

### 8.1.4.5 Tobermorite group of silicates

The silicates from the above group are listed in Table 1. For crystal structures and lattice parameters see Table 3.

#### 8.1.4.5.1 Crystal structures. Lattice parameters

The mineral group of tobermorites comprises **tobermorites** with its various hydration variants: 9 Å (riversideite), 11 Å (tobermorite) and 14 Å (plombierite) [54M1, 81H1, 88H1], **clinotobermorite** [97H1, 99M1, 00M1], **okenite**,  $\text{Ca}_{10}\text{Si}_{18}\text{O}_{46} \cdot 18\text{H}_2\text{O}$  [83M1], with tetrahedral sheets and double chains, both assembled of “dreiereinfachketten” (subcell space group  $P\bar{1}$ ), **nekoite**,  $\text{Ca}_3\text{Si}_6\text{O}_{15} \cdot 7\text{H}_2\text{O}$  [80A1], a sheet silicate obtained interconnecting “dreiereinfachketten” (space group  $P1$ ), **oyelite**,  $\text{Ca}_{10}\text{B}_2\text{Si}_8\text{O}_{29} \cdot 12\text{H}_2\text{O}$  [84K1] with orthorhombic cell dimensions close to 11 Å-tobermorite and **tacharanite**,  $\text{Ca}_{12}\text{Al}_2\text{Si}_{18}\text{O}_{33}(\text{OH})_{36}$  [75C1] with an A-centered monoclinic pseudo-cell ( $b$  is certainly,  $a$  and  $c$  are probably doubled in the true cell) the structure being also related to 11 Å-tobermorite. In [92T1] strong arguments were provided that also **jennite** should be considered as a member of the tobermorite group. Their structure (triclinic) was assumed to be similar to tobermorite to allow structural intergrowth resembling stacking faults along stacking direction of the  $\text{Ca}(\text{O},\text{OH})_{6-7} - \text{Si}_3(\text{O},\text{OH})_9$  layers [77G1]. The crystal structure of jennite was analyzed in Chap. 8.1.2.8 (subvolume 27I2) according to the classification given by [91N1]. The **calcium silicate hydrates** (CSH), with assumed  $[\text{Si}_3\text{O}_9]$  chain forming during the bending process, are in the above described tobermorite group of compounds as well as additional silicates which also exhibit the 7.3 Å periodicity [97H1].

#### Tobermorites

The crystal structure of powders and single crystals of tobermorites were studied [53T1, 54M1, 56M1, 64T1, 78M1, 81H1, 88H1, 95Z1, 97M1, 99M1, 01M1]. In [54M1] was reported that a pseudo-cell of  $a/2$  and  $b/2$  can be chosen because all the reflections with either  $h$  or  $k$  odd were very weak and diffuse. For the above mentioned unit cell the space group  $C222_1$  was suggested. A first structure determination [56M1] reported also that tobermorite shows a similar disorder phenomenon like wollastonite [53J1] (wollastonite possesses also “dreierketten”). In [58M1] the possibility of the existence of double chains in tobermorite was suggested which was observed in natural and synthetic specimens [68W1, 79W1].

The structure of tobermorite is strongly disordered, causing, in addition to the sharp X-ray reflections, diffuse streaks. If Bragg reflections and streaks were considered, the unit cell appears *pseudo-orthorhombic* ( $a = 11.3$  Å,  $b = 7.3$  Å,  $c = 22.6$  Å). If only the sharp Bragg reflections were considered, a subcell with  $a/2$  and  $b/2$  with space group  $\text{Imm}2$  was obtained [81H1]. Single crystal structure analysis performed on the subcell yielded an average structure characterized 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 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 were various possibilities how such an average structure can be interpreted in terms of long-range disordered domains. One *ordered tobermorite* model was proposed to have  $P2_1$  symmetry [81H1]. 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 Å (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.

Since the physical properties of 11 Å-tobermorite (sect. 8.1.4.5.2...8.1.4.5.4) will be discussed in correlation with the proposed model of Hamid [81H1], a short description of this structure will be given. As seen from Fig. 1 the structure has infinite  $\text{Si}_3(\text{O}/\text{OH})_9$  chains running parallel to  $b$  which are linked together by calcium atoms. The Ca1, Ca2, Ca3 and Ca4 atoms, in general, are coordinated with seven oxygen atoms. These are layers of “nonlabile” calcium (Ca1 to Ca4). Between these layers are located the “labile” Ca ions (Ca5 and Ca6) which are mobile in the interlayer space. The environments of Ca1 and Ca2 are very similar, while in case of Ca3 and Ca4, although coordinated by seven oxygens, have slightly different arrangements as compared to Ca1 and Ca2. In general Ca1, Ca2, Ca3 and Ca4 are coordinated with four co-planar oxygen atoms, two oxygens above and below, forming a dome and the seventh oxygen below or above the co-planar oxygen group forming a tetragonal pyramid – Fig. 1. The octahedral coordination of Ca5 and Ca6 (if they are present) is similar and is very distorted [81H1]. The  $^{29}\text{Si}$  MAS NMR study of synthetic tobermorite showed that single chains and/or double chains of tetrahedra may occur [87E1]. In other words, the Ca polyhedral sheet acts as a template for various arrangements

of tetrahedral chains or even layers [97H1]. As mentioned above, one calcium layer in three is “labile”, i.e. the calcium atoms are statistically distributed among the sites. At a Ca/Si ratio of 0.66, the labile layers are empty. As the Ca/Si ratio increases, the labile layers are progressively occupied. The maximum occupancy in natural tobermorites is seen for Ca/Si = 0.83. In this case sites Ca5 and Ca6 are 50 % occupied. For Ca/Si = 0.66, the oxygens O8, O9, O14, and O18 of the bridging tetrahedra (Si3 and Si5) are hydroxylated— Table 2. The incorporation of labile calcium atoms in the structure creates an excess of positive charge, which is compensated by the loss of the protons of these oxygens. The number of water molecules intercalated between the chains of tetrahedra and the labile calcium layers seems to be constant over the  $0.66 < \text{Ca/Si} < 0.83$  range. The  $\text{H}_2\text{O/Si}$  ratio is 0.33 [96F1]. The non-stoichiometric behaviour was supposed to be due to tetrahedral vacancies and omission of interlayer Ca [81H1, 92T1, 97H1].

Synthetic tobermorites form three modifications with different  $\text{H}_2\text{O}$  contents, where the  $\text{H}_2\text{O}$  concentration strongly influences the length of the  $c$ -axis [88H1]. Tobermorites with 0, 2 and 6  $\text{H}_2\text{O}$  have a  $c$ -axis of 18 Å, 22 Å and 28 Å, respectively – Table 3. These were identified based on the  $d$ -spacing of their (002) powder diffraction and were classified as 9Å-, 11Å-, and 14Å-tobermorites. Their characteristic basal spacings are really 9.3, 11.3 and 14.6 Å.  $\text{H}_2\text{O}$  loss and ion exchange experiments were performed to examine the mechanism at water storage and diffusion mechanisms.  $\text{H}_2\text{O}$  is released in two steps, from 14Å-tobermorite to 11Å-tobermorite at 353 K and then to 9Å-tobermorite at 553 K. The first step involves the interlayer  $\text{H}_2\text{O}$  release, whereas in the second step, the more firmly connected  $\text{H}_2\text{O}$  attached to the more rigid Ca layers is released [88H1]. The “dry” 9 Å phase is only metastable and rehydrates to the 11 Å phase with  $2\text{H}_2\text{O}$  per formula unit. Tobermorite minerals vary in some properties, notably in whether or not unidimensional lattice shrinkage occurs by about 573 K to give a 9 Å form. Specimens that do this are called *normal* and the ones that do not are called *anomalous* [74T1, 77E1]. The term *mixed tobermorite* is used for samples showing various kinds of intermediate behaviour, of which the most usual was a change in the basal plane reflection to a broad peak about 10.5 Å, at 573 K [77E1].

The **clinotobermorite** was first reported by [89H1, 92H1], who studied its chemical and crystallographic properties and indicated the composition  $\text{Ca}_5\text{Si}_6(\text{O},\text{OH})_{18}\cdot 5\text{H}_2\text{O}$ . A Cc or C2/c-type structure was proposed. The unit cell parameters show a 7.3 Å translation – Table 3 – which is typical of the wollastonite-like silicate chains, “dreierketten”, according to the terminology of [56L1]. Another natural clinotobermorite (Wessels mine) was studied [97H1]. Diffuse and weak reflections, of the type hkl with  $h, k = 2n+1$  were observed. Neglecting these reflections, determined the family structure of the clinotobermorite in space group I2/m with  $A_s = a/2 = 5.638$  Å,  $B_s = b/2 = 3.672$  Å,  $C_s = c = 22.629$  Å,  $\beta_s = 97.03^\circ$ . The refinement of the family structure corresponding to halved  $a$  and  $b$  parameters [97H1] did not allow to determine definitely whether single or double chains of silicate tetrahedra actually occur in clinotobermorite. The presence of structural disorder (evidenced by the diffuseness of reflections with  $k$  odd), prevented the determination of its real structure.

In clinotobermorite there are four sevenfold coordinated crystallographically independent calcium polyhedra (Ca1, Ca3, Ca1A and Ca3A). In two of them, i.e. those centered by Ca3 and Ca3A, calcium cations lie in the center of the basal plane of the pyramid. The polyhedra centered by Ca1 and Ca1A are better described as monocapped trigonal prisms. The  $\text{Ca}^{2+}$  cations, in this case, do not lie in the basal plane of the “pyramid”, but are displaced towards the center of the trigonal prisms. The “capping” ligand is a  $\text{H}_2\text{O}$  molecule W6 or W6A. Both types of polyhedral models were considered according to their capability to describe various structural features. The peculiar way in which the calcium polyhedral layers are built is evidenced in Fig. 2 [00M1]. In clinotobermorite, the infinite silicate tetrahedral chains of wollastonite type, i.e. with repeat of every fourth tetrahedron (“dreierketten”), run along  $b$  on both sides of the calcium polyhedral layers. The wollastonite chains attached to successive calcium layers and facing each other are condensated through the bridging oxygen O5, thus giving rise to double chains of  $[\text{Si}_6\text{O}_{17}]^{10-}$  composition. A comparison of the silicate chains in some related silicates is shown in Fig. 2b [00M1]. The chains in xonotlite (Chap.8.1.4.6) are squeezed between two successive calcium polyhedral layers, 7Å apart, whereas in clinotobermorite the double chains present a larger width connecting calcium polyhedral layers more than 11Å apart. Similar chains have been found in the structure of 11Å-tobermorite. A common feature of the three above structures is the way by which the “paired” tetrahedra are attached to calcium layers. In the above cases, the paired tetrahedra are bonded to oxygen of the “dome” edges on both sides of the layers with a relative displacement by  $b/4$  [00M1]. 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  $\text{H}_2\text{O}$  molecules W5, W7 and W8. The W5 one is placed in the center 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 tetrahedral chains. The “zeolitic” components play an important role for the stability of the

whole structure. The half occupancies and unreliably short cation-H<sub>2</sub>O and H<sub>2</sub>O-H<sub>2</sub>O distances involving the Ca2 and H<sub>2</sub>O (W5, W7, W8) placed in the cavity point to a symmetry reduction and to an actual ordered distribution obtained by releasing the inversion center with decrease of the space group symmetry to C1 (triclinic polytype). In another situation some short Ca-O distances occur between the calcium cations in the half-occupied Ca2 and H<sub>2</sub>O 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 molecules occupy only one of the two positions related by the inversion center. A monoclinic structure is present. The lattice sites for triclinic clinotobermorite are given in Table 2d [00M1]. The same sites are present in the monoclinic lattice but generally with different atomic coordinates.

The application of the OD theory [56D1, 64D1, 72D1] to tobermorites allowed the determination of real structures of various phases [97M1, 99M1, 00M1, 01M1]. The various phases present OD structures consisting of layers of one kind. In these structures, adjacent layers may be arranged in two geometrically equivalent ways, which give rise to a family of possible structures, differing in the stacking of the layers. The symmetry features common to all members, are dealt with the OD theory which focus attention on space transformations which convert any layer into itself or into the adjacent one. Such space transformations are the so-called  $\lambda$  (symmetry operations of the single layer, corresponding to one of the 80 layer group) and  $\sigma$ -POs (partial operations which are not necessarily valid for the whole structure). The  $\sigma$ -operations convert a layer into the adjacent one and are fully described by the OD groupoid family symbol [72D1]. The various possible structures (ordered or disordered of the whole OD family) present common reflections, which always appear sharp, in the same position and with the same intensity (family reflections) and differ in the position and intensity shape of other reflections. The family reflections correspond to the so-called family structure, more loosely denoted as subcell structure [01H1]. The symmetry properties of the building layers, as well as the symmetry operations relating adjacent layers may be sometimes derived through a careful consideration of the diffraction patterns. In case of 11Å-tobermorite, it has been shown that the C centering condition is valid for the whole pattern [54M1]. The analyses of the data, obtained for various tobermorites, suggest a reliable structure for the single layer of 11Å-tobermorite having layer group symmetry C2m(m) [01M1]. In case of the OD groupoid family of 11Å-

tobermorite this is  $C\ 2\ m\ (m)$  where  $n$  indicates a glide normal to  $a$ , with translational components  $\{2_{1/2}\ n_{2,1/2}\ (n_{1/2,1/2})\}$

$rb/2 + c_o$ . The symbol 2 indicates a screw parallel to  $b$  with translation component  $rb/2$  ( $r = 1/2$ ). The parentheses in the third position indicate that  $c_o$  is not a translation vector. Layers with C2mm symmetry may follow each other in the  $c$ -direction, related by the operator  $n_{1/2,1/2}$  ( $\equiv n_{1/2,-1/2}$  due to the C centering of the single layer) normal to  $c$  or by operator  $n_{1/2,-1/2}$  ( $\equiv n_{1/2,1/2}$ ). Pairs of layers related in both ways are geometrically equivalent. The layers related by the operators  $n_{1/2,1/2}$  and  $n_{1/2,-1/2}$  are translationally equivalent and stacked according to the vectors:  $t_1 = c_o + (a + b)/4$  and  $t_2 = c_o + (a - b)/4$ , respectively. According to the OD theory, there are two polytypes of maximum degree of disorder (MDO). The MDO<sub>1</sub> corresponds to the sequence in which the operators  $n_{1/2,1/2}$  and  $n_{1/2,-1/2}$  alternate or, equivalently, to the regular alternation of  $t_1$  and  $t_2$  stacking vectors. The MDO<sub>2</sub> corresponds to the sequence in which the operator  $n_{1/2,1/2}$  is constantly applied, or, equivalently, to the constant application of the  $t_1$  stacking vector [01M1]. The MDO<sub>1</sub> polytype of anomalous 11Å-tobermorites (Wessels mine) is orthorhombic having space group F2dd and the MDO<sub>2</sub> one is monoclinic (space group B11m), the same as of the MDO<sub>2</sub> polytype from Ural mine. The crystal structure of the monoclinic polytype MDO<sub>2</sub> of anomalous tobermorite is plotted in Fig. 3a, of normal tobermorite from Ural in Fig. 3b and of anomalous tobermorite (Wessels mine) in Fig. 3c [01M1]. A common feature of the structural arrangements in tobermorite group, as already mentioned, is the layer built up by sevenfold coordination calcium cations. Also, in clinotobermorite two distinct types of polyhedra (Ca1, Ca3) were observed whereas in tobermorites the polyhedra are of one kind, which were defined as mono-capped trigonal prisms [00M1]. Columns of mono-capped trigonal prisms run along  $b$ . Adjacent columns in each layer present the capping ligands on its opposite surfaces. In both polytypes of 11Å-tobermorites, very similar Ca-O distances occur and the capping ligands are W6 and O6. Infinite silicate tetrahedral chains of wollastonite type run along  $b$  on both sides of the calcium polyhedral layers. These chains may be described as built up by "paired" Si<sub>2</sub>O<sub>7</sub> tetrahedra (centered by Si1 and Si3 cations) connected by a "bridging" tetrahedron (centered by Si2). Each chain is firmly linked to a column of calcium trigonal prisms, with the "paired" tetrahedra grasped to it by sharing the oxygen atoms of the edges opposite to the capping ligands, while the bridging tetrahedron shares the capping O6 ligand of the adjacent column – Fig. 3d [01M1]. Successive tetrahedral chains on one side of the layer are shifted by  $b/2$ . The

tetrahedral chains on the hidden side are similarly connected to the layer, with paired tetrahedra grasped to the alternate columns and shifted by  $\pm b/4$  relatively to those on the visible side [01M1]. As in clinotobermorite, the wollastonite-like chains grasped to successive Ca layers and facing each other are condensed through the bridging oxygen O5 lying on the symmetry plane normal to  $c$ , thus building double chains with symmetry [2mm], to compare with the  $[-2/m-]$  symmetry of the corresponding double chains in clinotobermorite [01M1].

A model for the real structures of clinotobermorite was also proposed on the basis of OD theory [00M1]. Two polytypes with maximum degree of order (MDO) were confirmed by the structure refinements. The MDO<sub>1</sub>-polytype is monoclinic having space group Cc and MDO<sub>2</sub> one is triclinic with space group C1 – Table 3. These structures were already presented.

The main differences between the two structures of 11Å-tobermorites as well as of clinotobermorites is the content of cavities. In anomalous 11Å-tobermorite only water molecules are located in the cavities – Fig. 4a. The crystal chemical formula for 11Å-tobermorite (Wessels mine) is  $\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ . The cavities of 11Å-tobermorite from Ural mine contain “zeolitic” calcium cations, Ca2, in general position with occupancies  $\frac{1}{4}$ , W2 water molecules, with full occupancy and in position similar to that of the corresponding molecule in the sample from Wessels mine and W1, W3 water molecules, with occupancy  $\frac{1}{2}$ . Two distinct situations occur with the same probability. In one, the “zeolitic” calcium (Ca2) is located on either side of the reflection plane – Fig. 4b. In the other case Ca2 is absent (see 11Å-tobermorite from Wessels mine). When the Ca2 is located on the upper side, relatively to the reflection plane, W1 and W3 are located on the opposite side and form fairly strong bonds with Ca2 which is also firmly connected to W2, O2 and O6 and more loosely bonded to O1 and O7 – Fig. 4b [01M1]. The atomic configuration is closely similar to that realized in clinotobermorite (Wessels mine) – Fig. 4c. When Ca2 is absent, most probably W1 and W3 shift their positions towards the symmetry plane as shown in the 11Å-tobermorite (Wessels mine) – Fig. 4a. Therefore, considering Ca2 cations and O6 anions, there are two distinct situations, corresponding to the presence or absence of the “zeolitic” calcium cations: (1)  $\text{Ca}^{2+} + 2\text{O}^{2-}$ , as in case of clinotobermorite [00M1] and (2)  $\square + 2\text{OH}^-$  as in case of anomalous 11Å-tobermorite (Wessels mine). As both situations occur with the same frequency, the average results correspond to  $0.5\text{Ca}^{2+} + 1\text{O}^{2-} + 1\text{OH}^-$  and the composition of 11Å-tobermorite (Ural mine) is  $\text{Ca}_{4.5}\text{Si}_6\text{O}_{16}(\text{OH}) \cdot 5\text{H}_2\text{O}$ .

In case of partial substitutions of Si by Al, which mainly occurs in the bridging tetrahedron Si2 [85K3], general and local charge balance is restored through additional  $\text{OH}^-$  for  $\text{O}^{2-}$  substitutions in O6 site. These coupled substitutions justify the composition of 11Å-tobermorite (Ural mine), namely  $\text{Ca}_{4.42}\text{K}_{0.04}\text{Si}_{5.68}\text{Al}_{0.32}\text{O}_{15.56}(\text{OH})_{1.44} \cdot 5\text{H}_2\text{O}$  [01M1].

### Calcium silicate hydrate (CSH)

Calcium silicate hydrate (CSH) is the main component of cements and forms during the hydration of calcium silicate present in Portland cements. They are characterized by an X-ray diffraction pattern with few peaks [53T1]. Without being amorphous they therefore have a structure organized over distances of less than 100 Å. According to [81J1] CSH consists of nanometer-thick, micrometer-sized foils which intergrow and densify during the hydration. It is generally accepted that silicate anions (tetrahedra) present in CSH are polymerized and their degree of polymerization increased with time [78D1, 83H1]. The X-ray diffraction studies have not resolved their structure, but have demonstrated structural similarities with tobermorite, confirmed also by  $^{29}\text{Si}$  MAS NMR spectroscopy [89G1, 94O1, 95C1].

CSH's have a variable stoichiometry [50T1, 65G1] and were commonly defined by their Ca/Si ratio. The major phases forming during the binding process of Portland cements are 14Å- and/or 11Å-tobermorite  $\text{Ca}_{4.5}\text{Si}_6\text{O}_{15}(\text{OH})_3 \cdot x\text{H}_2\text{O}$  [69T1, 81H1, 92T1, 97T1] and jennite  $\text{Ca}_9\text{Si}_6\text{O}_{16}(\text{OH})_{10} \cdot 6\text{H}_2\text{O}$  [76G1, 77G1]. According to low-pressure and temperature conditions during their formation in the cement, these compounds are polycrystalline (like gels) or assemble of fragments with  $[\text{Si}_2\text{O}_7]$  groups which form first, developing to longer species which finally form infinite chains [86T1]. In [92T1] CSH(I) gels were defined as structurally closer to tobermorite and CSH(II) gels as closer to jennite. Most of CSH silicates are known to form during the cement binding process but they also occur in nature as hydrothermal alteration products of calcium carbonate rocks and vesicle fillings in basaltic rocks. Many authors have attempted to synthesize CSH, at or near room temperature, from various starting materials [50T1, 65G1, 81F1, 89A1, 93S1]. In [89A1] CSH was synthesized by the hydrolysis of mixed alkoxide precursors. In [93S1] 14Å-tobermorite was synthesized like CSH by room temperature titration of NaOH to a mixture of monomeric silicic acid  $[\text{Si}(\text{OH})_4]$  and  $\text{CaCl}_2$  solutions as the starting materials.

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Ion exchange reactions were analyzed in tobermorites. Mechanisms of the ion exchange reaction in 11Å-tobermorite were proposed first by [57K1, 82K1, 83K1]. The mechanism of  $\text{Cs}^+$  uptake was explained by  $\text{Al}^{3+}$  substitution for  $\text{Si}^{4+}$ , i.e.,  $\text{H}_3\text{O}^+$  subsequently participating in exchange with  $\text{Cs}^+$ . In [57K1] was pointed out that in order to maintain electrical neutrality, the possible substitutions are  $(\text{Al}^{3+}+\text{H}^+)$  for  $\text{Si}^{4+}$ ,  $2\text{Al}^{3+}$  for  $(\text{Si}^{4+}+\text{Ca}^{2+})$  or  $4\text{Al}^{3+}$  for  $3\text{Si}^{4+}$ . Unsubstituted 11Å-tobermorite also exhibits cation exchange although it does not contain aluminium. The thermal data remain practically unchanged after exchange, indicating that water does not take part in the exchange process [91L1]. Some investigations [85K1, 85S1, 86S1, 88L1, 89L1, 89L2, 91L1, 91S1, 93R1], however, confirmed the release of  $\text{Ca}^{2+}$  ions in almost equivalent amounts to balance the charge. The mechanism of exchange reaction in 11Å-tobermorite was thus interpreted starting from the structure reported by [81H1]. It was expected that the interlayer calcium content is responsible for charge balance in cation exchange [91L1]. Exchange experiments on 11Å-tobermorite with  $\text{Fe}^{3+}$  resulted in a maximum uptake of 16 % with almost intact crystallinity [91L1], while  $\text{Mg}^{2+}$  showed an even higher uptake, up to 21 % [91S1]. According to [91L1] the most probable sites for introduced  $\text{Fe}^{3+}$  ions are the interlayer spaces vacanted by releasing Ca atoms. The exchange relation of 11Å-tobermorite can be represented by the equilibrium relation:  $2\text{Fe}_{\text{solution}}^{3+} + 3\text{Ca}_{\text{tobermorite}}^{2+} \leftrightarrow 2\text{Fe}_{\text{tobermorite}}^{3+} + 3\text{Ca}_{\text{solution}}^{2+}$ . The average value of free energy for the above reaction is negative which indicates affinity of the exchange toward  $\text{Fe}^{3+}$  cations. In [97L1] the cation  $\text{Fe}^{3+} \leftrightarrow \text{Ca}^{2+}$  exchange mechanisms in CSH samples were also analyzed. The first one is typical for the labile calcium ions (Ca5, Ca6):  $3\text{Ca}_{\text{labile}}^{2+} \leftrightarrow 2\text{Fe}_{\text{labile}}^{3+} + \text{VCa}_{\text{labile}}^{2+}$  where VCa is a calcium vacancy created in the CSH lattice. The second mechanism applies to the non labile Ca ions and involves the hydroxyl groups of the bridging silicon atoms. The Ca1 and Ca4 ions can be replaced by  $\text{Fe}^{3+}$ , the charge compensation being achieved by removal of a proton from the structure:  $\text{Si3-O9H-Ca1} \leftrightarrow \text{Si3-O9-Fe1}$ ;  $\text{Si5-O18H-Ca4} \leftrightarrow \text{Si5-O18-Fe4}$ . The third mechanism involves Ca2 and Ca3, the charge compensation being achieved by removal of a proton after dissociation of a structural  $\text{H}_2\text{O}$ :  $\text{Ca2-H}_2\text{O}(1) \leftrightarrow \text{Fe2-O1H}$ ;  $\text{Ca3-H}_2\text{O}(2) \leftrightarrow \text{Fe3-O2H}$ . This mechanism was suggested also to occur in the labile plane with Ca5 and Ca6. In 15% ( $\text{Na}^+$ ,  $\text{Al}^{3+}$ ) substituted tobermorites [91T1],  $2\text{Cs}^{1+}$  were exchanged for  $1\text{Ca}^{2+}$ . In [93T1], also using synthetic (Na,Al) substituted tobermorite, a high selectivity decreasing from  $\text{Ba}^{2+}$  to  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  was discovered in exchange experiments.

### Okenite

In [56G1] the composition  $\text{Ca}_9(\text{Si}_6\text{O}_{15})_3 \cdot 18\text{H}_2\text{O}$  was proposed for okenite, and a triclinic-type structure was suggested. Later on, in [83M1] was shown that okenite has the composition  $\text{Ca}_{10}\text{Si}_{18}\text{O}_{46} \cdot 18\text{H}_2\text{O}$  and crystallizes in a triclinic lattice, having space group  $\text{P}\bar{1}$ . The structure is composed of the following structural units: (1) tetrahedral sheets S, with composition  $(\text{Si}_6\text{O}_{15})^{6-}$ , characterized by five- and eight-membered rings of silicate tetrahedra, with five tetrahedra pointing in one direction and one tetrahedron pointing in the other direction; (2) three-repeat double chain C, with composition  $(\text{Si}_6\text{O}_{16})^{8-}$  and characterized by four- and six-membered rings, made up by pairing two wollastonite chains, which points in opposite directions; (3) octahedral double chains O, formed by two strands of octahedra. These structural units are connected by corner sharing to give the complex layer SOCOS with composition  $[\text{Ca}_8(\text{Si}_6\text{O}_{16})(\text{Si}_6\text{O}_{15})_2(\text{H}_2\text{O})_6]^{4-}$ . Such complex layers alternate in the structure with sheets  $[\text{Ca}_2(\text{H}_2\text{O})_9 \cdot 3\text{H}_2\text{O}]^{4+}$ . The lattice parameters in  $\text{P}\bar{1}$  subcell are listed in Table 3. Careful examination of the X-ray spectra indicates that the true cell is triclinic with parameters derived from those of the subcell by means of the transformation matrix  $[110/0\bar{2}0/001]$ . In order to maintain the same orientation of the subcell an equivalent C centered cell may be chosen ( $\text{C}\bar{1}$ ) with doubled  $a$  and  $b$  parameters relative to the subcell parameters.

The dehydration and thermal decomposition of okenite was analysed [80P1]. Three kinds of structural water were shown. The conversion of anhydrous okenite to wollastonite and cristobalite begins at 855 °C with a maximum at 890 °C and completion at about 915 °C.

### Nekoite

The crystal structure of nekoite,  $\text{Ca}_3\text{Si}_6\text{O}_{15} \cdot 7\text{H}_2\text{O}$ , was hypothesized on the basis of chemical composition and unit cell dimensions [58M1]. Later on, the crystal structure was solved [80A1] and it was shown that in many respects it is different from the structural model of [58M1]. The crystal structure of nekoite consists of tetrahedral sheets interlayered with octahedral chains. The tetrahedral  $\text{Si}_6\text{O}_{15}$  sheets are obtained by interconnecting a “dreierkette” so as to form alternating bands of 5- and 8-membered rings. Ca-octahedral chains, which crosslink the tetrahedral sheets are formed by a double strand of octahedra of which three out of four are occupied and the fourth is empty. Water molecules occupy the empty spaces between the chains. The balance of electrostatic valences suggests that only oxygen atoms occupy the vertices of the tetrahedral sheet, while only water molecules occur outside the tetrahedral sheet. [80A1].

#### 8.1.4.5.2 Magnetic properties

The magnetic properties of synthetic **Fe-substituted calcium silicate hydrate** having a composition close to 11Å-tobermorite were studied [97L1]. The chemical analysis of the lyophilised solid yields  $(\text{Fe}+\text{Ca})/(\text{Al}+\text{Si}) = 1$ ,  $\text{Fe}/\text{Ca} = 4$  and  $\text{Al}/\text{Si} = 0.2$  ratios. The X-ray analysis shows the absence of any well crystallized phase.

The magnetization isotherm at 1.8 K shows no tendency to saturation up to a field of  $\mu_0 H = 5.5$  T – Fig. 5. Above 3 T a linear field variation of magnetization  $M = M_0 + \chi_{\text{HF}} H$  was observed with  $M_0 = 10$  emu/cm<sup>3</sup> and a high-field susceptibility  $\chi_{\text{HF}} = 17.6 \cdot 10^{-5}$  emu T<sup>-1</sup>/cm<sup>3</sup>. The coercive field is found as  $\mu_0 H_c = 0.17$  T. The zero-field cooled (ZFC) and field cooled (FC) susceptibility curves, in a field of  $\mu_0 H = 10^{-3}$  T, are shown in Fig. 6. The ZFC curve has a maximum at  $T_m \approx 10$  K and the susceptibilities decrease at higher temperatures. The FC curve follows the same thermal variation as the ZFC curve down to  $T_m$ , and then steeply increases as temperature decreases below  $T_m$ . In the high-temperature range (20...320 K),  $\chi^{-1}$  vs  $T$  follows a Curie-Weiss-type behaviour with  $\Theta = -1.6$  K – Table 4. The small value of the magnetization at 1.8 K and its linear variation in high fields are characteristic for a nearly antiferromagnetic-type structure involving  $\text{Fe}^{3+}$  moments. Below an “irreversibility temperature”, slightly above  $T_m$ , the biggest particles start to “freeze” with their magnetization preferentially along the direction of the field, and the FC curve departs from the ZFC curve and increases rapidly with decreasing temperatures. Thus, the Fe substituted CSH shows a behaviour characteristic of superparamagnetic small particles. The blocking temperature was identified with the temperature at which the ZFC magnetization is maximum. The experimental data were analyzed in a simple model for isolated spherical particles [81D1] considering a log-normal particle size distribution with  $d_0 = 5$  nm, log-normal root mean square deviation  $\sigma = 0.1$  and an anisotropy constant  $K \approx 4.4 \cdot 10^5$  erg/cm<sup>3</sup>. The magnetically ordered particles can be either nanometric crystallographically ordered domains embedded in an amorphous matrix as evidenced by TEM of CSH paste [96X1] or aggregated independent single particles. In the above model, the high-temperature Curie-Weiss law as well as the maximum of ZFC curve and the irreversibility point are well reproduced, whereas the low-temperature FC and ZFC branches (dashed lines in Fig. 6) are overestimated and underestimated, respectively. The low-field magnetization below  $T_m$  is dominated by the contribution of the smallest superparamagnetic particles and one can expect that the magnetic moment value for these particles is larger than the average value due to the growing relative importance of the unpaired spins at the surface. This effect can explain the observed discrepancy between the experimental data and calculated curves below  $T_m$ . The observed Curie-Weiss law corresponds to a mean magnetic moment per particle  $p_p = 70 \mu_B$ , using the determined mean particle diameter  $d_0 = 5$  nm.

#### 8.1.4.5.3 Nuclear gamma resonance (NGR) data

According to [85P1] the  $^{57}\text{Fe}$  NGR study of Fe substituted **tobermorite** evidenced the presence of tetrahedrally coordinated  $\text{Fe}^{3+}$ . In some samples – Table 5 – octahedrally coordinated  $\text{Fe}^{3+}$  was also observed and attributed to the presence of goethite. Later on, the  $^{57}\text{Fe}$  NGR spectra of iron exchanged tobermorite, at RT, were fitted considering two doublets [91L1]. The doublet with relative intensity  $A = 29(5)\%$  was attributed to  $\text{Fe}^{3+}$  cations situated in nondistorted octahedra and the second one with  $A = 71(5)\%$  to  $\text{Fe}^{3+}$  surrounded by distorted oxygen octahedra. Thus, it was concluded that  $\text{Fe}^{3+}$  takes the position of released  $\text{Ca}^{2+}$  ions. The iron present in place of the Ca5 was expected to be present in the distorted octahedral surrounding while the rest of iron might be present in place of Ca4 or other Ca sites.

The  $^{57}\text{Fe}$  NGR spectrum of a synthetic iron-substituted CSH having  $(\text{Fe}+\text{Ca})/(\text{Al}+\text{Si}) = 1$ ,  $\text{Fe}/\text{Ca} = 4$  and  $\text{Al}/\text{Si} = 0.2$  was fitted at  $T > 30$  K, with two doublets typical for  $\text{Fe}^{3+}$  – Table 5 [97L1]. When decreasing the temperature from 300 K, the spectra remain unchanged down to 30 K, except for a small increase in the mean quadrupolar splitting. It was suggested that Fe in CSH substitutes both the labile and nonlabile calcium sites [91L1, 97L1]. At 4.2 K, a magnetic hyperfine pattern was observed, the  $\text{Fe}^{3+}$  sublattice being ordered at this temperature – Fig. 7. The spectrum was decomposed in two sextets, the hyperfine fields being characteristic of those found in  $\text{Fe}^{3+}$  oxides – Table 5. On heating, one observes a progressive broadening of the magnetic hyperfine spectrum, together with the growth of quadrupole doublets. In the temperature range 15...25 K both a magnetic sextet and a quadrupole doublet coexist. In this temperature range, the spectra were fitted as a distribution of the magnetic hyperfine patterns and of the quadrupole patterns. Typical hyperfine fields histograms for the magnetic component are shown in Fig. 8a. The mean hyperfine field decreases and a bump at low fields develops as the temperature increases. The thermal variation of the relative percentage,  $f_p(T)$ , of the quadrupole doublet is shown in Fig. 8b. The thermal variation of  $f_p(T)$  is reproduced satisfactorily (solid line) according to the relations:

$$f_p(T) = \int_0^{v_b(T)} n(v) dv; \quad v_b(T) = \frac{k_B T}{K} \ln(\tau/\tau_0)$$

where  $n(v)$  is the volume distribution for the particle sizes and  $v_b(T)$  is the blocking volume at temperature  $T$ , above which the particle magnetization is “frozen” ( $\tau > \tau_0$ ). A value  $\tau_0 = 10^{-12}$  s was used. The computed data, denoted by a solid line, were obtained by using the same parameters as derived from the fit of the susceptibility curves ( $K = 4.4 \cdot 10^5$  erg/cm<sup>3</sup>,  $d_0 = 5$  nm and  $\sigma = 0.1$ ).

#### 8.1.4.5.4 Nuclear magnetic resonance (NMR) data

##### Tobermorites

The  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR studies were performed on tobermorites and aluminium substituted tobermorites [82W1, 85K2, 85K3, 91T2]. The existence of Si-O-Si bridges proposed by [74T1] in non-shrinking 11Å-tobermorite has been evidenced by  $^{29}\text{Si}$  MAS NMR spectroscopy [82W1]. The substitution of aluminium for silicon in the tetrahedral coordination has been also evidenced by the  $^{27}\text{Al}$  MAS NMR method [85K2].  $\text{Al}^{3+}$  ions were found to substitute for tetrahedral Si atoms in these bridges ( $\text{Q}^3$  sites) and atoms ( $\text{Q}^2$  sites) within the  $\text{Si}_3(\text{O}/\text{OH})_9$  chain [82W1, 85K3]. A cavity is formed by the  $\equiv \text{Si}-\text{O}-\text{Si} \equiv$  bridges and the  $\text{Si}_3(\text{O}/\text{OH})_9$  chain in the tobermorite structure [89K1]. The resultant deficiency in charge, arising from the Al substitution, may be compensated by alkali cations [82K1, 83K1, 85K1, 87K1], which are responsible for the ion exchange reaction. Hence the ion exchange sites for alkali metal and other ions exist in the cavity.

Some  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR data on tobermorites or substituted tobermorites, normal (N) or anomalous (A), are listed in Table 6. According to [85K3], in 11Å-tobermorites substituted by aluminium,  $^{27}\text{Al}$  MAS NMR data clearly showed that aluminium is tetrahedrally coordinated. Two different resonances (except for one sample) were observed, suggesting the presence of aluminium in two distinct local environments. These results seem to be in agreement with the suggestion of two different tetrahedral environments for aluminium in Al-substituted tobermorites [85K2]. Tobermorites prepared without Al addition also showed  $^{27}\text{Al}$  resonances which were attributed to the trace amounts of aluminium present as impurities in the reactants [85K3]. The  $^{27}\text{Al}$  MAS NMR spectra showed also that Al is incorporated in tetrahedral sites up to 15 mol % Al substituting Si in the structure, as indicated by the resonance around 55(10) ppm [91T1]. At 20 mol % Al for Si substitution, a small resonance at 1.5 ppm is due to octahedrally-coordinated Al and this resonance was attributed to hydrogarnet formation in addition to tobermorite – Fig. 9.

The  $^{29}\text{Si}$  chemical shifts in tobermorites were studied [82W1, 85K3]. Samples without added aluminium exhibit two resonances at –85.7 ppm and –95.7 ppm. These resonances arise from chain middle group ( $\text{Q}^2$ ) and branching sites ( $\text{Q}^3$ ), respectively [82W1]. Since these tobermorites exhibit anomalous thermal behaviour [77E1], they are expected to have Si-O-Si branching sites and NMR results showed their presence. The ratio  $\text{Q}^2/\text{Q}^3$  is  $\approx 2$ , as expected for tobermorites with  $\text{Ca}/\text{Si} \approx 0.83$ . The substitution of Al in sample<sup>8)</sup> (for composition see Table 6) caused a low-field resonance shift of the  $\text{Q}^3(0\text{Al})$  resonance from –95.7 to –91.5 ppm which was assigned to  $\text{Q}^3(1\text{Al})$  and suggest a regular ordering  $\text{Si}_3\text{Al}_1$  [85K3]. In anomalous tobermorites<sup>9,10)</sup>, four different resonances were observed and assigned to  $\text{Q}^2(0\text{Al})$ ,  $\text{Q}^2(1\text{Al})$ ,  $\text{Q}^3(0\text{Al})$  and  $\text{Q}^3(1\text{Al})$ . In case of Al-substituted normal tobermorite<sup>11)</sup>, the presence of only  $\text{Q}^2(0\text{Al})$  and  $\text{Q}^2(1\text{Al})$  resonances were observed [85K3]. In this

sample, there are no  $Q^3$  branching sites. These results were confirmed later [91T1]. The tobermorite with 1 mol % Al substituted for Si shows two resonances attributed to chain middle group ( $Q^2$ ) and branching sites ( $Q^3$ ). In case of a sample with 5 mol % Al, in addition, there is a shoulder on  $Q^2$  resonance attributed to  $Q^2(1Al)$  and for samples with 10 mol % Al or more four resonances were observed – Table 6 – suggesting that Al is substituting for Si in both the chain middle groups and branching sites.

The  $^{29}\text{Si}$  MAS NMR study on normal 14Å-tobermorite showed that this consists predominantly of middle units  $Q^2$  representative of chains of silicate tetrahedra [80L1, 82W1, 85K3, 87K2] and jennite synthesized at 353 K was found to contain both dimer and/or end units ( $Q^1$ ) as well as middle units  $Q^2$  [87K2] – Table 6.

### Calcium silicate hydrates (CSH)

The  $^{29}\text{Si}$  MAS NMR spectroscopy was used to monitor the development of amorphous CSH during the hydration of tricalcium silicate [89G1, 94O1, 95C1]. In [85B1] was shown that hydration begins with the production of the relatively simple monomeric hydrate ( $Q^0$ ), which tends to persist, followed at later stages by a combination of a dimer and/or end units ( $Q^1$ ) and middle units ( $Q^2$ ) which become increasingly abundant with time of hydration. According to [82L1, 88Y1] no significant monomer develops during the hydration reaction. Both above studies show an early development of dimer ( $Q^1$ ) followed by the development of middle units ( $Q^2$ ) after 15 h of reaction. In [80S2] was reported that CSH with Ca/Si = 1.3, precipitated at 273 K, consisted primarily of a monomer which quickly condensed to disilicate anions ( $Q^1$ ) with lesser amounts of polysilicate anions  $Q^2$  forming with time. In [80S1, 85S2], describing both 353 K and 423 K material, was suggested that the structure of CSH with Ca/Si > 1.1 consisted of a fixed ratio (1.2) of polysilicate ( $Q^2$ ) to disilicate anions ( $Q^1$ ), while materials with Ca/Si ratio ≤ 1.0 tend to be richer in polysilicate ( $Q^2$ ). In [80H1] the nature of phases was described which formed when fumed colloidal silica was allowed to react with  $\text{Ca}(\text{OH})_2$  solutions at 353 K. They observed that 14Å-tobermorite formed at Ca/Si ≤ 0.9 and jennite at Ca/Si = 1.1...1.5. In the presence of excess colloidal silica, a very low Ca/Si ratio (1.0), highly polymerized CSH formed [84W1]. Later on, reaction products, formed in a series of fully “equilibrated” room-temperature hydrated, fumed colloidal silica plus lime water mixtures, were examined by using  $^{29}\text{Si}$  MAS NMR spectroscopy [89G1]. As seen from Fig. 10, the spectra suggest that two structurally distinct CSH phases exist [91T2]. We note that the spectrum of hydrous silica (Ca/Si = 0.02) shows peaks at –100.7 and –114.5 ppm which were attributed to  $\text{HOSi}(\text{OSi})_3$  and  $\text{Si}(\text{OSi})_4$ , respectively, which are characteristic of tertiary ( $Q^3$ ) and quaternary ( $Q^4$ ) networks of silica tetrahedra found in silicate gel. For the sample with Ca/Si = 0.12 (hydrous silica + CSH + solution) an additional peak at –85.0 ppm was seen, characteristic of secondary  $Q^2$  chains of silicate tetrahedra [89G1].

The  $^{29}\text{Si}$  MAS NMR spectra reveal that two structural distinct CSH phases exist in the  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  system. The spectra of more silica rich CSH (Ca/Si = 0.65 ÷ 1.00) are dominated by a single  $Q^2$  peak which represents chains of silica tetrahedra similar to those found in “normal” 14Å-tobermorite [82W1, 87K2]. The spectra of more lime-rich CSH (Ca/Si = 1.1 ÷ 1.3) consists of two peaks having  $Q^2/Q^1$  peak height ratio of 0.7. This suggest that the samples are dominated by dimer and/or end groups ( $Q^1$ ) and the structure of CSH is relatively insensitive to changes in composition. The spectra are similar to synthetic jennite [87K2] although in the last case the  $Q^2/Q^1$  ratio is 1.5. The transition from the state with “one-peak” to the “two-peak” is abrupt [89G1].

In [96F1] molecular dynamics has been used to simulate the structure of CSH having Ca/Si ratios 0.66 and 0.83. In the absence of labile calcium,  $^{29}\text{Si}$  MAS NMR shows that the tetrahedral chains move closer together than predicted by the tobermorite model. This proximity may lead to bridging between chains. In the presence of labile calcium, there is partial rupture of the chains, as seen by NMR and the formation of  $Q^1$  tetrahedra. The break occurs between the Si3 and Si1 tetrahedra via a water molecule, which dissociates, thereby enabling four-coordination to be preserved for each tetrahedron. The hydrogens released by the dissociation allow the formation of two new OH bonds with the two  $Q^1$  tetrahedra. As Si3 already has on OH group, two types of  $Q^1$  tetrahedra are created by rupture of the chains ( $\text{Si3} \rightarrow Q^1(2\text{H})$ ,  $\text{Si1} \rightarrow Q^1(1\text{H})$ ).

### 8.1.4.5.5 Optical properties

For IR studies of 14Å-tobermorite see [75G1, 93S1]. For refractive indices of oyelite see Table 6 of Chap. 8.1.4.6.