

Clinotobermorite, $\text{Ca}_5[\text{Si}_3\text{O}_8(\text{OH})]_2 \cdot 4 \text{H}_2\text{O} - \text{Ca}_5[\text{Si}_6\text{O}_{17}] \cdot 5 \text{H}_2\text{O}$, a natural C–S–H(I) type cement mineral: determination of the substructure

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Abstract. The substructure of natural clinotobermorite $\text{Ca}_5[\text{Si}_3\text{O}_8(\text{OH})]_2 \cdot 4 \text{H}_2\text{O} - \text{Ca}_5[\text{Si}_6\text{O}_{17}] \cdot 5 \text{H}_2\text{O}$ from the Wessels mine, Kalahari manganese field, South Africa, was determined from single-crystal X-ray data. The diffraction pattern (monoclinic: $a = 11.19 \text{ \AA}$, $b = 7.29 \text{ \AA}$, $c = 22.46 \text{ \AA}$, $\beta = 96.97^\circ$) is characterised by rather diffuse reflections of the type hkl with $h, k = 2n + 1$. The substructure (space group $I2/m$, $Z = 1$, $a/2 = 5.593(6) \text{ \AA}$, $b/2 = 3.645(4) \text{ \AA}$, $c = 22.46(3) \text{ \AA}$, $\beta = 96.97(2)^\circ$) was solved from the sharp Bragg reflections (hkl , with $h, k = 2n$) and refined on the basis of 1877 unique reflections to $R(F) = 6.7\%$.

The structure of clinotobermorite is closely related to the one of so called 11 Å tobermorite $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 2 \text{H}_2\text{O}$ (pseudo-orthorhombic, $a = 11.17 \text{ \AA}$, $b = 7.38 \text{ \AA}$, $c = 22.6 \text{ \AA}$). In both minerals layers parallel (001), formed by seven-fold co-ordinated Ca, are flanked on either side by wollastonite-like $[\text{Si}_3\text{O}_9]$ single chains (ca. $7.3 \text{ \AA}$ periodicity along b) creating a sandwich-like assemblage. The short $b/2$ axis ($3.645 \text{ \AA}$) and the short $a/2$ axis ($5.593 \text{ \AA}$) of the subcell are caused by an overlay of two half-occupied single chains of tetrahedra with one shifted by $b/2$ against the other. In clinotobermorite the sandwich-like layers are stacked along c yielding an interlayer distance of $4.5 \text{ \AA}$ with a free aperture of $3.2 \text{ \AA}$ where additional Ca ions and H_2O molecules connect the sandwich units. Clinotobermorite with 4–5 H_2O represents a much denser structure than 11 Å tobermorite with only 2 H_2O or 14 Å tobermorite with ca. 6 H_2O (pseudo-orthorhombic, $a = 11.17 \text{ \AA}$, $b = 7.38 \text{ \AA}$, $c = 27.94 \text{ \AA}$). The substructure of clinotobermorite can be interpreted as either composed of 'Dreiereinfachketten' leading to the formula $\text{Ca}_5[\text{Si}_3\text{O}_8(\text{OH})]_2 \cdot 4 \text{H}_2\text{O}$, or of 'Dreierdoppelketten' leading to the formula $\text{Ca}_5[\text{Si}_6\text{O}_{17}] \cdot 5 \text{H}_2\text{O}$, or of a mixture of both variants.

The surface structure of clinotobermorite was studied by atomic force microscopy (AFM) where low magnifications reveal a complex layering or twinning parallel (001).

High resolutions scans parallel (100) establish enhanced contrast fringes with a periodicity of ca. $10 \text{ \AA}$ interpreted as the repeat distance of the Ca polyhedral layers parallel to c .

Introduction

The major phases forming during the binding process of Portland cements are 14 Å and/or 11 Å tobermorite $\text{Ca}_{4.5}\text{Si}_6\text{O}_{15}(\text{OH})_3 \cdot x \text{H}_2\text{O}$ (Hamid, 1981; Taylor, 1992) and jennite $\text{Ca}_9\text{Si}_6\text{O}_{16}(\text{OH})_{10} \cdot 6 \text{H}_2\text{O}$ (Gard, Taylor, Cliff, Lorimer, 1977). According to low pressure and temperature conditions during their formation in the cement these compounds are poorly crystalline (like gels) or assemble only to structural fragments (Taylor, 1986; 1992). Structural fragments with $[\text{Si}_2\text{O}_7]$ groups form first developing to longer species which finally form infinite chains (Taylor, 1986). These poorly crystalline materials are generally called C–S–H phases according to their components CaO, SiO_2 and H_2O . Taylor (1992) defined C–S–H(I) gels as structurally closer to tobermorite and C–S–H(II) gels as closer to jennite.

Most of the C–S–H minerals are known to form during the cement binding process but they also occur in nature as hydrothermal alteration products of calcium carbonate rocks and as vesicle fillings in basaltic rocks. Tobermorite received its name after the type locality, Tobermory, Isle of Mull, Scotland. Henmi and Kusachi (1992) described clinotobermorite from Fuka, Japan as a new mineral, associated with tobermorite, plombierite, apophyllite, and calcite in gehlenite-spurrite-bearing skarns. A second occurrence of this mineral is in fissures of the Wessels mine, South Africa. A clinotobermorite sample of yellowish-colourless intergrown (001) plates from this locality was provided by R. Dixon and is investigated in this study. The same mineral was originally described as plombierite from the Wessels mine (Bezing, Gutzmer, 1994). On other samples from the same locality clinotobermorite coexists with xonotlite and datolite.

The structure of tobermorite is strongly disordered causing, in addition to the sharp X-ray reflections (Bragg

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reflections), diffuse streaks. If Bragg reflections and streaks are considered, the unit cell appears pseudo-orthorhombic with $a = 11.3 \text{ \AA}$, $b = 7.3 \text{ \AA}$, $c = 22.6 \text{ \AA}$. If only the sharp Bragg reflections are considered a subcell with $a/2$ and $b/2$ with space group $Imm2$ is obtained (Hamid, 1981). Single-crystal structure analysis performed for the subcell yielded an average structure characterised by a polyhedral Ca layer where half-occupied $[\text{Si}_3\text{O}_6]$ chains above and below are shifted by $b/2$ against each other and are thus superimposed. In addition, the chains are disordered by a mirror plane perpendicular to a which causes the a periodicity to be halved in the substructure. There are various possibilities how such an average structure can be interpreted in terms of long-range disordered domains. One ordered tobermorite model was proposed by Hamid (1981) to have $P2_1$ symmetry with $a = 6.69 \text{ \AA}$, $b = 7.39 \text{ \AA}$, $c = 22.770 \text{ \AA}$, $\gamma = 123.49^\circ$. All possible models have the Ca polyhedral sheet in common, but the $[\text{Si}_3\text{O}_9]$ wollastonite-like chains with a periodicity of $7.39 \text{ \AA}$ (twice $b/2$ of the subcell) can be attached in different ways. The resulting sandwich layers composed of polyhedral Ca sheets and $[\text{Si}_3\text{O}_9]$ chains on both sides are stacked along c with additional Ca accommodated in the interlayer space. ^{29}Si MAS (magic angle spinning) NMR spectra of synthetic tobermorites have shown (Engelhardt, Michel, 1987) that single chains and/or double chains of tetrahedra may occur. In other words the Ca polyhedral sheet acts as a template for various arrangements of tetrahedral chains or even layers.

Both natural and synthetic $11 \text{ \AA}$ tobermorites show marked deviation from $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 2 \text{ H}_2\text{O}$ stoichiometry. The limiting compositions (Taylor, 1992) are probably between $\text{Ca}_5\text{Si}_{5.5}\text{O}_{15}(\text{OH})_2 \cdot 2 \text{ H}_2\text{O}$ and $\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 2 \text{ H}_2\text{O}$. The mechanisms for this non-stoichiometric behaviour are explained by tetrahedral vacancies and omission of interlayer Ca. Synthetic tobermorite forms three modifications with different H_2O contents (Hamid Rahman, Beyrau, 1988) where the H_2O concentration strongly influences the length of the c -axis. Tobermorite with 0, 2, and 6 H_2O has a c -axis of $18 \text{ \AA}$, $22 \text{ \AA}$, and $28 \text{ \AA}$, respectively. These phases are identified based on the d -spacing of their (002) powder diffraction peaks and thus classified as $9 \text{ \AA}$, $11 \text{ \AA}$, and $14 \text{ \AA}$ tobermorites. H_2O loss and ion exchange experiments on tobermorite were performed to examine the mechanisms of water storage and diffusion mechanisms. H_2O is released in two steps, from $14 \text{ \AA}$ tobermorite to $11 \text{ \AA}$ tobermorite at 353 K then to $9 \text{ \AA}$ tobermorite at 553 K . The first step involves the interlayer H_2O whereas in the second step more firmly connected H_2O , attached to the more rigid Ca layers, is released (Hamid Rahman, Beyrau, 1988). The 'dry' $9 \text{ \AA}$ phase is only metastable and rehydrates to the $11 \text{ \AA}$ phase with $2 \text{ H}_2\text{O}$ per formula unit (pfu).

Exchange experiments on $11 \text{ \AA}$ tobermorite with Fe^{2+} resulted in a maximum uptake of $16\% \text{ Fe}^{2+}$ with almost intact crystallinity (Labhasetwar, Shrivastava, 1991) while Mg^{2+} showed an even higher uptake of 21% (Shrivastava, Komarneni, Breval, 1991). In $15\% \text{ Na}^+$, Al^{3+} substituted tobermorites (Tsuji, Komarneni, 1991) 2 Cs^+ were exchanged for 1 Ca^{2+} . Tsuji, Komarneni (1993), also using synthetic Na, Al substituted tobermorite, discovered in ex-

change experiments a high selectivity decreasing from Ba^{2+} to Sr^{2+} and Mg^{2+} . This selective ion exchange property might become interesting in waste treatment in cements because critical ions could be selectively extracted from solution while harmless ions are released.

The goal of this investigation is two-fold: firstly, to solve the substructure of clinotobermorite based on single-crystal X-ray data and to compare it with the known substructures of pseudo-orthorhombic tobermorite in order to discuss the possible similarities in properties and use; secondly, to give a short overview of cement minerals which have the characteristic $7.3 \text{ \AA}$ ($7.3/2 \text{ \AA}$) cell dimension in common.

Experimental

Electron microprobe analysis

Three small plates (ca. $1 \times 2 \times 0.3 \text{ mm}^3$) were selected for electron microprobe analysis to determine the chemical composition of clinotobermorite. Under a focused electron beam at 15 kV and 20 nA the sample released volatiles, thus the investigation was performed with a defocused electron beam of $10 \text{ }\mu\text{m}$ diameter using natural wollastonite as the standard. The analysis of the major elements ($\text{SiO}_2 = 47.44 \text{ wt\%}$, $\text{CaO} = 36.53 \text{ wt\%}$, and FeO , MnO , $\text{Na}_2\text{O} < 0.1 \text{ wt\%}$) leads to the chemical formula $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 5 \text{ H}_2\text{O}$ (based on 6 Si pfu). The H_2O content was estimated from the difference of the analysis for 100% . The calculated H_2O content is ca. $5.5 \text{ H}_2\text{O}$ pfu. and was reset to $5 \text{ H}_2\text{O}$ in accordance with Henmi and Kusachi (1992). As shown in subsequent sections, the H_2O content of the crystal fragment studied by single-crystal X-ray methods is between $4 \text{ H}_2\text{O}$ and $5 \text{ H}_2\text{O}$ pfu depending on the model for the substructure. The variable H_2O content is due to the substitution $2 \text{ OH}^- \leftrightarrow \text{O}^{2-} + \text{H}_2\text{O}$ which preserves the charge balance and keeps the number of O constant. The only coexisting phase sufficient in size to be analysed and stable under the electron beam is pure calcite.

Atomic Force Microscopy (AFM)

An examination of the clinotobermorite crystal surface was performed using the AFM method. The AFM scans with a sharp cantilever tip under current across a surface in such a short distance that it interacts with the substrate and the attracting and repulsing forces of the surface atoms direct the up and down movement of the tip according to the surface structure. In this technique either the position of the tip is kept stable and the variation of attracting or repulsing forces is measured or the forces are kept constant and the up and down movement of the cantilever is recorded with a position sensitive method (in our case a laser beam reflected by the top side of the cantilever is used).

A series of surface scans were taken under air for different orientations of a $1.2 \times 2 \times 0.5 \text{ mm}^3$ crystal of a clinotobermorite fragment which was cut shortly before the measurement. The scan width was varied stepwise

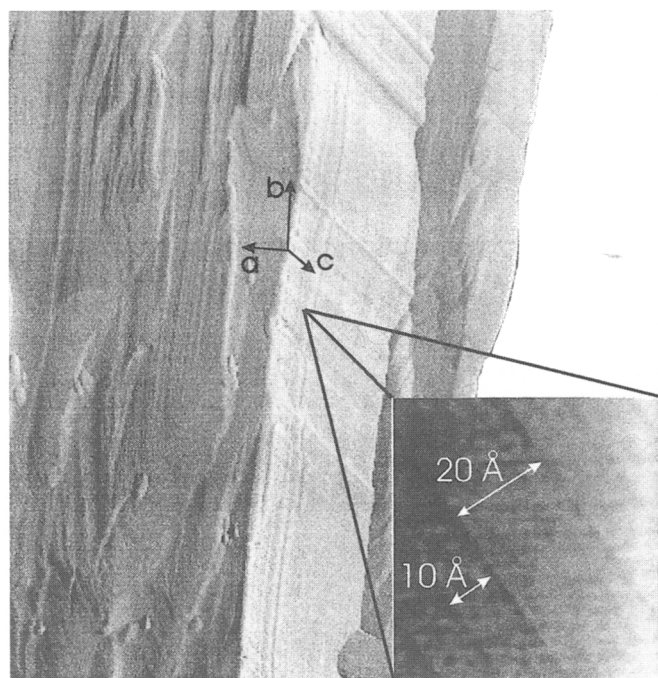


Fig. 1. A crystal of clinotobermorite is displayed using AFM methods. The image is taken under air with a scan width of 5781 nm. The b - c plane is zoomed out on a 5 nm scale to demonstrate the stacking of the fully occupied Ca layers. The image is rotated about 45° to avoid artifacts. In the image centre a stacking fault with doubled spacing is visible.

from 5781.14 nm to 5 nm (Fig. 1). The first image with 5781.14 nm scan width shows the rough surface of the a - b plane and a complex layering, intergrowth, or twinning. Scans of 5 nm width were performed with the crystal oriented parallel to (100). In this orientation the fully occupied Ca1 layers with ca. 10 Å distances can be detected by enhanced contrast fringes. A doubled Ca1-Ca1 layer distance of ca. 20 Å is interpreted in terms of a stacking fault of the layered structure.

X-ray data collection and structure solution

A clinotobermorite single-crystal, $0.17 \times 0.1 \times 0.04 \text{ mm}^3$ in size, was cut out of the core of a larger platy crystal ($1.2 \times 2 \times 0.5 \text{ mm}^3$) with slit edges parallel to b and was mounted on a glass fibre. A preliminary rotation photograph about b (the elongated direction) was recorded on a SIEMENS CCD X-ray imaging system yielding sharp Bragg reflections on hkl layers with $k = 0, 2, 4, \dots$ (even) and streaks with superimposed sharp Bragg reflections on hkl layers with $k = 1, 3, 5, \dots$ (odd). Considering only the sharp Bragg reflections the distances of the $k = 2n$ layers are characteristic of the subcell with $b/2 = 3.645 \text{ Å}$ whereas the distance of 7.29 Å accounts for the whole unit cell (Fig. 2). First layer equi-inclination Weissenberg photographs ($h1l$) with the crystal rotated about the b axis show continuous smearing of $11l, 31l, 51l, 71l$ etc. reciprocal lattice rows, though with variable intensity. In addition, these diffuse rows are decorated by weak reflections. Streaking on $1kl$ and $3kl$ layers of corresponding precession photographs is always along c^* . Thus the structure of clinotobermorite is disordered along c^* . Precession photographs of $0kl$ and $hk0$ layers reveal also weak reflections

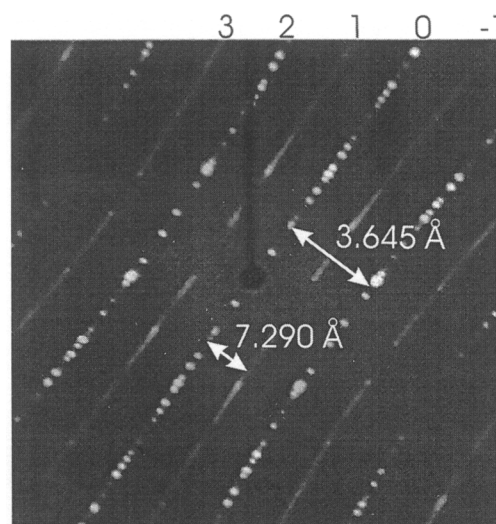


Fig. 2. CCD rotation photograph of the rotation axis b with an inclination of 54° . All hkl , $k = 0, 2, 4, \dots$ show sharp Bragg reflections; all hkl , $k = 1, 3, 5, \dots$ show streaks with superimposed sharp Bragg reflections. The intensities of the k even layers are considerably higher than those of the k odd layers.

violating I centring of the subcell. However, all reflections of the true structure fulfil requirements of C centring.

X-ray data were collected on a SIEMENS-P4R single-crystal diffractometer equipped with a rotating anode (50 kV, 200 mA) producing graphite monochromatized $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ Å}$) radiation. The subcell was refined from 47 Bragg reflections to $a/2 = 5.593(6) \text{ Å}$, $b/2 =$

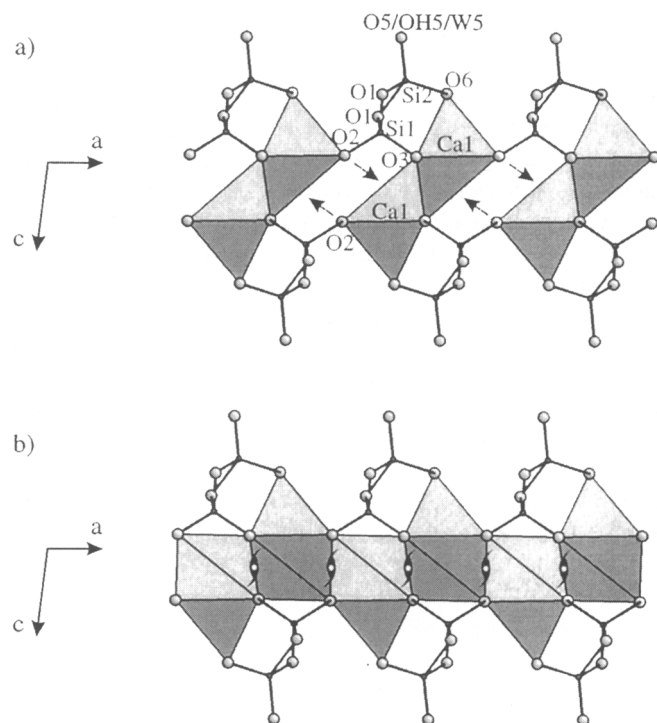


Fig. 3. A schematic model of the clinotobermorite substructure is displayed parallel to b . **a)** The Ca1 has an octahedral co-ordination to the closest oxygen atoms building edge-connected octahedral double chains. **b)** The distance to the adjacent octahedral double chain (in the same layer) is so close that an additional O2 is included into the co-ordination sphere of each Ca1 resulting in an edge-connected undulated Ca layer. Screw axes (2_1) exist at the shared edge parallel to b .

Table 1. Cell parameters and refinement parameters of clinotobermorite.

Space group	<i>I</i> 2/ <i>m</i>
<i>a</i> [Å]	5.593(6)
<i>b</i> [Å]	3.645(4)
<i>c</i> [Å]	22.456(27)
β [°]	96.97(2)
<i>Z</i>	1
Volume [Å ³]	454.4(9)
Formula wt	744.65
Diffractionmeter with rotating anode	
Current [mA], voltage [kV]	200, 50
Crystal size [mm]	0.17 × 0.1 × 0.04
<i>h</i> (min, max)	−11, 12
<i>k</i> (min, max)	−5, 7
<i>l</i> (min, max)	−13, 48
Reflections measured	5841
Reflections observed	2598
No. of reflections [<i>F</i> _o > 4σ(<i>F</i> _o)]	1877
<i>F</i> (000)	379
No. of parameters	79
<i>R</i> _{int} ^a	0.0227
<i>R</i> _w (<i>F</i> ²)(obs)/(all) ^b	0.1667/0.1807
<i>R</i> (<i>F</i>)(obs)/(all) ^c	0.0671/0.0838
<i>Goof</i> (obs)/(all) ^d	0.838/0.775

a: $R_{\text{int}} = (\sum (|F^2 - (F^2)_{\text{mean}}|) / (\sum F^2))$
b: $R_w(F^2) = \{(\sum (\text{weight} [|F_{\text{obs}} - F_{\text{calc}}|]^2) / (\sum (\text{weight} \cdot F_{\text{obs}}^2)))\}^{1/2}$
c: $R(F) = (\sum [|F_{\text{obs}} - F_{\text{calc}}|] / (\sum F_{\text{obs}}))$
d: $Goof = \{(\sum (\text{weight} [|F_{\text{obs}} - F_{\text{calc}}|]^2) / (\text{reflections}_{\text{obs}} - \text{parameters}_{\text{ref}}))\}^{1/2}$

3.645(4) Å, *c* = 22.456(27) Å, β = 96.97(5)°, *V* = 454.4(9) Å³, *Z* = 1 (space group *I*2/*m*), where *a* and *b* are doubled in the real cell considering the diffuse reflections. For the structure determination only the sharp Bragg reflections of the subcell were measured. A total of 5841 reflections of a hemisphere in reciprocal space (−11 ≤ *h* ≤ 12, −5 ≤ *k* ≤ 7, −13 ≤ *l* ≤ 48) were collected up to θ = 51° at room temperature. Data reduction, including background and Lorentz-polarisation corrections, was performed with the program XSCANS (SIEMENS, 1994). An empirical absorption correction using the ψ -scan technique was applied resulting in *R*_{int} = 0.0227 and *R*_σ = 0.0405. A total number of 2598 reflections with 1877 observed intensities (> 4σ(*F*_o)) were used for the structure solution. Direct methods (SHELXTL PCTM, Release 4.1, 1990) were utilised to locate the primary atoms Ca1, Si1, Si2. By subsequent difference-Fourier summa-

tions with the program SHELXL-93 (Sheldrick, 1993) the oxygen atoms O1 to O6 of the Ca1 and Si co-ordination as well as Ca2, located in the interlayer space, were found. Finally two H₂O oxygens were determined, one half occupied and disordered, connected to Ca1 and the second in the interlayer space. The latter H₂O (W7) is more or less centred in the interspace cavity whereas Ca2 is shifted by 2.038(4) Å from this H₂O position. As H₂O (W7) is half and Ca2 is one quarter occupied, both positions host the same average number of electrons. Thus the proper assignment had to be made based on interatomic distances. The shortest Ca–O distance for the assigned Ca2 position is 2.156 Å to the fully occupied (O5/OH5/W5) which is too short for a H₂O...O contact. Furthermore, the larger displacement parameter for the chosen H₂O position (W7) is in agreement with the lower weight and the weaker bonding of H₂O compared to Ca.

Table 2. Atomic coordinates and *B*_{eq} values of clinotobermorite.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq}	Occupancy
Ca1	0.5282(1)	0	0.29487(3)	1.473(7)	1
Ca2	0.3385(5)	0	0.4632(1)	2.67(5)	1/4
Si1	0.4453(2)	0.0798(3)	0.15732(4)	1.04(1)	1/2
Si2	0.5628(3)	1/2	0.07108(7)	1.24(2)	1/2
O1	0.4238(6)	0.145(1)	0.0941(1)	1.80(4)	1/2
O2	0.2304(3)	0	0.1953(1)	1.38(2)	1
O3	0.6957(3)	0	0.19738(9)	1.39(2)	1
O4	0.4156(8)	1/2	0.1313(2)	1.52(5)	1/2
O5/OH5/W5	1/2	1/2	0	2.99(8)	1
O6	0.841(1)	1/2	0.0925(3)	2.03(7)	1/2
W6	0.921(2)	1/2	0.0950(5)	6.1(3)	1/2
W7	0.495(2)	1/2	0.4805(5)	5.1(2)	1/2

$B_{\text{eq}} = 8/3 \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$
W is used to describe the oxygen position of the H₂O molecule.

Distance [Å]		Distance [Å]	
Ca1–O2	2.353(2)	Ca2 ^b –(O5/OH5/W5)	2.156(3)
Ca1–O2	2.353(2)	Ca2 ^b –W7 ^a	2.346(7)
Ca1–O2	2.620(3)	Ca2 ^b –W7 ^a	2.346(7)
Ca1–O3	2.381(2)	Ca2 ^b –O6 ^a	2.306(6)
Ca1–O3	2.381(2)	Ca2 ^{b,c} –O6 ^a	2.900(8)
Ca1–O3	2.484(3)	Ca2 ^{b,d} –W6 ^a	2.938(12)
Ca1 ^c –O6 ^a	2.546(8)	Ca2 ^b –O1 ^a	2.754(8)
Ca1 ^d –W6 ^a	2.461(13)	"Ca2 ^b –O4 ^a	2.407(5)
		"Ca2 ^b –O1 ^a	2.981(4)
		+Ca2 ^b –O1A ^a	2.242(4)
		+Ca2 ^b –O1B ^a	2.242(4)
average	^{o1} 2.445/ ^{o2} 2.433	average	^{o1} "2.541 ^c / ^{o1} +2.363 ^{o2} "2.547 ^d / ^{o2} +2.368
Si1 ^a –O2	1.584(2)	Si2 ^a –O6 ^a	1.571(5)
Si1 ^a –O3	1.596(2)	Si2 ^a –(O5/OH5/W5)	1.592(2)
Si1 ^a –O1 ^a	1.629(3)	Si2 ^a –O1 ^a	1.626(3)
Si1 ^a –O4 ^a	1.642(2)	Si2 ^a –O1 ^a	1.626(3)
average	1.612	average	1.604

W is used to describe the oxygen position of the H₂O molecule;

a: half occupied position;

c: O6 is present;

b: 1/4 occupied position;

d: W6 is present;

due to disorder either "(O4 + O1) or +(O1A + O1B) is present.

The least squares refinement was carried out with the program SHELXL-93 converging at a conventional $R(F)$ factor of 6.71%. Structure analysis of the average structure and chemical analyses clearly point to 5 Ca, 6 Si, and 22 O pfu. Of the 22 O pfu, at least 4 O are assigned to H₂O molecules because they are bonded to only one Ca (or to two 1/4 occupied Ca sites) and they display increased atomic displacement parameters due to the weaker bonding properties. The experimental parameters are listed in Table 1 and the refined atomic parameters are given in Table 2.¹ Selected atomic distances are summarised in Table 3.

Structure description of clinotobermorite

The Ca arrangement in the polyhedral layer

The clinotobermorite structure consists of a polyhedral layer formed by edge-connected Ca1 octahedral double chains running parallel to b . Ca1–O distances are between 2.353(2) Å and 2.546(6) Å. The co-ordination polyhedra are angularly distorted and have a two-fold screw-axis parallel to b , passing through the shared octahedral edge (Fig. 3). As the double chains of Ca1 octahedra are very close to each other, O2 of the equatorial oxygens in the neighbouring double chain is only 2.620(3) Å apart from the distorted octahedron (Fig. 3). Thus O2 of the neighbouring double chain is included into the Ca co-ordination sphere leading to seven-fold co-ordinated Ca1. The resulting Ca1 polyhedra are edge connected to every

Table 3. Selected cation-anion distances for clinotobermorite.

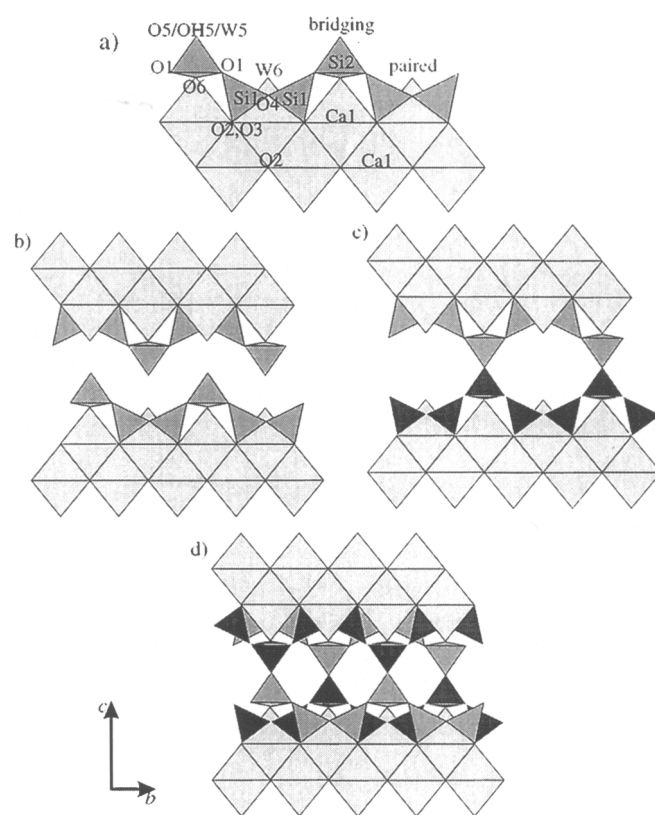


Fig. 4. Schematic drawing of the sandwich layer arrangement in clinotobermorite projected parallel to a . **a)** The Ca polyhedral layer with the attached 'Dreiereinfachkette' is displayed. This $[\text{Si}_3\text{O}_9]$ chain consists alternately of two 'paired' (Si1) and one 'bridging' (Si2) tetrahedra. The sandwich layers are stacked parallel to c . **b)** A bridging tetrahedron of the top layer can face two paired tetrahedra on the bottom. **c)** Two bridging tetrahedra can face each other, leading to eight membered rings. **d)** The two arrangements are superimposed and cannot be distinguished in the substructure.

neighbouring Ca1 polyhedron building an undulated fully occupied Ca–O layer expanding infinitely along the a – b plane, stacked along c (Fig. 4).

¹ Additional material to this paper can be ordered referring to the no. CSD 403090, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of F_o/F_c -data is available from the author up to one year after the publication has appeared.

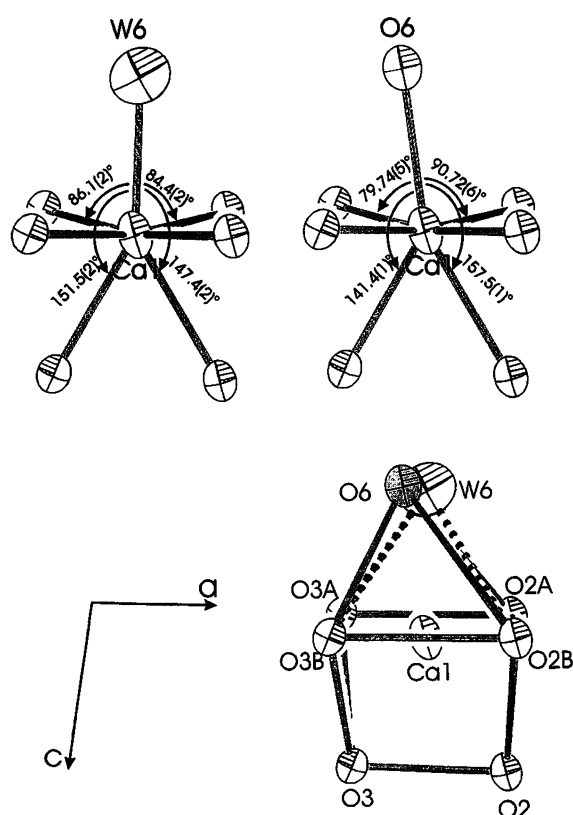


Fig. 5. The seven-fold co-ordination of Ca1 has a tetragonal pyramid as the top part and a dome as the bottom part. The pyramidal top shows positional disorder and is either occupied by W6 or O6. The displacement ellipsoids are drawn with 80% probability.

The seven-fold Ca1 co-ordination polyhedron has a pyramidal part on one side and a dome part on the other side joining the equatorial oxygen atoms (Fig. 3, 5). The Ca1–O distances of the equatorial oxygen atoms (representing the pyramidal and dome base) are $2 \times 2.353(2)$ Å to O2 and $2 \times 2.381(2)$ Å to O3. The dome apices O2 and O3 have Ca1–O distances of 2.620(3) Å and 2.484(3) Å. The opposite pyramidal apex of the Ca1 polyhedron is formed by O6 with a Ca1–O distance of 2.546 Å. The O6 position is only half occupied and exhibits positional disorder with a half occupied H₂O (W6) position, 0.44(1) Å apart from O6. The O6/W6 disorder is caused by the doubled periodicity of the [Si₃O₉] ‘Dreiereinfachkette’ parallel to *b* relative to the Ca1 polyhedral layer (Fig. 4). Thus, only each second O6 is attached to Si2 and the pyramidal Ca1 apex in between is formed by W6 (Fig. 4).

The tetrahedral chains

Si-tetrahedra forming infinite ‘Dreiereinfachketten’ expanding parallel to *b* are attached to the undulating Ca1 layers. These [Si₃O₉] chains flank the Ca layers on either side resulting in a sandwich like arrangement. The chain topology can be described as two ‘paired’ [Si_{1.5}O₇] tetrahedra connected by a ‘bridging’ tetrahedron. In other words, one ‘bridging’ [Si₂O₃(OH)] tetrahedron connects two ‘paired’ [Si_{1.5}O₇] tetrahedral units to form a wave-like infinite single chain (Fig. 4a). This nomenclature is very common in cement research and is adopted from Taylor

(1992). The ‘Dreiereinfachkette’ is linked to the Ca layer alternating with the paired and bridging tetrahedra. The paired tetrahedra are connected to O2 and O3 of the dome whereas the bridging tetrahedron joins the pyramidal apex O6. Both connection modes alternate leaving every second Ca1 polyhedron apex unconnected to the bridging tetrahedron; this apex is now able to house a H₂O molecule (W6). The starting point for the attachment to the Ca1 layers is not fixed, hence either a bridging tetrahedron or two paired tetrahedra can be attached to one Ca1 polyhedron with the same probability. In the clinotobermorite substructure the two variants can not be distinguished leading to half occupied superimposed ‘Dreiereinfachketten’ showing positional disorder along the chain by being statistically shifted by *b*/2 (Fig. 4c).

The apex O5 (Si2–O5 = 1.592(2) Å) of the bridging tetrahedron points into the interlayer space towards the next polyhedral layer (Figs. 3, 4a–c). The opposite chain in the neighbouring sandwich layer behaves the same. Assuming an ordered structure, the bridging tetrahedron can: (a) point parallel to *c* towards the paired tetrahedra leading to an interlayer space with wavy surface (Fig. 4b) thus the composition is Ca₅[Si₃O₈(OH)]₂ · 4 H₂O with all OH at O5; (b) by considering the possible shift of *b*/2 the bridging tetrahedron of one sheet can also meet the opposite bridging tetrahedron by joining the apex O5 (Fig. 4c). Thus, double chains with eight-membered rings are formed. This arrangement leads to the formula Ca₅[Si₆O₁₇] · 5 H₂O with O5 alternating in chain direction as O^{2–} and H₂O (W5). In case (a) O5 is connected to only one Si2 and the disordered Ca2. Consequently, O5 is strongly underbonded and is capable of bearing an OH group. In model (b) O5 as interconnecting oxygen resides on a twofold axis at 1/2, 1/2, 0 in the middle of the interlayer space and apparently connects two parallel layers via an energetically unfavourable Si–O–Si angle of 180°. As the displacement parameters of O5 (Table 3) are considerably smeared out in the *a*–*b* plane the 180° angle is probably prevented by O5 positional disorder.

The interlayer cavities

Due to the monoclinic angle of 96.97° parallel sandwich layers have an offset along *a* of 1.23 Å leading to a wavy interlayer providing space for disordered cations and H₂O. The relatively rigid sandwich layers are held together either by OH...O bonds and the interlayer Ca2 or by the [Si₆O₁₇]^{10–} double chains (model b) forming eight-membered rings (Fig. 4c). The interlayer cavities are occupied by a 1/4 populated Ca2 and a half occupied W7; the interlayer distances are about 4.55 Å with a free aperture of ca. 3.2 Å (calculated from the covalent oxygen radii). In the cavities Ca2 is located on a 1/4 occupied split position shifted from the centre of the cavity. The Ca2 oxygen co-ordination is seven-fold and therefore similar to Ca1, though more strongly distorted. Ca2–O distances range from 2.156(3) Å to 2.900(8) Å or 2.938(12) Å depending on whether O6 or W6 is present. The Ca2–O distances to the second O6 or W6 group are 2.306(6) Å or 1.984(12) Å, respectively. This indicates that this latter Ca2 site can only be populated if W6 is vacant and O6 is

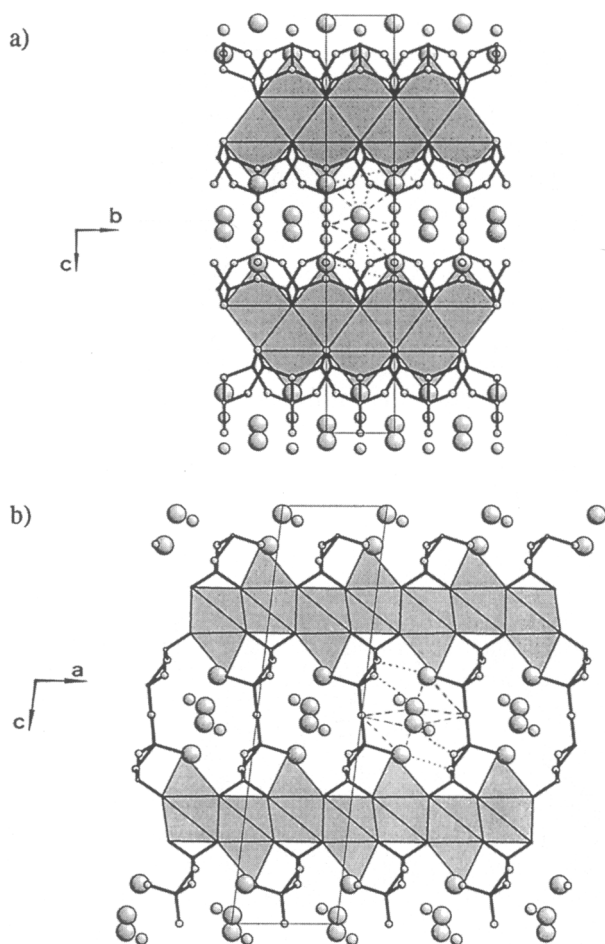


Fig. 6. The Ca1 co-ordination of the clinotobermorite substructure is represented by polyhedra. Balls and sticks are used for the $[\text{Si}_3\text{O}_9]$ 'Dreiereinfachketten'. The large spheres are H_2O , W6 at the Ca1 pyramidal top, and W7 in the interlayer cavities. The smaller spheres in the interlayer space symbolise the 1/4 occupied Ca2. **a)** A view parallel to *a* with the Ca1 layers flanked by $[\text{Si}_3\text{O}_9]$ 'Dreiereinfachketten'. In the centre of the interlayer cavity resides the half occupied H_2O (W7), represented by large spheres. **b)** View of the clinotobermorite substructure parallel to *b*. The offset of the sandwich layers due to the monoclinic angle is displayed. W7 is located in the interlayer centre and next to it, with smaller spheres, the 1/4 occupied Ca2 is shown.

filled. Depending on whether the paired or the bridging tetrahedra of the 'Dreiereinfachkette' are close to the occupied Ca2 site either $2 \times \text{O}1$ with $2 \times 2.242(4) \text{ \AA}$ or $\text{O}4$ and $\text{O}1$ with $2.407(4) \text{ \AA}$ and $2.981(4) \text{ \AA}$ are connected to Ca2.

The interlayer H_2O position and the $\text{OH} \dots \text{O}$ bonds

The interlayer H_2O molecule W7 refined to a position with two symmetry equivalent half occupied sites $0.87(2) \text{ \AA}$ part from each other. It participates in the Ca2 co-ordination and contributes with $2 \text{ H}_2\text{O}$ pfu to the H_2O content of clinotobermorite. $\text{OH} \dots \text{O}$ bonds from W7 can be predicted to $\text{O}1$ and $\text{O}5/\text{OH}5/\text{W}5$ with distances of $2.760(10) \text{ \AA}$ and $3.347(7) \text{ \AA}$, $\text{O}1$ and W6 ($2.760(10) \text{ \AA}$ and $2.686(9) \text{ \AA}$, $2 \times \text{O}6$ ($2 \times 2.686(9) \text{ \AA}$) or less probably to $2 \times \text{W}6$ ($2 \times 2.570(11) \text{ \AA}$). The choice as to which $\text{OH} \dots \text{O}$ bonds locally develop depends on the arrangement of the 1/2 occupied W7 relative to the local arrangement of Ca2, O6 and W6. If OH5 or W5 are present they

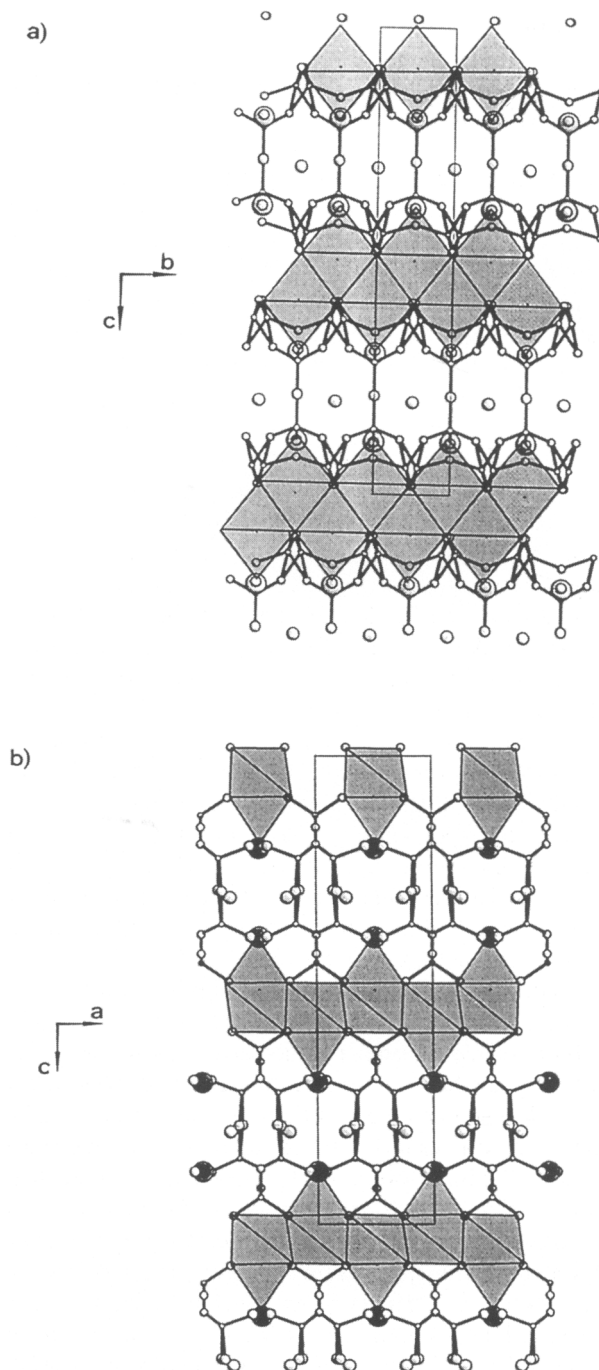


Fig. 7. **a)** The tobermorite substructure (Hamid, 1981) parallel to *a* is displayed showing the same sandwich arrangement as in Fig. 6a for clinotobermorite. The disordered half occupied Ca occupies the cavity centres. **b)** Parallel to *b* the second mirror plane related position of the bridging tetrahedron of the 'Dreiereinfachkette' is visible. Only Ca is situated in the interlayer space.

can either hydrogen bond to W7 or W6 with distances of $3.347(7)$ or $2.980(11) \text{ \AA}$. W6 can either bond to W7 ($2.686(9) \text{ \AA}$) and $\text{O}4$ ($2.785(10) \text{ \AA}$), or to $\text{O}5/\text{OH}5/\text{W}5$ ($2.980(10) \text{ \AA}$) and W7 ($2.570(11) \text{ \AA}$), or to $\text{O}4$ ($2.785(11) \text{ \AA}$) and $\text{O}5/\text{OH}5/\text{W}5$ ($2.980(11) \text{ \AA}$). The possible $\text{OH} \dots \text{O}$ bonds are shown as dashed lines in Fig. 6a and 6b. A definite distribution of H atoms, a correct system of hydrogen bonds and, a reliable description of the Ca2 co-ordination will only be possible after the understanding of the full structure.

Discussion

Structural comparison of clinotobermorite and 11 Å tobermorite

Clinotobermorite (**ct**) is structurally closely related to 11 Å tobermorite (**t**). The sandwich assemblage of Ca layers, perpendicular to *c*, flanked by $[\text{Si}_3\text{O}_9]$ 'Dreiereinfachketten' on either side pointing into the interlayer space are the central structural units for both minerals. Thus, the clinotobermorite subcell structure could be regarded as a squeezed derivative of the 11 Å tobermorite subcell structure (Hamid, 1981), though with shifted sandwich layers. Accordingly, the corresponding sandwich layers are very similar with the same Ca co-ordinations and with only slightly different distortions. Thus in a projection of the subcells parallel to *a* the only visible difference between clinotobermorite (Fig. 6a) and 11 Å tobermorite (Fig. 7a) is the additional H_2O in the interlayer space of **ct**.

In 11 Å tobermorite the Ca atoms of the neighbouring layers are stacked exactly above each other whereas a layer shift along *a* occurs in **ct** due to the monoclinic angle. In the orthorhombic space group of the **t** subcell *Imn2* (Hamid, 1981), the bridging tetrahedron has an additional position, mirror plane related to the first, leading to disorder along the *a* direction thus doubling the *a* axis in the ordered super-structure. This mirror plane does not exist in **ct**. The doubling of the subcell parallel to *a* in the monoclinic phase is caused by *b*/2 shifts of two neighbouring $[\text{Si}_3\text{O}_9]$ chains on the same side of the Ca polyhedral unit. The interspace diameter is 3.2 Å for clinotobermorite and 3.0 Å for tobermorite (calculated from O to O minus the covalent oxygen radii).

In both structures the disordered Ca positions in the interlayer space have a seven-fold surrounding as found for the fully occupied Ca positions within the layers. The half occupied Ca position in **t** is centred in the interspace cavity (Fig. 7a, b) as observed for the H_2O position in **ct** (Fig. 6a, b). Ca2 in **ct** is separated by 2.038(4) Å from the H_2O position. In **t** the H_2O site attached to the Ca polyhedral layer is only occupied if the bridging Si tetrahedron is absent (due to *b*/2 shifts). This leads to a higher water content in clinotobermorite (4 or 5 H_2O pfu depending on the structural model) than in tobermorite with only 2 H_2O pfu. Owing to the higher H_2O content in **ct**, the density increases to 2.80 g/cm³ whereas **t** has a density of 2.43 g/cm³. As **ct** and **t** are frequently associated minerals it seems highly unlikely that the more dense phase (**ct**) is formed under a significantly higher pressure than **t**. The most probable explanation is a different linkage of the sandwich layers in both structures. Tobermorite exists in two varieties, so called normal **t** and anomalous **t**, where the first variety shows ion diffusion and ion/water exchange capabilities which is not the case for the second (Mitsuda, Taylor, 1978; Taylor, 1992). Both have the same subcell but in anomalous **t** the bridging $[\text{SiO}_4]$ tetrahedra may form double chains with eight-membered rings (Engelhardt, Michel, 1987) that prevent the channel atoms from migrating through. Due to the high probability of tetrahedral double chains in **ct** (model b), **ct** is not expected to expand parallel to *c* as observed for the 14 Å **t**

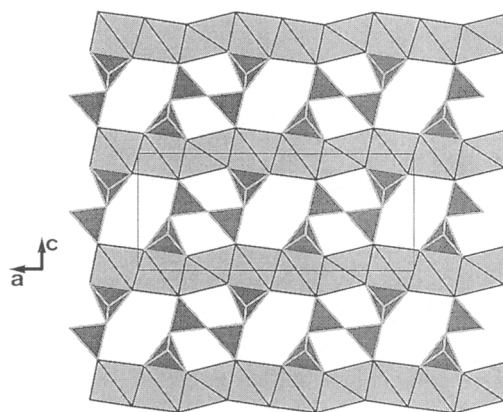


Fig. 8. The substructure of xonotlite (Eberhard, Hamid, Röttger, 1981) parallel to *b* is shown with $[\text{Si}_6\text{O}_{17}]$ tetrahedral double chains linking the 'wave-like' Ca layers.

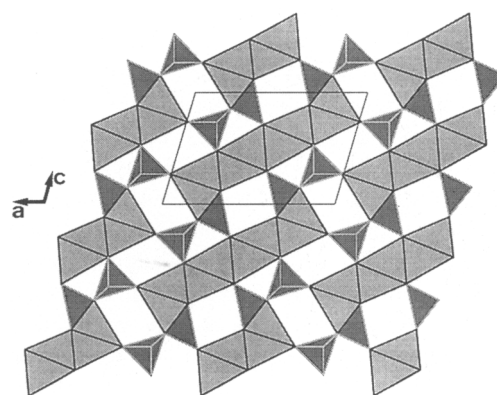


Fig. 9. Image of the foshagite structure (Gard, Taylor, 1960) with interrupted Ca sheets linked by 'Dreiereinfachketten'.

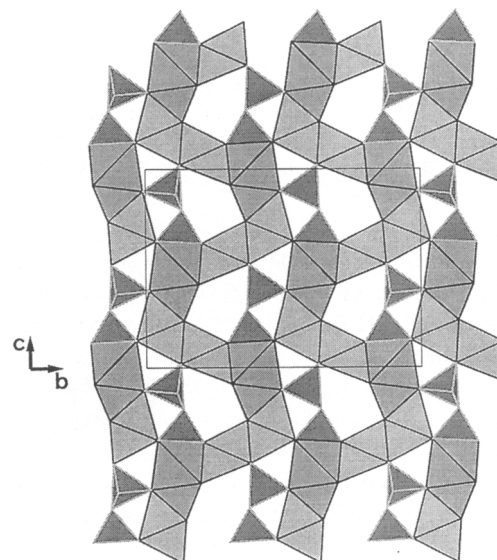


Fig. 10. The substructure of hillebrandite (Dai, Post, 1995) with corrugated edge-connected Ca layers corner-linked to the neighbouring layer forming tunnels which house the $[\text{Si}_3\text{O}_9]$ single chains.

modification. Furthermore, the **ct** structure is also stabilised against dehydration because possible double chains will prevent contraction along the *c* direction as observed for 9 Å **t**.

The silanol groups

Recently Nyfeler and Armbruster (1997) studied the influence of silanol groups on the Si–O bond lengths in various silicate structure types and found that a $\text{SiO}_3(\text{OH})$ tetrahedron linked to two additional SiO_4 tetrahedra (characteristic of single chains) has an average Si–O distance of 1.619 Å (excluding the Si–OH bond) whereas the Si–OH bond is elongated to 1.638 Å. The same type of analysis for $\text{SiO}_3(\text{OH})$ tetrahedra linked to three additional tetrahedra (characteristic of layers or double chains) led also to average Si–O distances of 1.619 Å (without the Si–OH bond) whereas the Si–OH bond was shortened to 1.604 Å. In case of **ct** the average Si–O bond lengths of 1.612 Å for SiO_4 and 1.608 Å for $\text{Si}_2(\text{O},\text{OH})_4$ are close to the $\langle\text{Si–O}\rangle$ distances determined statistically by Nyfeler and Armbruster (1997). The Si2–OH5 distance of 1.592 Å in clinotobermorite is significantly shortened and therefore different to the average Si–OH distances (1.638 Å) found in tetrahedral single chains. This observation should be considered a strong argument for a possible double chain arrangement in clinotobermorite.

El-Hemaly, Mitsuda and Taylor (1977) determined experimentally that normal tobermorite with Si–OH groups at the bridging tetrahedron forms as a precursor of anomalous tobermorite with double chains. Thus for a natural sample of sufficient crystal size the anomalous variety should be expected. Liebau (1980) concluded that in pyroxenoids with unbranched single chains and an odd number of $[\text{SiO}_4]$ in the repeat unit of the chains silanol groups are preferred at the paired tetrahedra because the folding of the chains offers favourable intra-chain hydrogen bonds. Such silanol groups in clinotobermorite are unlikely because hydrogen bonds would be developed parallel to a Ca1 polyhedral edge (O2–O2 or O3–O3). Furthermore, such hydrogen bonds should decrease the cell dimension parallel to the chain direction by ca. 0.25 Å (Liebau, 1980) which is not found in clinotobermorite.

Other C–S–H minerals with the 7.3 Å axis length feature

The tobermorite group is structurally not well defined because only few crystal structures or substructures have been solved (Taylor, 1992). Based on the scarce data some common structural principles can be identified. This group is composed of ribbons of $\text{Ca}(\text{O},\text{OH})_{6-7}$ polyhedra building sheets where above and below the sheet wollastonite-related $[\text{Si}_3\text{O}_9]$ chains ('Dreiereinfachketten') with a periodicity of ca. 7.3 Å are attached forming a sandwich-like assemblage. In addition, the $[\text{Si}_3\text{O}_9]$ chains may be polymerised with each other to form double chains or even tetrahedral layers. Between these sandwich-like units additional Ca and H_2O may be accommodated. This mineral group comprises tobermorite with its various hydration variants (Hamid, 1981; Hamid Rahman, Beyrau, 1988), clinotobermorite (this study), plombierite – a hardened gel – with a chemical composition close to 14 Å tobermorite (McConnell, 1954), riversideite – probably identical or strongly related to 9 Å tobermorite – (McConnell, 1954), okenite $\text{Ca}_{10}\text{Si}_{18}\text{O}_{46} \cdot 18 \text{H}_2\text{O}$ (Merli-

no, 1983) with tetrahedral sheets and double chains, both assembled of 'Dreiereinfachketten' (subcell space group $P\bar{1}$, $a = 9.69$ Å, $b = 7.28$ Å, $c = 22.02$ Å, $\alpha = 92.7^\circ$, $\beta = 100.1^\circ$, $\gamma = 110.9^\circ$), nekoite $\text{Ca}_3\text{Si}_6\text{O}_{15} \cdot 7 \text{H}_2\text{O}$ (Alberti, Galli, 1980) a sheet silicate obtained by interconnecting 'Dreiereinfachketten' (space group $P1$, $a = 7.588$ Å, $b = 9.793$ Å, $c = 7.339$ Å, $\alpha = 111.77^\circ$, $\beta = 103.50^\circ$, $\gamma = 86.53^\circ$), ovelite $\text{Ca}_{10}\text{B}_2\text{Si}_8\text{O}_{29} \cdot 12 \text{H}_2\text{O}$ (Kusachi, Henmi, Henmi, 1984) with orthorhombic cell dimensions close to 11 Å tobermorite ($a = 11.25$ Å, $b = 7.25$ Å, $c = 5.911$ Å), and tacharanite $\text{Ca}_{12}\text{Al}_2\text{Si}_{18}\text{O}_{33}(\text{OH})_{36}$ (Cliff, Gard, Lorimer, Taylor, 1975) with an *A*-centred monoclinic pseudo-cell ($a = 17.07$ Å, $b = 3.65$ Å, $c = 27.9$ Å, $\beta = 114.1^\circ$; b is certainly, a and c are probably doubled in the true cell), the structure is also related to 11 Å tobermorite. Taylor (1992) provides strong arguments that also jennite should be considered as a member of the tobermorite group. The structure (triclinic cell parameters $a = 10.593$ Å, $b = 7.284$ Å, $c = 10.839$ Å, $\alpha = 99.67^\circ$, $\beta = 97.65^\circ$, $\gamma = 110.11^\circ$) is assumed to be similar to tobermorite to allow structural intergrowth resembling stacking faults along the stacking direction of the $\text{Ca}(\text{O},\text{OH})_{6-7}$ – $\text{Si}_3(\text{O},\text{OH})_9$ layers (Gard, Taylor, Cliff, Lorimer, 1977).

The C–S–H cement minerals with assumed $[\text{Si}_3\text{O}_9]$ chains forming during the binding process are the above described tobermorite group compounds and additional minerals which also exhibit the 7.3 Å periodicity. Xonotlite $\text{Ca}_6[\text{Si}_6\text{O}_{17}](\text{OH})_2$, (e.g., Eberhard, Hamid, Röttger, 1981) has 'Dreiereinfachketten' connected to double chains (Fig. 8) and exhibits manifold ways of polytypes (subcell space group $C2/m$, $a = 17.03$ Å, $b/2 = 3.678$ Å, $c/2 = 7.003$ Å, $\beta = 90.32^\circ$). Kudoh and Takéuchi, (1979), refined the structure of an $A\bar{1}$ polytype ($a = 8.712$ Å, $b = 7.363$ Å, $c = 14.023$ Å, $\alpha = 89.99^\circ$, $\beta = 90.36^\circ$, $\gamma = 102.18^\circ$). ^{29}Si MAS NMR spectra on xonotlite confirmed the double chains giving rise to two maxima with chemical shifts $\delta(\text{ppm})$ at -86.8 and -97.6 and an intensity ratio 2:1 for the two paired SiO_4 tetrahedra with two Si neighbours each and one bridging SiO_4 tetrahedron with three Si neighbours (Engelhardt, Michel, 1987). Tokkoite $\text{K}_2\text{Ca}_4[\text{Si}_7\text{O}_{18}(\text{OH})](\text{F},\text{OH})$ (Rozhdestvenskaya, Nikishova, Lazebnik, Lazebnik, 1989) also joins the xonotlite group but with a hybrid 'Dreierdoppelkette' where the paired tetrahedra are connected by two bridging tetrahedra (space group $P\bar{1}$, $a = 10.438$ Å, $b = 12.511$ Å, $c = 7.112$ Å, $\alpha = 89.92^\circ$, $\beta = 99.75^\circ$, $\gamma = 92.89^\circ$).

Foshagite $\text{Ca}_4[\text{Si}_3\text{O}_9](\text{OH})_2$ (Gard, Taylor, 1960) belongs to the wollastonite group and has undulated Ca octahedral layers (Fig. 9) with attached $[\text{Si}_3\text{O}_9]$ 'Dreiereinfachketten' (space group $A\bar{1}$, $a = 10.32$ Å, $b = 7.36$ Å, $c = 14.07$ Å, $\alpha = 90^\circ$, $\beta = 106.4^\circ$, $\gamma = 90^\circ$). There is, however, no interlayer space in this structure. The Ca polyhedral layers with attached OH groups are interrupted and connected by $[\text{Si}_3\text{O}_9]$ chains.

Although most of the C–S–H(I) structures have rather plain or undulated Ca layers or, layer fragments, hillebrandite $\text{Ca}_2\text{SiO}_3(\text{OH})_2$ (Dai, Post, 1995) exhibits a corrugated Ca polyhedral sheet (Fig. 10) connected by the $[\text{Si}_3\text{O}_9]$ 'Dreiereinfachketten' (subcell space group $Cmc2_1$, $a = 3.639$ Å, $b = 16.311$ Å, $c = 11.829$ Å).

Conclusions

Clinotobermorite is one more example for the structural variety of C—S—H phases in nature. Although, at first glance clinotobermorite and tobermorite seem to be structurally very similar and consequently seem to have similar physical and chemical properties, on closer inspection, however, important differences can be seen: The higher H₂O content in clinotobermorite compared with the tobermorite structure leads to a higher density. Obviously, there seems to be no tendency to expand the interlayer distances in clinotobermorite, on the contrary, the sandwich layers are just shifted against each other. The closer packing of sandwich layers in clinotobermorite is most probably caused by the formation of 'Dreierdoppelketten' as already established for xonotlite (Kudoh, Takéuchi, 1979; Engelhardt, Michel, 1987). Consequently, clinotobermorite cannot be expected to have the same properties as tobermorite which is worth examination in greater detail by ²⁹Si MAS NMR spectroscopy to obtain information as to the environment of the disordered tetrahedra and to determine the exact chain topology.

The crystal structure analysis of the substructure of clinotobermorite clearly points to 5 Ca, 6 Si, 22 O, and 10 H (for charge balance). This composition can be interpreted as Ca₅[Si₃O₈(OH)]₂ · 4 H₂O with 'Dreiereinfachketten', as Ca₅[Si₆O₁₇] · 5 H₂O with 'Dreierdoppelketten', or as a combination of both variants. The electron microprobe analyses performed by us and the chemical analyses by Henmi and Kusachi (1992), however, indicate 23 O for the same number of Si and Ca which may be indicative for chemical and structural variations in the bulk sample.

Provided the phases are not pure, clinotobermorite and tobermorite are difficult to distinguish in a powder diffraction pattern as the lattice parameters for both are very similar. The peak splitting of the monoclinic powder pattern is not well pronounced due to the monoclinic angle of 96.97°, particularly in poorly crystallised material. The measured peak intensities are the major difference between *ct* and *t* powder diffractograms (Henmi, Kusachi, 1992). In phase mixtures — as it appears in synthetic cement — the peaks may overlap and intensities are less reliable. Consequently, clinotobermorite in artificial cements is difficult to detect. On the other hand, however, the anomalous tobermorite phase which shows no exchange properties is well known in cement research (Taylor, 1992) and we would expect that this tobermorite variety is either structurally close to clinotobermorite or even identical to it.

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