CALCIUM SILICATE HYDRATES:
CRYSTAL STRUCTURE AND THERMAL BEHAVIOUR

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INTRODUCTION

Calcium silicate hydrates (C-S-H) are a series of natural and synthetic phases (Fig. 1), characterized by a high scientific and technological interest; in particular, the compounds belonging to the tobermorite group are intensively studied for their relationship with the C-S-H phase formed during the hydration of the ordinary Portland cement and for their potential technological applications (*e.g.* as cation exchangers).
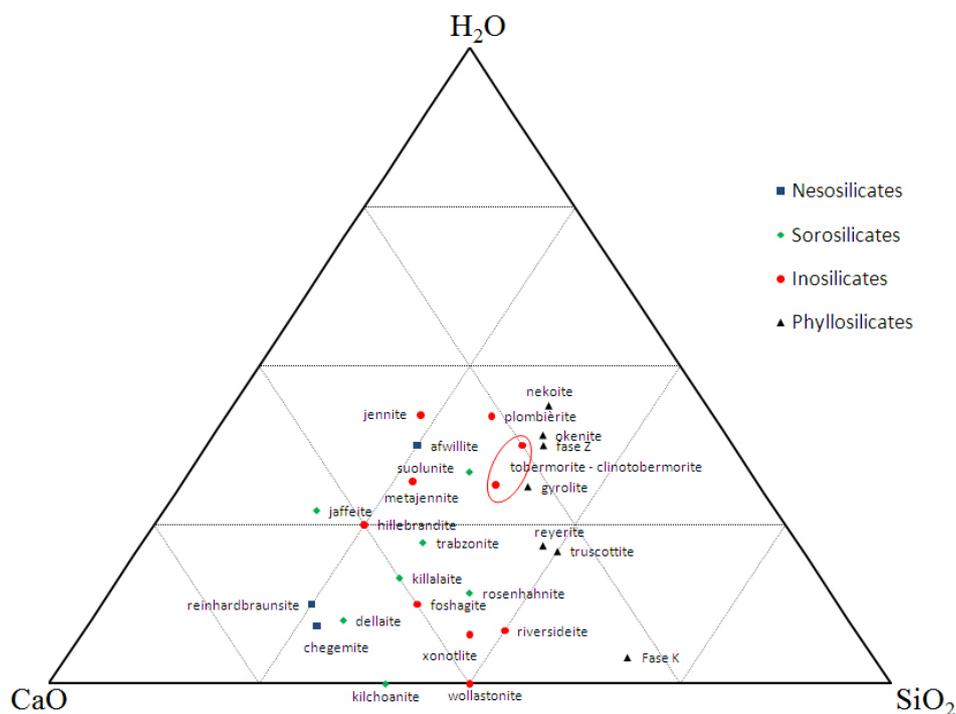

Fig. 1 - CaO-SiO$_2$-H$_2$O triangular diagram, showing the molar composition of C-S-H phases.

The natural C-S-H phases form typically through the action of hydrothermal fluids during the late stages of the evolution of different geological environments; they are particularly frequent in veins and amygdales of basaltic rocks and near to contact aureoles around magmatic intrusions.

The study of these phases is made difficult by the specimen morphology, usually not suitable for single-crystal studies. These crystallographic techniques are the only ones that allow the full understanding of the very complex crystallographic issues (twinning, structural disorder, polytypism) shown by the minerals of the tobermorite group. Moreover, their fibrous and microcrystalline nature makes the accurate chemical characterization quite difficult for the frequent association with other C-S-H phases.

The aims of this study are the crystal-chemical characterization of natural samples of calcium silicate hydrates, paying special attention to those belonging to the tobermorite group, and the accurate study of their thermal behaviour. These goals were achieved through different analytical techniques: X-ray diffraction (both on

powder and single crystal), EDS chemical analyses, ^{29}Si NMR and micro-Raman spectroscopies, and TG-DTA studies.

THE TOBERMORITE GROUP: CRYSTAL STRUCTURE AND NOMENCLATURE

The tobermorite group includes a series of calcium inosilicates, characterized by the presence of wollastonite-like chains, bonded to layers of seven-fold coordinated calcium polyhedra. Claringbull & Hey (1952) showed the similarity between the X-ray powder pattern of tobermorite and that of the C-S-H (I) phase, synthesized by Taylor (1950). Cement chemist observed the existence of three hydration states of the C-S-H compounds, characterized by different basal spacings. Phases with basal spacings of 14.0, 12.6, 11.3, 10.2, and 9.3 Å were described and assigned to the tobermorite group. Actually, only the 14, 11, and 9 Å phases are known in nature, whereas the relationship between the synthetic compounds with basal spacing of 12.6 and 10.2 and the natural counterpart (tacharanite and oyelite, respectively) are still debatable.

Crystal structure of the tobermorite group phases

The phases of the tobermorite group are characterized by a common structural unit, called "complex module" by Bonaccorsi & Merlino (2005), built up by a calcium polyhedral layer (a continuous layer, in the plane (001), of seven-fold coordinated calcium cations), with wollastonite-like tetrahedral chains grasped on both sides of it. The "complex module" is *C*-centered, with cell parameter $a = 11.2$ Å, $b = 7.3$ Å, and width $c_0 = 11.2$ Å.

The calcium cations polyhedra can be described as monocapped trigonal prisms; they are bonded through edge-sharing and form columns running along [010]. Along this direction, the capping ligands are alternatively H_2O molecules and anions (O^{2-} or OH^-). Adjacent columns are connected through edge-sharing and have the capping ligands on opposite sides of the calcium polyhedral layer.

Wollastonite-like chains run along [010], on both sides of the calcium polyhedral layer; each chain can be described as formed by paired tetrahedra connected by bridging tetrahedra.

It is important to stress that there are two geometrically distinct ways to place the "bridging" tetrahedron with respect to the paired tetrahedra on the two sides of the calcium layer: in the first one, the "bridging" tetrahedron is placed at right on one side and at left on the other side (or *vice versa*), with respect to the paired tetrahedra, giving rise to the "complex module" of type A; in the second one, the "bridging" tetrahedron is placed on both sides at left (or at right) with respect to the paired tetrahedra ("complex module" of type B). Types A and B "complex modules" occur in the phases with monoclinic and orthorhombic subcells, respectively (Bonaccorsi & Merlino, 2005). The stacking of the "complex modules" gives rise to the different structure known in the tobermorite group (Fig. 2).

Wollastonite-like chains can be single, like in the 14 and 9 Å phases, or double, like in the 11 Å compounds. In the latter, the framework, formed
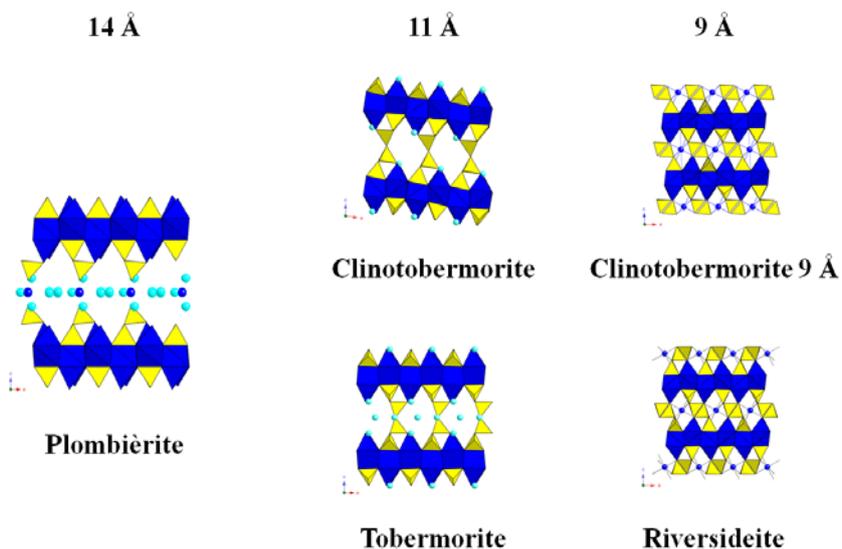

Fig. 2 - Crystal structures of the phases of the tobermorite group.

by the calcium polyhedral layers and the double chains, forms structural cavities that host "zeolitic" water molecules and additional calcium cations.

The nomenclature of the tobermorite group minerals

The phases belonging to the tobermorite group are traditionally classified on the basis of their basal spacings; the latter can be 14.0, 11.3, and 9.3 Å, corresponding to the natural phases plombièrite, tobermorite, and riversideite (McConnell, 1954), respectively. A dimorph of the 11 Å phase, clinotobermorite, was described by Henmi & Kusachi (1992). This is the only mineral species of the tobermorite group approved after the institution of the IMA-CNMNC, in 1959; the other three minerals are considered *grandfathered*.

Plombièrite was described by Daubrée (1858) as a gelatinous matter formed by the interaction between thermal springs and cement of Roman age at Plombières (Vosges, France). McConnell (1954) used this name for two different phases: a poor-crystallized gelatinous phase (probably corresponding to the plombièrite of Daubrée) and a phase characterized by a basal spacing of 14 Å. Successively, the use of plombièrite as a mineralogical name to indicate the 14 Å tobermorite has become the routine. Bonaccorsi *et al.* (2005) solved the crystal structure of plombièrite from Crestmore (Riverside County, California). Notwithstanding the doubtful relationship between the crystalline 14 Å phase and the gel described by Daubrée (1858), it is clear that plombièrite is a valid mineral.

On the contrary, the true nature of riversideite is still questionable. Riversideite was described by Eakle (1917) but the specimens were successively identified as an intergrowth of tobermorite and ellestadite-(F) by Taylor (1953). According to McConnell (1954), the occurrence of the 11 Å phase in the specimen studied by Taylor was due to the rehydration of the 9 Å phase, consequent to an inappropriate storing of this mineral. Up to now, an accurate description of natural riversideite is still missing and the status of this mineral species is probably questionable.

Finally, tobermorite was described by Heddle (1880); Claringbull & Hey (1952), studying Heddle's specimens, observed a basal spacing of 11 Å. Successively, McConnell (1954) used the name tobermorite for the 11 Å phase. However, a wide composition variability was observed in this mineral, due to different Ca:Si ratio and Al content. The scrutiny of literature data allows to hypothesize that tobermorite is actually a series between two end-members, tobermorite-□, $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$, and tobermorite-Ca, $Ca_5Si_6O_{17} \cdot 5H_2O$. Sometimes, alkali-bearing tobermorites were observed, suggesting the possible existence of terms such as "tobermorite-(K,Na)".

Relationship between tobermorite and clinotobermorite

Clinotobermorite and tobermorite are the two dimorphs of the 11 Å phase. These two species can be distinguished on the basis of their X-ray powder diffraction patterns. Clinotobermorite is rarer than tobermorite and it has been reported only from a few localities worldwide. During this study, some specimens composed by admixture of tobermorite and clinotobermorite were identified. These specimens come from Bazhenovskoe asbestos deposit (Ural, Russia), and from the two Italian localities of San Vito di Leguzzano (hereafter SVL) and Gambellara (Veneto). Whereas the specimens from Russia and SVL can be studied only with X-ray powder techniques, due to their microcrystalline morphologies, the specimens from Gambellara show tabular crystals suitable for single-crystal studies. The latter unequivocally showed the coexistence, in the same crystal, of both tobermorite and clinotobermorite. Further studies will be necessary to understand the actual relationship between the two dimorphs.

In addition, also the chemical variability of clinotobermorite should be studied. In fact, the quantitative ratio tobermorite:clinotobermorite, obtained through Rietveld refinement, is 1:1, whereas the average Ca content is around 4.1-4.2 apfu. This low calcium content can be the consequence of the coexistence of "zeolitic" Ca-free domains associated with "zeolitic" Ca-bearing domains, or of the homogeneous distribution of the small amounts of "zeolitic Ca" in the whole structure. In the latter case, also clinotobermorite may be a series, namely between clinotobermorite-□ (still not described in nature) and clinotobermorite-Ca.

THE TOBERMORITE GROUP: THERMAL BEHAVIOUR OF THE 11 Å PHASES

The difference between tobermorite-□ and tobermorite-Ca is closely related to the differences in their thermal behaviour. Mitsuda & Taylor (1978) distinguished three kinds of tobermorite, based on the heating product at 300°C: "normal", "anomalous", and "mixed" tobermorites. According to Merlino *et al.* (2001), the difference between "normal" and "anomalous" thermal behaviour is related to the content of Ca^{2+} cations in the structural cavities. These calcium cations are bonded to "zeolitic" H_2O molecules. If Ca^{2+} is present, the dehydration induces an uncompleted coordination around these cations, causing a rearrangement of the crystal structure, with the decondensation of the silicate chains and the contraction of the 11 Å phase to a 9 Å tobermorite. On the contrary, if Ca is not present, the dehydration does not affect (at 300°C) the basal spacing of tobermorite.

The study of synthetic tobermorites, and in particular of alkali-substituted tobermorites, showed that also the kind of "zeolitic" cation hosted in the structural cavities is important in determing the thermal behaviour. As pointed out by Merlino *et al.* (2008), the actual thermal behaviour of tobermorites is more complex than that outlined above.

The thermal behaviour of several natural tobermorites, both "anomalous" and "normal", were studied through *in situ* X-ray powder diffraction analyses, in order to achieve an accurate understanding of the processes involved.

Fig. 3 - X-ray powder diffraction patterns (λ = 0.6873 Å) of the specimen from NCIIM, from 25 up to 960°C.

"Anomalous" thermal behaviour

According to Mitsuda & Taylor (1978), a tobermorite is "anomalous" if, after heating at 300°C, it maintains its basal spacing of $\sim$ 11.3 Å.

"Anomalous" tobermorites from N'Chwaning II mine (Kalahari Manganese Field, Republic of South Africa; hereafter NCIIM) and SVL were studied *in situ* (Fig. 3 and 4, respectively) at the GILDA beamline (ESRF, Grenoble, France), using the experimental apparatus described by Meneghini *et al.* (2001). These two samples were chemically characterized and their crystal chemical formulae were ideally $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$ and $Ca_4(Al_{0.5}Si_{5.5})O_{14.5}(OH)_{2.5} \cdot 5H_2O$, respectively.

Both the samples maintained their 11 Å periodicity at 300°C, in agreement with their "anomalous" nature. Some differences must be stressed:

- at T > 420°C, the sample from NCIIM shrinked to a 10 Å phase (hereafter called tobermorite 10 Å), whereas the sample from SVL maintained its 11 Å basal spacings;
- tobermorite 10 Å was stable at high T, transforming into wollastonite at 1200°C, whereas tobermorite 11 Å from SVL transformed into wollastonite at lower T (800°C);
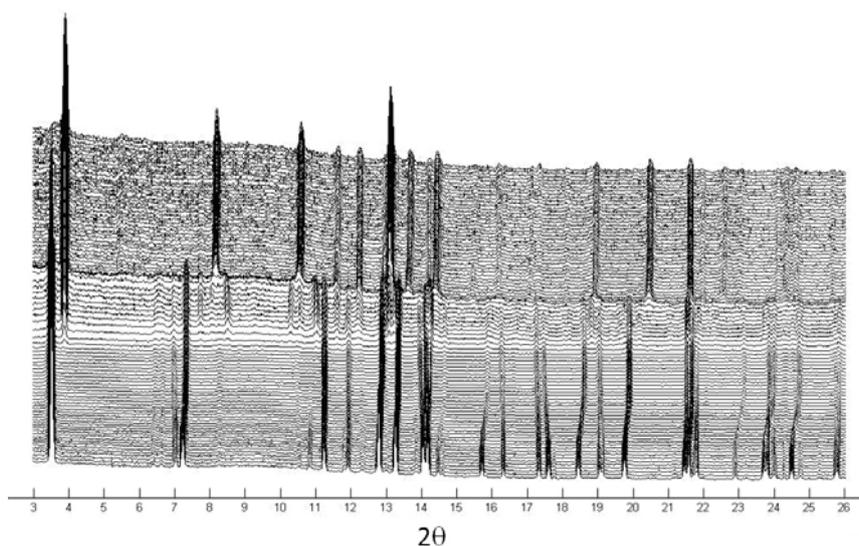
- the TG-DTA studies showed that tobermorite from NCIIM lost ~10 wt.%, corresponding to 4 H_2O molecules, whereas tobermorite from SVL lost ~ 8 wt.%, corresponding to 3 H_2O molecules.

As written above, the sample from SVL is actually a mixture of tobermorite and clinotobermorite. Clinotobermorite disappears at about 380-400°C. On the contrary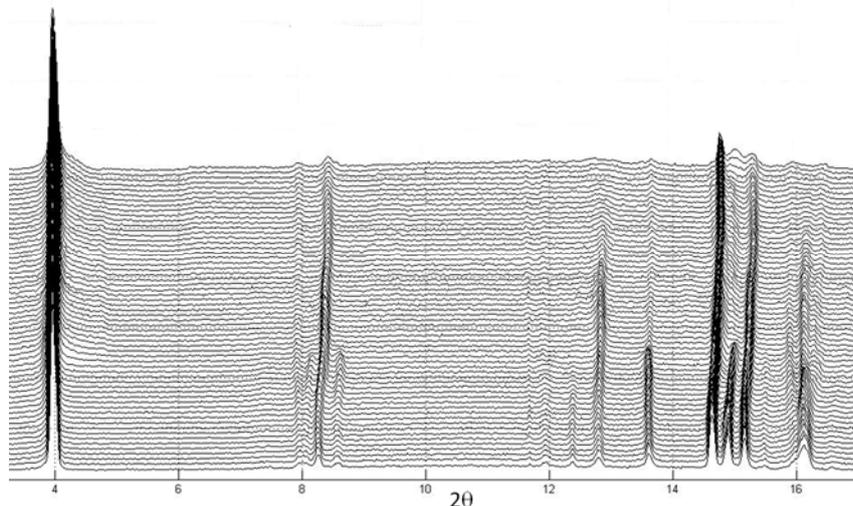, a clinotobermorite-like phase appears before tobermorite 10 Å in the specimen from South Africa. The configuration of the wollastonite-like chains in clinotobermorite may facilitate the contraction of the crystal structure, giving rise to the appearance of the 10 Å phase.

Fig. 4 - X-ray powder diffraction patterns ($\lambda = 0.7835$ Å) of the specimen from SVL, from 30° up to 950°C.

The "anomalous" behaviour was also shown by other specimens; it is interesting to stress that this kind of behaviour was observed in K,Al-bearing tobermorites. In particular, a specimen of tobermorite from Urals (Russia), with chemical composition $K_{0.40}Ca_{3.98}(Al_{0.76}Si_{5.24})O_{14.60}(OH)_{2.40} \cdot 5H_2O$, was "anomalous". This result is in agreement with those obtained by Mitsuda (1970), who synthesized an alkali-rich tobermorite which showed an "anomalous" thermal behaviour; in addition, the synthetic compounds synthesized by Ferreira *et al*. (2003) and having a tobermorite-like structure, with K^+ ions hosted into the structural cavities, were "anomalous".

Tobermorite 10 Å and its relationship with oyelite

Tobermorite 10 Å was synthesized by Jauberthie *et al*. (1996) and Garbev (2004); the relationships between it and the "natural tobermorite 10 Å", known as oyelite (Kusachi *et al*., 1980), are still debatable. In order to solve the crystal structure of the synthetic 10 Å phase and to unravel the relationship with oyelite, crystals of tobermorite 10 Å, obtained through *ex situ* heating experiments, were used for single-crystal studies. Through Weissenberg photographs, the unit cell parameters are $a = 11.2$, $b = 3.67$, and $c = 20.1$ Å; the b periodicity is characteristic of the wollastonite-like chains. Unfortunately, the crystal structure of tobermorite 10 Å could not be solved due to the widespread disorder originated by the thermal treatment.

Due to the lacking of a long-range periodicity, ^{29}Si NMR and micro-Raman spectroscopies were used to study the local environments of this phase. Both these methods indicate that double wollastonite-like chains and water (as hydroxyl groups or water molecules) are present.

Diffractometric, chemical, spectroscopic, and thermogravimetric studies were conducted on oyelite specimens from NCIIM.

Due to the small crystal size and the polycrystalline nature of the oyelite crystals, its crystal structure is still unsolved. However, some considerations allow to verify that oyelite is not the natural counterpart of tobermorite 10 Å. In fact:

- Ca:Si ratio is 4:6 in tobermorite 10 Å, whereas it is 5:4 in oyelite (or 5:5 if boron is assumed in tetrahedral coordination);
- oyelite contains boron as essential element;

- new data collected through micro-Raman spectroscopy showed that tobermorite 10 Å has double silicate chains, whereas oyelite probably shows single silicate chains. ^{29}Si NMR spectra collected only on one sample of tobermorite 10 Å are in agreement with these results.

Normal thermal behaviour

According to Mitsuda & Taylor (1978), a tobermorite is "normal" if, after heating at 300°C, it shrinks to a 9 Å phase. As stated above, this behaviour has been related to the occurrence of "zeolitic" calcium in the structural cavities. Specimens of "normal" tobermorite from Montalto di Castro (Latium, Italy), Vallerano (Latium, Italy), and Grolla quarry (Veneto, Italy) were studied. The two specimens from Latium have chemical composition $Ca_5AlSi_5O_{16}(OH)\cdot5H_2O$, whereas that from Veneto has a formula corresponding to $Ca_{4.5}Al_{0.5}Si_{5.5}O_{15.5}(OH)_{1.5}\cdot5H_2O$.

The thermal behaviour of a powder sample of the tobermorite from Montalto di Castro was followed through an *in situ* study (Fig. 5), performed at the GILDA beamline. Tobermorite 9 Å appeared at ~ 240°C and completely substituted the 11 Å phase at 300°C, in agreement with the "normal" behaviour of this sample. At 800°C, wollastonite became the only phase present in the powder sample. These results are in agreement with the thermogravimetric studies. Specimens from Vallerano and Grolla quarry showed similar TG-DTA curves.
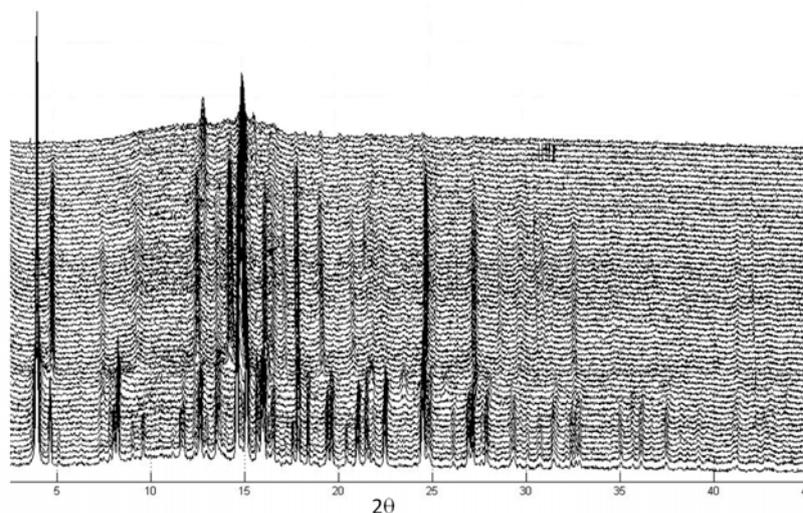
Fig. 5 - X-ray powder patterns (λ = 0.7835 Å) of the specimen from Montalto di Castro, from 32 up to 843°C.

It is interesting to note that the accurate scrutiny of the diffraction pattern collected during the *in situ* study of the sample from Montalto di Castro revealed that probably a clinotobermorite-like phase appears before the shrinking of the structure from the 11 Å to the 9 Å tobermorite, in the temperature range between 180 and 240°C.

The aluminium content in tobermorite

In tobermorite, aluminium replaces silicon in one of the bridging tetrahedron of the double wollastonite-like chains. In agreement with the Loewenstein rule (Loewenstein, 1954), the maximum value of the Al:(Al+Si) ratio should be 1/6. Therefore, the specimens from Montalto di Castro and Vallerano, having 1 Al pfu, show the highest possible aluminium content in tobermorite.

Micro-Raman spectra collected on these Al-rich samples seem to indicate a lower degree of polymerization or the presence of defects in the wollastonite-like chains, in agreement with Black *et al.* (2005). The lower degree of polymerization is not related to the "normal" thermal behaviour of these specimens. In fact, micro-Raman spectra collected on crystals of "normal" clinotobermorite from Wessels mine (the same specimen studied by Merlino *et al.*, 2000), clearly showed the presence of double wollastonite-like chains.

Mixed thermal behaviour

In some cases, tobermorite samples heated up to 300°C show the coexistence of the 11 Å and the 9 Å basal reflections, indicating that a part of the crystal structure has shrinked, whereas the other maintains its

original basal spacing. This kind of tobermorite was called "mixed" by Mitsuda & Taylor (1978). Some samples from the Gambellara and Grolla quarries, and in particular from Höwenegg (Hegau, Germany), show this thermal behaviour. Probably it can be explained as the result of an inhomogeneous distribution of "zeolitic" calcium cations into the structural cavities; the "zeolitic" Ca-rich domains collapsed due to the water loss, whereas the "zeolitic" Ca-poor regions maintained their 11 Å basal spacing.

DISCUSSION

Table 1 summarizes the results of the thermal behaviour studies.

It is clear that the definitions given by Mitsuda & Taylor (1978) describe the behaviour of tobermorite at 300°C; instead, more complex behaviours were observed at higher temperatures, *i.e.* either the appearance of tobermorite 10 Å or the preservation of the 11 Å basal spacing.

Table 1 - Thermal behaviour of the studied specimens.

Thermal behaviour	Locality	(Ca+alkali):(Si+Al)	Si:Al	K+Na (*apfu*)	d_{002} (Å) 300°C	d_{002}(Å) 500°C
"anomalous"	N'Chwaning II mine	4 : 6	6 : 0	0	11.3	10.2
	San Vito di Leguzzano	4.1 : 6	5.5 : 0.5	0	11.3	11.3
	Urals	4.4 : 6	5.25 : 0.75	0.4	11.1	
	Gambellara	4.1 : 6	5.5 : 0.5	0	11.3 (11 + 9)	
"mixed"	Höwenegg	4.8 : 6	5.1 : 0.9	0.4	11 + 9	
"normal"	Grolla quarry	4.5 : 6	5.5 : 0.5	0	9.6 (11 + 9)	
	Montalto di Castro	5 : 6	5 : 1	0	9.5	9.5
	Vallerano	5 : 6	5 : 1	0.1	9.6	

The brace indicates that "mixed" thermal behaviours were observed not only for tobermorite from Höwenegg, but also in some samples from the Gambellara and Grolla quarries, that usually displayed an "anomalous" and "normal" behaviour, respectively.

Churakov (2009) discussed the important role of "zeolitic" water in stabilizing the water molecules bonded to the calcium layer of tobermorite. The different weight loss of the two "anomalous" specimens from NCIIM and SVL can be related to the loss of four and three water molecules, respectively; in the first case, all the three "zeolitic" water molecules were lost plus one of the two water molecules bonded to the calcium layer, whereas only the "zeolitic" water were lost in the second case. Naturally occurring tobermorites usually contains small amounts of aluminium, whereas the specimen from NCIIM is Al-free. Therefore, it is possible that the heterovalent substitution $Si^{4+}+O^{2-}\rightarrow Al^{3+}+OH^{-}$ gives rise to additional hydrogen bonds, that can inhibit the loss of the water molecules bonded to the calcium polyhedral layer, stabilizing the 11 Å phase.

Another important topic related to the tobermorite group is that concerning the stability field of clinotobermorite; its rarity in nature, in comparison with the more common tobermorite, and its appearance as an intermediate phase between the 11 Å phase and compounds with a shorter basal spacings (both the 10 and 9 Å forms), may suggest a possible metastability of clinotobermorite at room temperature.

Further studies will be necessary to understand the relationship between chemical composition and high-temperature thermal behaviour (taking into account, in particular, the role of aluminium), the degree of condensation of wollastonite-like chains in Al-bearing tobermorite, and the actual thermodynamic relation between the two 11 Å dimorphs. Finally, a new nomenclature of the members of the tobermorite group, taking

into account the important role of the "zeolitic" cations and the eventually natural occurrence of tobermorite 9 Å (riversideite), is desiderable.

REFERENCES

Black, L., Stumm, A., Garbev, K., Stemmermann, P., Hallam, K.R., Allen, G. (2005): X-ray photoelectron spectroscopy of aluminum-substituted tobermorite. *Cem. Concr. Res.*, **35**, 51-55.

Bonaccorsi, E. & Merlino, S. (2005): Modular microporous minerals: cancrinite-davyne group and C-S-H phases. *Rev. Mineral. Geochem.*, **57**, 241-290.

Bonaccorsi, E., Merlino, S., Kampf, A.R. (2005): The crystal structure of tobermorite 14 Å (plombierite), a C-S-H phase. *J. Amer. Ceram. Soc.*, **88**, 505-512.

Churakov, S.V. (2009): Structural positions of H_2O molecules and hydrogen bonding in anomalous 11 Å tobermorite. *Am. Mineral.*, **94**, 156-165.

Claringbull, G.F. & Hey, M.H. (1952): A re-examination of tobermorite. *Mineral. Mag.*, **29**, 960-962.

Daubrée, M. (1858): Mémoire sur le relation des sources thermal de Plombières avec les filons métalliféres et sur la formation contemporaine des zéolithes. *Ann. Mines*, **13**, 227-256.

Eakle, A.S. (1917): Minerals associated with the crystalline limestone at Crestmore, Riverside County, California. *Bull. Dep. Geol.*, *Univ. California*, **10**, 327-360.

Ferreira, A., Ananias, D., Carlos, L.D., Morais, C.M., Rocha, J. (2003): Novel microporous lanthanide silicates with tobermorite-like structure. *J. Am. Chem. Soc.*, **125**, 14573-14579.

Garbev, K. (2004): Struktur, Eigenschaften und quantitative Rietveldanalyse von hydrothermal kristallisierten Calciumsilikathydraten (C-S-H Phasen). Ph.D. Dissertation, Ruprecht-Karls-University, Heidelberg.

Heddle, M.F. (1880): Preliminary notice of substances which may prove to be new minerals. *Mineral. Mag.*, **4**, 117-123.

Henmi, C. & Kusachi, I. (1992): Clinotobermorite, $Ca_5Si_6(O,OH)_{18} \cdot 5H_2O$, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineral. Mag.*, **56**, 353-358.

Jauberthie, R., Temimi, M., Laquerbe, M. (1996): Hydrothermal transformation of tobermorite gel to 10 Å tobermorite. *Cem. Concr. Res.*, **26**, 1335-1339.

Kusachi, I., Henmi, C., Henmi, K. (1980): 10 Å tobermorite from Fuka, the town of Bitchu, Okayama Prefecture. *J. Mineral. Soc. Jap.*, **14**, 314-322.

Loewenstein, W. (1954): The distribution of aluminum in the tetrahedra of silicates and aluminates. *Am. Mineral.*, **39**, 92-96.

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

Meneghini, C., Artioli, G., Balerna, A., Gualtieri, A., Norby, P, Mobilio, S. (2001): Multipurpose imaging-plate camera for in-situ powder XRD at the GILDA beamline. *J. Synchr. Rad.*, **8**, 1162-1166.

Merlino, S., Bonaccorsi, E., Armbruster, T. (2000): The real structure of clinotobermorite and tobermorite 9 Å: OD character, polytypes, and structural relationship. *Eur. J. Mineral.*, **12**, 411-429.

Merlino, S., Bonaccorsi, E., Armbruster, T. (2001): The real structure of tobermorite 11Å: normal and anomalous forms, OD character and polytypic modifications. *Eur. J. Mineral.*, **13**, 577-590.

Merlino, S., Bonaccorsi, E., Merlini, M., Marchetti, F., Garra, W. (2008): Tobermorite 11 Å and its synthetic counterparts: structural relationships and thermal behaviour. *In*: "Minerals as advanced materials I", S. Krivovichev, ed. Springer, Berlin, 37-44.

Mitsuda, T. (1970): Synthesis of tobermorite from zeolite. *Mineral. Mag.*, **6**, 143-158.

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

Taylor, H.F.W. (1950): Hydrated calcium silicates. Part I. Compound formation at ordinary temperature. *J. Chem. Soc.*, **1950**, 3682-3690.

Taylor, H.F.W. (1953): Crestmoreite and riversideite. *Mineral. Mag.*, **30**, 155-165.