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The tobermorite supergroup: a new nomenclature

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ABSTRACT

The name 'tobermorites' includes a number of calcium silicate hydrate (C-S-H) phases differing in their hydration state and sub-cell symmetry. Based on their basal spacing, closely related to the degree of hydration, 14, 11 and 9 Å compounds have been described. In this paper a new nomenclature scheme for these mineral species is reported. The tobermorite supergroup is defined. It is formed by the tobermorite group and the unclassified minerals plombièrite, clinotobermorite and riversideite. Plombièrite ('14 Å tobermorite') is redefined as a crystalline mineral having chemical composition $Ca_5Si_6O_{16}(OH)_2{\cdot}7H_2O$. Its type locality is Crestmore, Riverside County, California, USA. The tobermorite group consists of species having a basal spacing of ~11 Å and an orthorhombic sub-cell symmetry. Its general formula is $Ca_{4+x}(Al_ySi_{6-y})O_{15+2x-y}{\cdot}5H_2O$. Its endmember compositions correspond to tobermorite $Ca_5Si_6O_{17}{\cdot}5H_2O$ ($x = 1$ and $y = 0$) and the new species kenotobermorite, $Ca_4Si_6O_{15}(OH)_2{\cdot}5H_2O$ ($x = 0$ and $y = 0$). The type locality of kenotobermorite is the N'Chwaning II mine, Kalahari Manganese Field, South Africa. Within the tobermorite group, tobermorite and kenotobermorite form a complete solid solution. Al-rich samples do not warrant a new name, because Al can only achieve a maximum content of 1/6 of the tetrahedral sites ($y = 1$). Clinotobermorite, $Ca_5Si_6O_{17}{\cdot}5H_2O$, is a dimorph of tobermorite having a monoclinic sub-cell symmetry. Finally, the compound with a ~9 Å basal spacing is known as riversideite. Its natural occurrence is not demonstrated unequivocally and its status should be considered as "questionable". The chemical composition of its synthetic counterpart, obtained through partial dehydration of tobermorite, is $Ca_5Si_6O_{16}(OH)_2$. All these mineral species present an order-disorder character and several polytypes are known. This report has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification.

KEYWORDS: plombièrite, tobermorite, kenotobermorite, clinotobermorite, riversideite, tobermorite supergroup, C-S-H phases.

Introduction

MINERALS of the tobermorite group ('tobermorites') are calcium silicate hydrate (C-S-H) compounds of which the main interest is related to their close relationships with the C-S-H phases formed during the hydration of Portland cement (e.g. Richardson, 2008). In addition, they may act as cation exchangers and have potential applications in waste disposal.

'Tobermorites' are structurally characterized by layers of seven-coordinate, calcium-centred polyhedra, parallel to (001), decorated on both sides by wollastonite-like chains (*dreier* single chains, in the terminology of Liebau (1985); Fig. 1); this common structural module was called a "complex module" by Bonaccorsi and Merlino (2005). The nomenclature of these minerals relies on their water content, structurally conditioning their basal spacings; the greater the hydration, the wider the basal spacing.

Taking into account the different hydration states (as also described by Taylor (1953*b*) for synthetic C-S-H (I) compounds), McConnell

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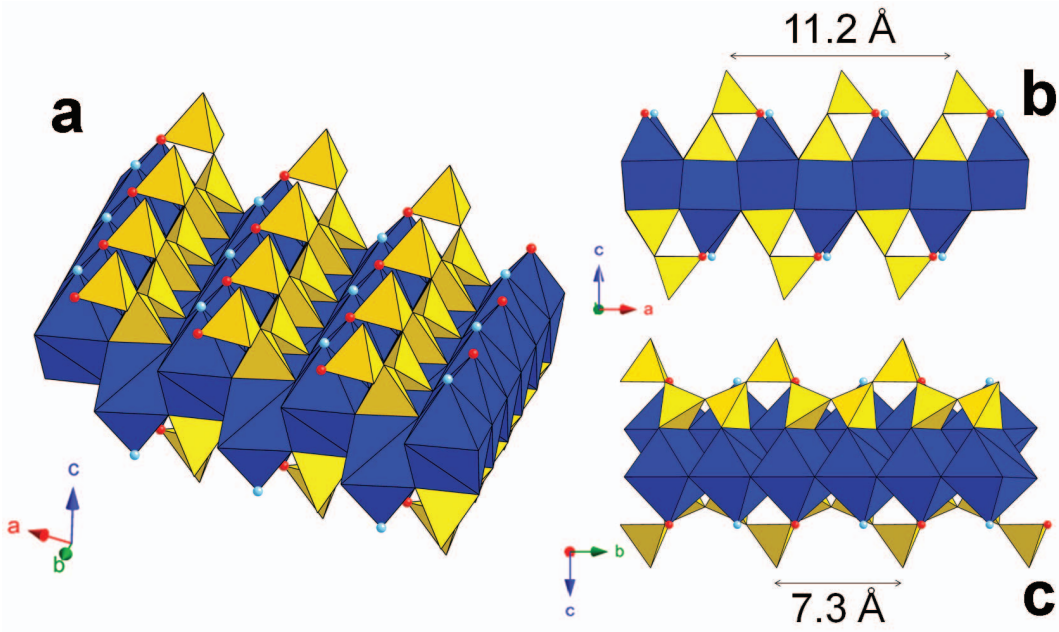


FIG. 1. The fundamental building unit in the crystal structure of tobermorites, the so-called "complex module". The sheet of seven-coordinate Ca-centred polyhedra is shown in blue, whereas wollastonite-like silicate chains are shown in yellow. (*a*) An oblique projection of the complex module; the complex module is seen down [010] and [100] in (*b*) and (*c*), respectively. The two fundamental repeat units of the complex module are shown. Circles represent water molecules (light blue) and oxygen atoms or hydroxyl groups (red) bonded to the apical sites of Ca-centred polyhedra.

(1954) proposed the names plombièrite, tobermorite and riversideite for the three different known hydration states, corresponding to basal spacings of 14, 11 and 9 Å, respectively. However, McConnell (1954) did not distinguish between crystalline and amorphous C-S-H compounds, as noted by Taylor (1964) who stressed the existence of nomenclature problems related to the poorly defined nature of some phases.

Bonaccorsi and Merlino (2005) pointed out that none of the mineral names and species belonging to the 'tobermorite group' were officially approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA), with the exception of the approved mineral clinotobermorite (Henmi and Kusachi, 1992). In the IMA CNMNC *List of Mineral Names* (http://http://ima-cnmnc.nrm.se/imalist.htm), updated on March 2014, plombièrite, riversideite and tobermorite were considered as grandfathered species.

Important progress in the knowledge of the structural arrangement of the minerals belonging to the tobermorite group has been achieved in the last few decades, with the determination of the actual crystal structure of tobermorites by Merlino *et al*. (1999, 2000, 2001) and Bonaccorsi *et al*. (2005), allowing a deeper understanding of the chemical and structural variability of the members of this group. Therefore, a re-definition of the endmember formulae, in agreement with crystal-structure data, seems desirable.

This report has been approved by the IMA CNMNC and rationalizes the current nomenclature scheme of tobermorites, well known to the mineralogical community as well as to cement chemists, taking into account the group nomenclature rules of Mills *et al*. (2009).

Basic structural features of tobermorites

The complex module (Fig. 1*a*), common to all tobermorites, is *C* centred, with periods $a \approx 11.2$ Å, $b \approx 7.3$ Å (Fig. 1*b*, 1*c*) and width $c_0 \approx 11.2$ Å (Merlino *et al*., 1999, 2000, 2001). The coordination polyhedra in the calcium layer may be described as consisting of a pyramidal part on

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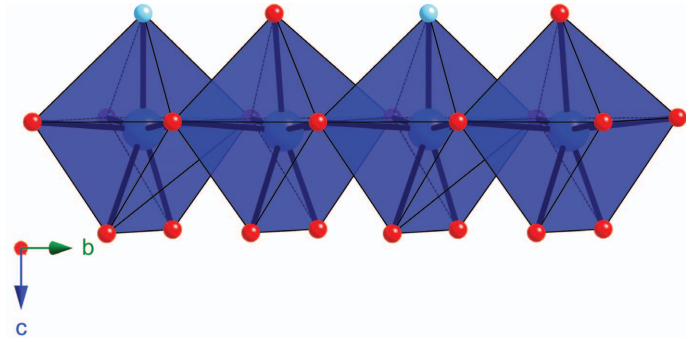


FIG. 2. The column of Ca-centred polyhedra running along **b**. The polyhedra can be described as being formed by a pyramidal part on one side and a domatic part on the other. The apical ligands, on the pyramidal parts, are represented by H_2O molecules (in light blue) and (O^{2-},OH^{-}) anions (in red), alternating along [010].

one side and a domatic part on the other side, forming monocapped trigonal prisms (coordination number, CN = 7). These polyhedra are connected through edge-sharing and form columns running along **b** (Fig. 2). Along this direction, two types of polyhedra alternate; one shows the pyramidal apical site occupied by a water molecule, whereas an oxygen or hydroxyl group occupies the other apical site. Wollastonite-like chains decorate the calcium polyhedra layer on both sides. Using the terminology of cement chemists, the chains are formed by paired tetrahedra connected by bridging tetrahedra. Silicate chains are connected to the calcium polyhedra layers with the paired tetrahedra sharing the dome edges and the bridging tetrahedra sharing the apical oxygen- or hydroxyl-hosting apex.

The various members of the 'tobermorite group' present an order-disorder (OD) character (Dornberger-Schiff, 1956, 1964, 1966; Ferraris *et al*., 2004) related to the metrical relationships between the calcium polyhedral module, with a repeat of 3.65 Å, and the wollastonite-like chains, with a periodicity of 7.3 Å. The chains can be connected to the calcium layers in two distinct but equivalent positions, shifted by 3.65 Å in the **b** direction. Consequently, all the various phases of the tobermorite group can be described in terms of OD layers which may stack in two different ways along **c***, giving rise to a whole family of disordered or ordered sequences (polytypes). In each family of polytypes, two main polytypes exist, corresponding to the MDO (Maximum Degree of Order) structures. A detailed description of the polytypism in tobermorites is reported in Merlino *et al*. (1999, 2000, 2001) and Bonaccorsi and Merlino (2005).

Two distinct kinds of complex module exist, differing in terms of the way in which the bridging tetrahedron is placed with respect to the paired tetrahedra on the two sides of the calcium polyhedra layers (Fig. 3): (1) complex module of type A (Fig. 3*a*); the bridging tetrahedra are placed at the right on one side and at the left on the other side (or *vice versa*) with respect to the paired tetrahedra of the corresponding chains. This kind of complex

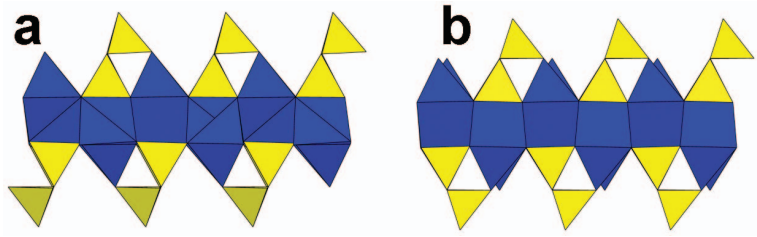


FIG. 3. Complex modules of type A (*a*) and B (*b*). Polyhedra: blue = Ca-centred polyhedra; yellow = Si-centred tetrahedra.

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layer occurs in phases with a monoclinic sub-cell (or family cell, in agreement with the OD terminology) symmetry; (2) complex module of type B (Fig. 3*b*); the bridging tetrahedra on both sides are all placed at the left (or right) with respect to the corresponding paired tetrahedra. This kind of complex layer occurs in the phases presenting an orthorhombic sub-cell symmetry.

In the crystal structure of the 11 Å phases (i.e. tobermorite and clinotobermorite), the stacking of the complex modules gives rise to the condensation of wollastonite-like chains, with the formation of double chains. In the resulting framework, structural cavities occur, hosting additional water molecules and cations (usually calcium). In the crystal structure of the 14 Å tobermorite, the complex modules are separated by a layer containing additional calcium cations and a larger amount of water molecules with respect to the 11 Å phases, i.e. five water molecules with respect to three water molecules. Finally, in 9 Å tobermorite, adjacent complex modules are wedged together, the ridges of one fitting in the hollows of the other. No water molecules occur, the apical sites being occupied only by hydroxyl groups; the additional calcium cation is six-coordinated by the oxygen atoms of the framework. The crystal structure of these different tobermorites are shown in Fig. 4.

Chemical composition and recalculation of the crystal-chemical formulae

Tobermorites usually occur as small fibrous crystals, sometimes associated intimately with calcite and other C-S-H phases (e.g. Biagioni, 2011). Consequently, owing to the usually small amount of homogeneous material available, a full chemical characterization may be very difficult.

Two possible strategies for the recalculation of the chemical formulae of tobermorites can be followed: (1) recalculation based on the number of anions. This method is sensitive to the difficulty in the accurate determination of the water content, related to the usually small amount of homogeneous available material; (2) recalculation based on the number of cations. Considering this strategy, there are various possibilities (e.g. considering the total number of cations) but, owing to the wide chemical variability of the

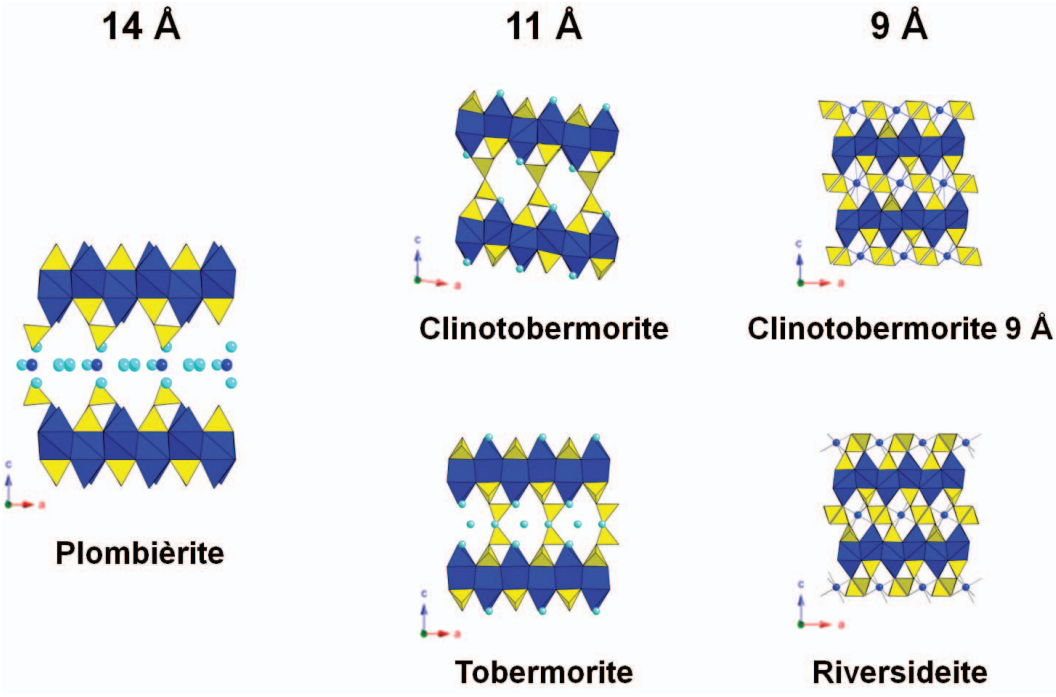


FIG. 4. Crystal structures of tobermorites, as seen down **b**. For polyhedra, colours are as in Fig. 1. Circles: light blue = water molecules; blue = fifth calcium cations (not shown in the crystal structures of the 11 Å phases).

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tobermorites, related to the possible occurrence of additional cations within the structural cavities or in the interlayers, a recalculation based on the number of tetrahedral cations seems the most reliable. Note that some structural data indicate the possibility of defects in the tetrahedral chains, with local omission of the bridging tetrahedra (e.g. Taylor, 1986). However, natural samples usually have good crystallinity and, as a first approximation, we can ignore possible defects of the tetrahedral chains, recalculating the chemical analyses on the basis of six tetrahedral atoms per formula unit (a.p.f.u.), assuming the possible substitution of Si^{4+} by Al^{3+}, in agreement with several authors (e.g. Diamond, 1964; Komarneni *et al*., 1985; Richardson *et al*., 1993; Faucon *et al*., 1999; Andersen *et al*., 2003).

Tobermorites: state of the art

The nomenclature schemes of tobermorites reported in the literature and the accepted species given in the IMA list (March 2014) are shown in Table 1.

The first nomenclature of the tobermorite group was proposed by McConnell (1954), who distinguished three phases on the basis of the basal spacing d_{002}, related to their hydration state. As already stated, McConnell (1954) did not distinguish between crystalline 14 Å tobermorite and the C-S-H gel plombièrite described by Daubrée (1858).

Taylor (1964) put forward a more complete nomenclature scheme, also considering the synthetic C-S-H compounds obtained by cement chemists. He divided the phases into three categories, taking into account the degree of crystallinity. He proposed using the name plombièrite to indicate an amorphous C-S-H gel and to adopt a new name for the 14 Å tobermorite.

Finally, in the IMA list (March 2014), the chemical formulae of tobermorites were only partially updated on the basis of the recent structural studies. As a matter of fact, plombièrite is considered as the crystalline phase studied by Bonaccorsi *et al*. (2005). In the following, more detailed information is given about the mineral species reported in the IMA list, pointing out the classification problems to be addressed.

Plombièrite

The name plombièrite was first used by Daubrée (1858) to indicate a silicate gel formed through the action of thermal springs on cementitious material of Roman age in Plombières, Vosges, France.

McConnell (1954, 1955) studied a natural gelatinous material from Ballycraigy, Larne, County Antrim, Ireland. On the basis of powder X-ray diffraction (XRD) data, he attributed the phase to the C-S-H (I) group. Moreover, taking into account its chemical composition, he identified the material as plombièrite. The author attributed this name indiscriminately to the gelatinous phase and to the most hydrated member of the C-S-H (I) compounds, i.e. crystalline 14 Å tobermorite. In fact, the powder XRD pattern collected for the specimen from Ballycraigy did not show the 14 Å basal reflection.

Consequently, according to Taylor (1964), the name plombièrite should indicate only the poorly crystalline phases, in agreement with the first description given by Daubrée (1858). According to Taylor (1964), the crystalline phase, characterized by a basal spacing of 14 Å, deserves a new name. Unfortunately, since the first descriptions of a natural crystalline 14 Å tobermorite (Heller and Taylor, 1956; Mitsuda *et al*., 1972), this phase has usually been referred to as plombièrite in the mineralogical literature. Bonaccorsi *et al*. (2005), using a specimen from Crestmore, Riverside County, California, USA, solved and refined the crystal structure of plombièrite (natural 14 Å tobermorite). The ideal crystal-chemical formula of plombièrite is $Ca_5Si_6O_{16}(OH)_2{\cdot}7H_2O$. Chemical variability is limited to small changes in the calcium content (usually between 4.5–5 a.p.f.u.) and to minor Al-for-Si substitution (Biagioni, 2011).

Tobermorite

Tobermorite was first described by Heddle (1880) from four Scottish localities, three near Tobermory, Isle of Mull and the fourth being Dunvegan, Isle of Skye.

Claringbull and Hey (1952) re-examined the Heddle's specimens, confirming the validity of tobermorite as a mineral species and reporting its powder XRD pattern, characterized by a 11.3 Å basal reflection. Moreover, they suggested the close similarity between tobermorite and the C-S-H (I) compounds synthesized and studied by Taylor (1950). Owing to the results of Claringbull and Hey (1952), McConnell (1954) used the name tobermorite for the C-S-H phases having a 11 Å basal spacing.

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TABLE 1. Nomenclature schemes for the tobermorite group proposed by McConnell (1954) and Taylor (1964), compared with the mineral species reported in the IMA CNMNC List of Mineral Names (March, 2014).

– McConnell (1954) –			——— Taylor (1964)* ———			——— IMA list ———	
d_{002} (Å)		H_2O:SiO_2 molar ratio		Mineralogical name	Chemical formula	Name	Chemical formula
Crystalline tobermorites							
9.6	Riversideite	0.5	9.3 Å tobermorite	Riversideite	$C_5S_6H_{0\text{-}2}$	Riversideite	$Ca_5Si_6O_{16}(OH)_2{\cdot}2H_2O$
11.3	Tobermorite	1.0	11.3 Å tobermorite	Tobermorite	$C_5S_6H_5$	Tobermorite Clinotobermorite	$Ca_5Si_6O_{16}(OH)_2{\cdot}nH_2O$ $Ca_5Si_6O_{17}{\cdot}5H_2O$
14.6	Plombierite	2.0	14 Å tobermorite		$C_5S_6H_9$	Plombièrite	$Ca_5Si_6O_{16}(OH)_2{\cdot}7H_2O$
Semicrystalline tobermorites							
			C-S-H(I)		Ca/Si < 1.5		
			C-S-H(II)		Ca/Si ⩾ 1.5		
Near-amorphous tobermorites							
Absent	Gels	Variable	Tobermorite gel	Plombierite	Ca/Si probably ⩾ 1.5		

* Taylor (1964) attributed the mineral species tacharanite and oyelite (basal spacing of 12 and 10 Å, respectively) to the tobermorite group. Owing to the lack of structural data, their relationships with the tobermorite group is only speculative.

The crystal structure determinations by Merlino *et al*. (1999, 2000, 2001) allowed a deeper understanding of the crystal chemistry of this phase and the interpretation of its thermal behaviour. Examination of chemical data reported in the literature (Biagioni, 2011) confirms the wide variability of calcium content, generally ranging between 4 and 5 a.p.f.u., in agreement with the crystal structure of tobermorite. Some analyses show small Ca contents, <4 a.p.f.u.; this is usually due to analysis of inhomogeneous material, with the admixture of Ca-poor phases. Analyses showing a Ca content >5 a.p.f.u. could be explained as the result of the close association of tobermorite with phases having a higher Ca:Si ratio (e.g. xonotlite, $Ca_6(Si_6O_{17})(OH)_2$) and/or calcite.

Substitution of Si^{4+} by Al^{3+} in the tetrahedral chains is widespread, with a maximum possible Al content of 1 Al a.p.f.u. Owing to a maximum Al content of 1/6 of the tetrahedral sites, it is worth noting that Al-rich samples do not warrant a new name. Al-free tobermorite is very rare, e.g. in the Kalahari Manganese Field, Republic of South Africa (Merlino *et al*., 2001). The general formula of tobermorite may be written as $Ca_{4+x}(Al_ySi_{6-y})O_{15+2x-y}(OH)_{2-2x+y}{\cdot}5H_2O$, with $0 \leqslant x \leqslant 1$ and $0 \leqslant y \leqslant 1$. The variable x represents the amount of additional calcium hosted in the structural cavities ['zeolitic' calcium, in agreement with Bonaccorsi and Merlino (2005)]. Consequently, tobermorite is actually a series between two endmembers, $Ca_4Si_6O_{15}(OH)_2{\cdot}5H_2O$ and $Ca_5Si_6O_{17}{\cdot}5H_2O$. As illustrated by Merlino *et al*. (2001), this chemical difference guides the thermal behaviour ["normal" or "anomalous", according to the definitions given by Mitsuda and Taylor (1978)] of tobermorite; phases having $x \sim 0$ show "anomalous" behaviour, whereas increasing Ca content favours "normal" behaviour.

Clinotobermorite

Clinotobermorite was first found at Fuka, Okayama Prefecture, Japan, by Henmi and Kusachi (1992). It is the monoclinic dimorph of tobermorite, characterized by the complex module of type A (Bonaccorsi and Merlino, 2005). The sub-cell structure of clinotobermorite was solved by Hoffmann and Armbruster (1997), whereas its real structure was determined by Merlino *et al*. (2000).

The natural occurrences of clinotobermorite are very rare and its genetic relationships with tobermorite are still unknown. According to Henmi and Kusachi (1992), clinotobermorite could be a low-temperature polymorph of tobermorite, whereas Biagioni *et al*. (2012) observed a clinotobermorite-like phase as the product of the thermal treatment of an "anomalous" tobermorite.

Chemically, clinotobermorite usually shows ~5 Ca a.p.f.u.; however, Biagioni (2011), using single-crystal XRD techniques, observed the coexistence of tobermorite and clinotobermorite in a crystal from Gambellara quarry, Veneto, Italy, having a calcium content of 4.2 a.p.f.u. In addition, clinotobermorite and tobermorite coexist in a specimen from San Vito di Leguzzano, Veneto, Italy; in this specimen, crystals are unsuitable for single-crystal studies and were used for the collection of powder XRD patterns. Refinement of their relative abundance with the Rietveld method indicated an ~50:50 ratio of these two phases. Owing to the fact the average content of calcium is 4.1 a.p.f.u., it is possible that clinotobermorite from this sample is Ca-poor (Biagioni, 2011).

Riversideite

Eakle (1917) described two new minerals from Crestmore, Riverside County, California, USA, and named them crestmoreite and riversideite. The latter differs from the former only in the smaller water content. Flint *et al*. (1938) concluded that crestmoreite and riversideite are the same phase and proposed dropping the name riversideite. Subsequently, Taylor (1953*a*) demonstrated that crestmoreite (and riversideite also) is an association, at submicroscopic scale, of tobermorite "with different hydration states" and wilkeite, a discredited phase corresponding to a phosphate-bearing ellestadite (Rouse and Dunn, 1982; Pasero *et al*., 2010). In particular, he observed basal reflections at 14.0 and 11.2 Å, indicating the coexistence of plombièrite and tobermorite. No 9.3 Å basal reflection was observed.

McConnell (1954) assumed that the phase studied by Eakle (1917) was actually the 9 Å phase, transformed into the more hydrated terms due to the lack of proper preservation. As a matter of fact, a 9 Å tobermorite was obtained easily through heating of "normal" tobermorite by several authors (e.g. McConnell, 1954; Biagioni, 2011). None of the specimens so obtained expands its basal spacing if kept at ambient

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conditions. According to our knowledge, only two possible natural occurrences of 9 Å tobermorite have been described: (1) Gross (1977) reported the occurrence of riversideite from the Hatrurim Formation, Israel, associated with other tobermorites. Unfortunately, no analytical data were given; (2) Marincea *et al*. (2001) described the occurrence of a 9 Å phase, in fibres up to 50 μm long, associated strictly with plombièrite. They reported only a chemical analysis, recalculated on the basis of the formula of riversideite proposed by Mandarino (1999), i.e. $Ca_5Si_6O_{16}(OH)_2{\cdot}2H_2O$.

Merlino *et al*. (2000) determined the crystal structure of 9 Å clinotobermorite, obtained through thermal treatment of clinotobermorite at 300ºC. According to these authors, the chemical formula of the 9 Å phase with monoclinic sub-cell should be $Ca_5Si_6O_{16}(OH)_2$; the species with orthorhombic sub-cell should have the same ideal composition.

Potential new mineral species

Examination of the literature data and our research on tobermorites point to the potential existence of other members belonging to the tobermorite group: (1) Biagioni (2011) described the coexistence of a Ca-poor clinotobermorite, associated closely with tobermorite, from Gambellara quarry and San Vito di Leguzzano, Veneto, Italy. If confirmed, its ideal chemical composition would be $Ca_4Si_6O_{15}(OH)_2{\cdot}5H_2O$. (2) K-Al tobermorite was synthesized by Mitsuda (1970). Some natural phases containing K and Al have been described by Organova *et al*. (2002) and Biagioni (2011). In those cases, K^+ ions occupy <50% of the sites within the structural cavities, but the possible existence of tobermorites having a K^+ occupancy larger than 50% should be taken into account.

Revision of the nomenclature of the tobermorite supergroup

The increasing knowledge of the crystal-chemistry of tobermorites allows the introduction of a new nomenclature scheme.

Following Mills *et al*. (2009), we define the tobermorite supergroup from the name of the most common phase within it. The tobermorite supergroup is formed by the tobermorite group, and the unclassified minerals plombièrite, clinotobermorite, and riversideite. The new nomenclature

TABLE 2. New nomenclature scheme for the tobermorite supergroup. In italics, possible new mineral species of the tobermorite supergroup are given. As indicated, riversideite has to be considered as being of questionable status.

d_{002} (Å)		Mineral name	Simplified chemical formula	Structural chemical formula
14.0		Plombièrite	$Ca_5Si_6O_{16}(OH)_2{\cdot}7H_2O$	$[Ca_4Si_6O_{16}(OH)_2{\cdot}2H_2O]{\cdot}(Ca{\cdot}5H_2O)$
11.3	Tobermorite group	Tobermorite	$Ca_5Si_6O_{17}{\cdot}5H_2O$	$[Ca_4Si_6O_{17}{\cdot}2H_2O]{\cdot}(Ca{\cdot}3H_2O)$
		Kenotobermorite	$Ca_4Si_6O_{15}(OH)_2{\cdot}5H_2O$	$[Ca_4Si_6O_{15}(OH)_2{\cdot}2H_2O]{\cdot}3H_2O$
		Clinotobermorite	$Ca_5Si_6O_{17}{\cdot}5H_2O$	$[Ca_4Si_6O_{17}{\cdot}2H_2O]{\cdot}(Ca{\cdot}3H_2O)$
	Clinotobermorite group	*Kenoclinotobermorite*	$Ca_4Si_6O_{15}(OH)_2{\cdot}5H_2O$	$[Ca_4Si_6O_{15}(OH)_2{\cdot}2H_2O]{\cdot}3H_2O$
		Kalitobermorite	$KCa_4AlSi_5O_{15}(OH)_2{\cdot}5H_2O$	*$[Ca_4AlSi_5O_{15}(OH)_2{\cdot}2H_2O]{\cdot}(K{\cdot}3H_2O)$*
9.3		Riversideite (questionable)	$Ca_5Si_6O_{16}(OH)_2$	$[Ca_4Si_6O_{16}(OH)_2]{\cdot}Ca$

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for the tobermorites is summarized in Table 2 where the structural chemical formula is expressed by separating the content of the structural cavities or the interlayers (within round brackets) from the chemical composition of the complex modules (within square brackets).

In agreement with the structural and chemical data outlined above, the following can be stated:

(1) Plombièrite – notwithstanding the recommendation given by Taylor (1964), who suggested the use of the name plombièrite to indicate an amorphous C-S-H gel and the introduction of a new name to indicate the crystalline 14 Å tobermorite, the consolidated use of the term plombièrite to describe the latter phase suggests that it should be maintained. Consequently, plombièrite should be defined as the crystalline 14 Å tobermorite, with type locality Crestmore, Riverside County, California, USA. Neotype material is represented by the specimen studied by Bonaccorsi *et al.* (2005) and kept in the mineralogical collection of the Museo di Storia Naturale, Università di Pisa, catalogue number 19690.

(2) Tobermorite group – this group consists of two mineral species, kenotobermorite, $Ca_4Si_6O_{15}(OH)_2{\cdot}5H_2O$ and tobermorite, $Ca_5Si_6O_{17}{\cdot}5H_2O$. The prefix keno indicates the Ca-free nature of the structural cavities of this member of the tobermorite group. The name tobermorite is in agreement with the Ca-rich nature of the formula given in the IMA list. Tobermorite and kenotobermorite form a continuous solid solution. As regards the type material, it should be noted that a more accurate characterization of type tobermorite described by Heddle (1880) is mandatory in order to define the type specimens for the two new endmembers in the tobermorite group. If a re-study of the type material described by Heddle (1880) proves impossible, neotype specimens may be defined. In particular, we suggest that the type specimen of tobermorite could be that studied by Henmi and Kusachi (1992), who reported chemical analysis, unit-cell parameters and powder XRD data for tobermorite from Fuka, corresponding to the chemical composition, on the basis of (Si+Al) = 6 a.p.f.u., $(Ca_{4.85}Mg_{0.01})_{\Sigma 4.86}(Al_{0.15}Si_{5.85})_{\Sigma 6}O_{16.57}(OH)_{0.43}{\cdot}4.35H_2O$. Type material of kenotobermorite is represented by the specimen studied by Merlino *et al.* (2001) from the N'Chwaning II mine (and not the Wessels mine, as reported erroneously in that paper), Kalahari Manganese Field, South Africa; the type specimen is kept in the mineralogical collection of the Museo di Storia Naturale, Università di Pisa, catalogue number 19691. Finally, the possible existence of other members of the tobermorite group, having different zeolitic cations (e.g. K^+) should be considered; in this case a prefix (e.g. kali-) should be used.

(3) Clinotobermorite – this mineral is a dimorph of the members of the tobermorite group, being characterized by a different kind of complex module. As reported above, the possible existence of a Ca-poor analogue cannot be excluded. We propose maintaining the name clinotobermorite to indicate the Ca-rich endmember. The hypothetical Ca-poor endmember should be named 'kenoclinotobermorite'.

(4) Riversideite – its description is very incomplete and its natural occurrence is not

TABLE 3. Nomenclature scheme for natural polytypes in the tobermorite supergroup.

	a (Å)	*b* (Å)	*c* (Å)	α (º)	β (º)	γ (º)	Space group	Ref.
Plombièrite-4*O*	11.2	7.3	56	90	90	90	*F*2*dd*	[1]
Plombièrite-2*M*	6.735	7.425	27.987	90	90	123.25	*B*11*b*	[1]
Kenotobermorite-4*O*	11.265	7.385	44.970	90	90	90	*F*2*dd*	[2]
Kenotobermorite-2*M*	6.735	7.385	22.487	90	90	123.25	*B*11*m*	[2]
Tobermorite-2*M*	6.732	7.369	22.680	90	90	123.18	*B*11*m*	[2]
Clinotobermorite-2*M*	11.276	7.343	22.642	90	97.28	90	*Cc*	[3]
Clinotobermorite-1*A*	11.274	7.344	11.468	99.18	97.19	90.02	*C*1	[3]

[1] Bonaccorsi *et al.* (2005); [2] Merlino *et al.* (2001); [3] Merlino *et al.* (2000).

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demonstrated unequivocally. There is the possibility that natural 9 Å tobermorite will never be found at its type locality (Crestmore, Riverside County, California) or in other localities. However, owing to the consolidated use of the name riversideite to indicate natural 9 Å tobermorite, the name should be maintained and the species should be indicated as "questionable".

(5) Owing to the OD nature of 'tobermorites', several natural polytypes are known. Their nomenclature is given in Table 3.

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