterns seem to indicate minor differences in the structures. Such differences may be exactly understood only once the structural arrangements of both phases will be completely unravelled.

OD character of tobermorite 9 Å

After the transformation, which occurs topotactically at 225°C, the crystal appeared strongly fractured, with the different crystallites partially out of alignment. The reflections became broad, the spreading being particularly evident in the ω -scan mode, with peaks wider than 2°. In spite of that, the X-ray intensity data collections were performed for both MDO polytypes. It turned out that the product of the dehydration process of clinotobermorite has OD character, as do all the phases of the tobermorite-group, *i.e.* it consists of equivalent layers which can be stacked in two different, but geometrically equivalent, ways.

The heat-treated clinotobermorite shows family reflections corresponding to a family cell with $A = 5.58$, $B = 3.65$, $C = 18.78$ Å, $\beta = 92.8^\circ$, space group $A2/m$. Due to its crystal-chemical relationships to clinotobermorite, the shrunken phase should have building layers with the same translation vectors **a** and **b** as clinotobermorite ($a = 11.16$, $b = 7.30$ Å), but a distinct basis vector **c**₀ ($c_0 = C/2 = 9.39$ Å; layer spacing $c_0 \sin \beta$, with $\beta = 92.8^\circ$).

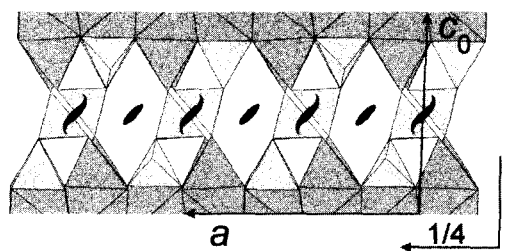


Fig. 10. Single layer in tobermorite 9 Å, as seen along *b*.

Due to these various constraints, the building layer should actually correspond to that sketched in Fig. 10, with symmetry $C12/m(1)$. The OD groupoid family compatible with the layer symmetry and space group of the 'family structure' is the same as found for clinotobermorite, *i.e.* layers with symmetry $C12/m(1)$ may follow each other in the *c* direction, related by the symmetry operator $2_{1/2}$ or by the operator $2_{1/2}$. Layers related by these operators are translationally equivalent and related, respectively, by the stacking vectors:

$$\begin{aligned} \mathbf{t}_1 &= \mathbf{c}/2 - \mathbf{b}/4 \\ \mathbf{t}_2 &= \mathbf{c}/2 + \mathbf{b}/4 \end{aligned}$$

Two MDO polytypes are possible in this family:

- 1) MDO₁ polytype, which corresponds to the sequence $\mathbf{t}_1\mathbf{t}_2\mathbf{t}_1\mathbf{t}_2\dots$; it presents $C2/c$ symmetry, with cell parameters $a = 11.16$, $b = 7.30$, $c = 18.78$ Å, $\beta = 92.8^\circ$;
- 2) MDO₂ polytype, which correspond to the sequence $\mathbf{t}_1\mathbf{t}_1\mathbf{t}_1\dots$ (the constant application of the vector $\mathbf{t}_2$ gives rise to the twin structure MDO₂); it presents $C1$ symmetry, with cell parameters $a = 11.16$, $b = 7.30$, $c = 9.58$ Å, $\alpha = 101.3$, $\beta = 92.8$, $\gamma = 90^\circ$.

Both polytypes, where the triclinic one exhibited twinning, were present in the specimen obtained by dehydration.

Triclinic polytype MDO₂

The cell parameters of the triclinic polytype of tobermorite 9 Å, obtained through least-squares refinement of 15 reflections with $20^\circ < 2\theta < 35^\circ$, were $a = 11.156(5)$, $b = 7.303(4)$, $c = 9.566(5)$ Å, $\alpha = 101.08(4)$, $\beta = 92.83(5)$, $\gamma = 89.98(4)^\circ$. The data collection was performed in ω - 2θ scan mode, with $3.5^\circ < 2\theta < 50^\circ$, scan speed $4^\circ/\text{min}$, scan range 2.2° . A total of 1338 unique reflections were measured, 1003 of them were considered as observed [$F_o > 4\sigma(F_o)$] and were used for the refinement (SHELXL-97; Sheldrick, 1997).

Separate scale factors for family and characteristic reflections were applied.

The refinement was carried out in space group $C1$, with the starting atomic coordinates derived from the OD model. A maximum of electron density, which was attributed to a calcium cation Ca2 with half occupancy, was found within the narrow structural cavity, slightly displaced from the inversion centre at $1/2, 1/2, 1/2$. Ordering of the Ca2 cations, with lowering of the symmetry to $C1$, is probable, but the quality of our data did not allow to reliably test this possibility.

After some minor adjustments and introduction of anisotropic displacement parameters for Ca1 and Ca3 and for the silicon atoms, the refinement converged to $R = 0.144$ for 1003 reflections with $F_o > 4\sigma(F_o)$. Taking into account that the starting crystal was quite disordered and that the dehydration process strongly damaged it, the results of the structural refinement are satisfactory. The atomic coordinates and displacement parameters are listed in Table 6, whereas the bond distances are reported in Table 7. In Fig. 11, two projections of the structure are sketched.

Monoclinic polytype MDO₁

The cell parameters of the monoclinic polytype, $a = 11.161(5)$, $b = 7.303(4)$, $c = 18.771(9)$ Å, $\beta = 92.91(5)^\circ$, were obtained by least-squares refinement of 15 reflections with $20^\circ < 2\theta < 35^\circ$.

Table 6. Tobermorite 9 Å, triclinic polytype MDO₂, space group $C1$: atomic coordinates and displacement parameters (U_{eq} for Si1, Si2, Si3, Ca1, Ca3 atoms, U_{iso} for all the others).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} or <i>U</i> _{eq}
Si1	0.3859(5)	0.2158(8)	0.2234(7)	0.013(1)
Si2	0.3181(6)	-0.0193(9)	0.4343(8)	0.025(2)
Si3	0.3883(5)	0.6416(8)	0.2173(8)	0.015(2)
O1	0.390(2)	0.150(2)	0.377(2)	0.030(4)
O11	0.390(2)	-0.209(2)	0.371(2)	0.024(4)
O2	0.499(2)	0.663(2)	0.121(2)	0.024(4)
O21	0.502(1)	0.152(2)	0.136(2)	0.018(4)
O3	0.268(1)	0.649(2)	0.118(2)	0.013(3)
O31	0.267(2)	0.163(2)	0.133(2)	0.018(4)
O4	0.403(2)	0.441(2)	0.277(2)	0.022(4)
O6	0.179(2)	-0.040(3)	0.384(2)	0.041(5)
OH6	0.152(2)	0.488(3)	0.390(3)	0.050(6)
Ca1	0.3713(4)	0.0981(6)	-0.1040(6)	0.017(1)
Ca2	0.499(1)	0.460(1)	0.502(2)	0.035(3)
Ca3	0.3647(4)	0.5966(6)	-0.1175(6)	0.017(1)

Table 7. Selected bond distances (in Å) in triclinic MDO₂ tobermorite 9 Å. e.s.d. are reported in parentheses.

Si1 - O1	1.63(2)	Si2 - O1	1.67(2)	Si3 - O11	1.65(2)
- O21	1.60(2)	- O11	1.63(2)	- O2	1.61(2)
- O31	1.56(2)	- O6	1.61(2)	- O3	1.62(2)
- O4	1.63(2)	- OH6	1.68(2)	- O4	1.68(2)
Ca1 - O2	2.30(2)	Ca3 - O2	2.43(2)	Ca2 - O1	2.62(2)
- O21	2.29(2)	- O2	2.65(2)	- O11	2.67(2)
- O21	2.63(2)	- O21	2.41(2)	- O4	2.32(2)
- O3	2.36(2)	- O3	2.38(2)	- O4	2.35(2)
- O31	2.38(2)	- O3	2.52(2)	- O6	2.34(3)
- O31	2.57(2)	- O31	2.38(2)	- O6	2.36(3)
- OH6	2.70(2)	- O6	2.54(2)		

An intensity data collection was performed in ω -2 θ scan mode, scan width 2.2°, scan speed 12°/min, up to 45° in 2 θ . The characteristic reflections of the monoclinic polytype were, in average, weaker and more diffuse than the characteristic reflections of the triclinic one, pointing to a smaller volume and a greater disorder in the former than in the latter. Consequently the refinement of this polytype was not satisfactory, resulting in a reliability index never less than 20 %.

Structure description

The structure of tobermorite 9 Å, obtained through the refinement of the triclinic polytype, presents some common features with clinotober-

morite, namely the calcium octahedral layers parallel to (001) with wollastonite chains attached to both sides of these layers. As in clinotobermorite, the chains are linked to the polyhedral walls with the 'paired' tetrahedra sharing the oxygen atoms of the 'dome' edge and the 'bridging' tetrahedron sharing the pyramidal apex O6.

However, a major structural difference is found between clinotobermorite and tobermorite 9 Å. Whereas clinotobermorite has 'Dreierdoppelketten', tobermorite 9 Å has 'Dreiereinfachketten' and the free apices OH6 of the bridging tetrahedra are connected to the opposite calcium polyhedral layer, just at the positions that, in clinotobermorite, were occupied by W6 and W6A H₂O molecules.

All H₂O molecules have been lost in the dehy-

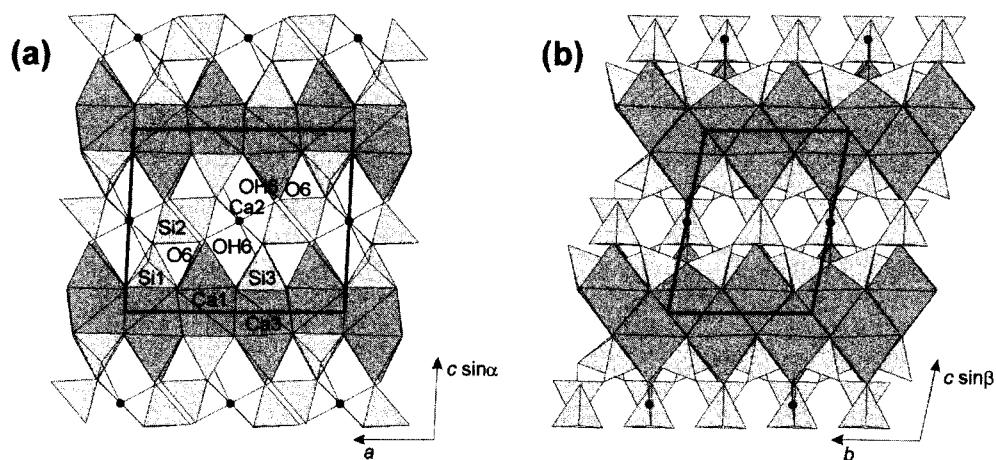


Fig. 11. Schematic drawing of the crystal structure of the triclinic polytype MDO₂ of tobermorite 9 Å, as seen along the **b** axis (a) and down the **a** axis (b). Single chains of tetrahedra (light grey) connect two layers of sevenfold coordinated calcium polyhedra (dark grey).

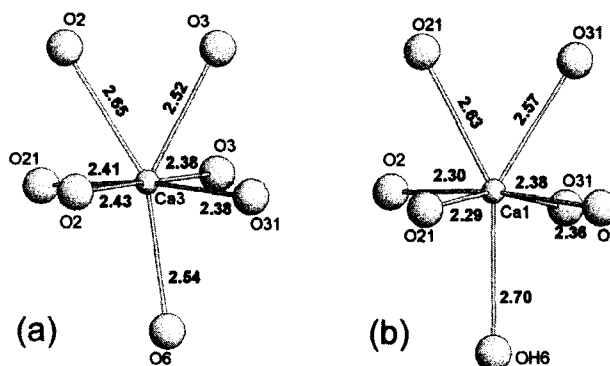


Fig. 12. Coordination of Ca in the polyhedral layers of tobermorite 9 Å: (a) Ca3 is placed within the basal pyramidal plane, whereas (b) Ca1 is displaced from the basal pyramidal plane, forming a trigonal prism monocapped by the hydroxyl group OH6.

dration process and Ca2 is now firmly linked to six oxygen atoms of the framework.

Looking at the bond-valence sums of all oxygen atoms, calculated according to the parameters proposed by Brese & O'Keefe (1991), we obtain two bond-valence sums considerably different from 2 v.u., *i.e.* 1.61 v.u. for O6 and 0.99 v.u. for OH6. This last anion obviously corresponds to a hydroxyl group, whereas O6, notwithstanding the undersaturation, is an oxygen anion. This assignment is confirmed by the examination of the coordination polyhedra of Ca1 and Ca3 cations (Fig. 12). These polyhedra present the features already discussed for clinotobermorite, *i.e.* shortening of the 'domatic' edge and different shapes for Ca1 and Ca3 polyhedra. Ca1 is displaced away from the centre of the basal pyramidal plane, thus causing a long Ca1-OH6 bond. Ca3 is placed within the basal pyramidal plane forming a shorter Ca3-O6 bond that contributes to attenuate the undersaturation of the O6 ligand. These observations support the interpretation given above and point to a crystal chemical formula of $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$ for tobermorite 9 Å.

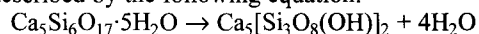
Conclusions

The application of OD procedures facilitated us to understand the complex diffraction patterns of clinotobermorite, and to correctly relate the observed characteristic reflections to different polytypes (MDO_1 , MDO_2 and MDO_2'), coexisting within the crystals. Moreover, a careful examination of the collected intensity data showed the presence of additional twinning, with (001) as

twin plane. Thus a macroscopic crystal may actually contain domains of six different individuals. Despite of these structural complexities, the refinements performed on the two MDO polytypes of clinotobermorite showed well-defined structural features, which could not be determined on the basis of the knowledge of the family structure only (Hoffmann & Armbruster, 1997).

In particular, it has been definitely confirmed that the wollastonite-like chains are linked to form 'Dreierdoppelketten' (Liebau, 1956), $[\text{Si}_6\text{O}_{17}]^{10-}$, running along **b**, with a conformation different from that of xonotlite ribbons (Kudoh & Takeuchi, 1979) as well as from that of the chains in tobermorite 11 Å (Merlino *et al.*, 1999). The various structural details - shapes of calcium polyhedra, hydrogen bond system, bond strength balance - indicate the absence of hydroxyl anions in clinotobermorite and point to the crystal chemical formula $\text{Ca}_5\text{Si}_6\text{O}_{17}\cdot 5\text{H}_2\text{O}$.

By heating crystals of clinotobermorite to 225°C we obtained, in a topotactical way, crystals of tobermorite 9 Å. This phase, too, has an OD character and, through the determination of the structural features of the triclinic polytype, the presence of wollastonite-type single chains and the occurrence of hydroxyl anions has been demonstrated. The dehydration reaction may be described by the following equation:



It seems interesting to recall that $[\text{Si}_3\text{O}_8(\text{OH})]^{5-}$ chains occur in the minerals of the serandite-pectolite-schizolite series, but in these cases the Si-OH group connects the 'paired' Si_2O_7 tetrahedra (Takeuchi & Kudoh, 1977) by a very strong infra-chain hydrogen bond. In tobermorite 9 Å the

Si-OH group occurs in the bridging tetrahedron and does not form strong hydrogen bonds.

The results we obtained in the study of clinotobermorite and tobermorite 9 Å provide a clear understanding of the structural relationships between the two phases. It could be shown that the main consequences of the dehydration process are the decondensation of the tetrahedral double chains and the closer approach of the calcium polyhedral layers, to offer a favourable coordination to the calcium cations Ca²⁺.

These results suggest also some preliminary considerations about the enigmatic behaviour of tobermorite 11 Å upon heating. It is well known that tobermorite 11 Å loses most of its H₂O molecules at 300°C: in some specimens – normal tobermorites – the loss of H₂O results in a decrease of the characteristic spacing from 11.3 Å to 9.3 Å, corresponding to the formation of tobermorite 9 Å, whereas in other specimens – anomalous tobermorites – there is no decrease in the basal spacing upon dehydration. It has been assumed that anomalous tobermorites should present ‘interlayer Si-O-Si linkages’. These linkages, present in the tetrahedral double chains, would prevent an approach of the adjacent calcium polyhedral layers after dehydration. In contrast, the absence of ‘interlayer Si-O-Si linkages’ in normal tobermorites, which therefore should be characterized by tetrahedral single chains, would allow such an approach upon dehydration, with a consequent decrease in the basal spacing to 9.3 Å.

The results described and discussed in the present paper make such an explanation untenable, as we have demonstrated that clinotobermorite, with tetrahedral double chains, does actually shrink to tobermorite 9 Å upon dehydration. An alternative explanation, based on the ‘zeolitic’ calcium content, may be put forward. As we have previously described, in clinotobermorite the ‘zeolitic’ Ca²⁺ is strongly bonded to three H₂O molecules; after dehydration it may reconstruct its coordination sphere only through a general rearrangement involving division of the double chains and approach of adjacent calcium polyhedral layers. A similar behaviour has to be expected for specimens of tobermorite 11 Å with high calcium content (Ca₅Si₆O₁₇·5H₂O) and full occupancy of the ‘zeolitic’ calcium site, whereas in case of specimens with few or no ‘zeolitic’ calcium cations [extreme composition Ca₄Si₆O₁₅(OH)₂·5H₂O] dehydration should not cause severe consequences on the whole structure and no rearrangement should be necessary.

This hypothesis is in agreement with the

observation that high Ca/Si ratios favour normal behaviour; moreover, it has received a consistent support by the results of our studies on a specimen of anomalous tobermorite from the Wessels mine with composition Ca₄Si₆O₁₅(OH)₂·5H₂O (Merlino *et al.*, 1999). However, more structural work on specimens of normal tobermorite and wide crystal chemical investigations on the various phases of the tobermorite group are necessary to present definite and sound conclusions on this problem.

Acknowledgements: This work was supported by MURST (Ministero dell’Università e della Ricerca Scientifica) through a grant to the national project “Relations between structure and properties in minerals: analysis and applications”. We thank S. Đurović, E. Makovicky, and E. Libowitzky, for their constructive suggestions and comments.

References

- Brese, N.E. & O’Keefe, M. (1991): Bond-valence parameters for solids. *Acta Cryst.*, **B47**, 192-197.
- Dornberger-Schiff, K. (1956): On the order-disorder (OD-structures). *Acta Cryst.*, **9**, 593.
- (1964): Grundzüge einer Theorie von OD-Strukturen aus Schichten. *Abhandlungen der Deutschen Akademie der Wissenschaften zu Berlin. Klasse für Chemie, Geologie und Biologie*, **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.
- Đurović, S. (1997): Fundamentals of the OD theory. in ‘Modular aspects of minerals - EMU Notes in Mineralogy, Vol. 1, S. Merlino ed., Eötvös University Press, Budapest, 3-28.
- Eberhard, E., Hamid, S.A., Röttger, B. (1981): Strukturverfeinerung und Polytypie von Xonotlit Ca₆Si₆O₁₇(OH)₂. *Z. Kristallogr.*, **154**, 271-272.
- Ferraris, G. & Ivaldi, G. (1988): Bond valence vs. bond length in O—O hydrogen bonds. *Acta Cryst.*, **B44**, 341-344.
- Henmi, C. & Kusachi, I. (1989): Monoclinic tobermorite from Fuka, Bitchu-cho, Okayama Prefecture, Japan. *Journ. Min. Petr. Econ. Geol.*, **84**, 374-379 (in Japanese).
- , — (1992): Clinotobermorite, Ca₅Si₆(O,OH)₁₈·5H₂O, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineral. Mag.*, **56**, 353-358.
- Hoffmann, C. & Armbruster, T. (1997): Clinotobermorite, Ca₅[Si₃O₈(OH)]₂·4H₂O-Ca₅[Si₆O₁₇]·5H₂O, a natural C-S-H(I) type cement mineral: determination of the substructure. *Z. Kristallogr.*, **212**, 864-873.

- Kudoh, Y. & Takeuchi, Y. (1979): Polytypism of xonotlite: (I) Structure of an A polytype. *Mineral. J.*, **9**, 349-373.
- Liebau, F. (1956): Bemerkungen zur Systematik der Kristallstrukturen von Silikaten mit hochkondensierten Anionen. *Physikal. Chem.*, **206**, 73-92.
- Mamedov, K.S. & Belov, N.V. (1955): The crystalline structure of xonotlite. *Doklady Akad. Nauk SSSR*, **104**, 615-618 (in Russian).
- McConnell, J.D.C. (1954): The hydrated calcium silicates riversideite, tobermorite, and plombierite. *Mineral. Mag.*, **30**, 293-305.
- 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. *Am. Mineral.*, **84**, 1613-1621.
- 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.
- Takeuchi, Y. & Kudoh, Y. (1977): Hydrogen bonding and cation ordering in Magnet Cove pectolite. *Z. Kristallogr.*, **146**, 281-292.
- Taylor, H.F.W. (1959): The dehydration of tobermorite. *Proc. 6th Nat. Conf. Clays and Clay Minerals*, Pergamon Press, 101-109.
- (1992): Tobermorite, jennite, and cement gel. *Z. Kristallogr.*, **202**, 41-50.

Received 21 July 1999

Modified version received 24 November 1999

Accepted 2 December 1999