1 **Revision 1**
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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 for 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 is composed by 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 should not deserve any new name, because Al could 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 unequivocally demonstrated and its status should be considered as 'questionable'. The chemical composition of its synthetic counterpart, obtained through partial dehydration of tobermorite, has chemical composition $Ca_5Si_6O_{16}(OH)_2$. All these mineral species present an OD character, and several polytypes are known. This report has been approved by the IMA CNMNC.

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 whose 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 the waste disposal.

'Tobermorites' are structurally characterized by layers of seven-fold coordinated calcium-centered 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 '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 described also by Taylor (1953b) for synthetic C-S-H (I) compounds], McConnell (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://pubsites.uws.edu.au/ima-cnmnc/), updated at 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), consenting 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 by the mineralogical community as well as by the cement chemists, taking into account the group nomenclature rules of Mills *et al.* (2009).

Basic structural features of 'tobermorites'

The 'complex module' (Fig. 1a), common to all 'tobermorites', is *C* centered, with periods $a \sim 11.2$ Å, $b \sim 7.3$ Å (Fig. 1b, 1c), and width $c_0 \sim 11.2$ Å (Merlino *et al.*, 1999, 2000, 2001). The coordination polyhedra in the calcium layer may be described as consisting of a pyramidal part on one side and a domatic part on the other side, being monocapped trigonal prisms (C.N. = 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

85   pyramidal apical site occupied by a water molecule, whereas an oxygen or hydroxyl group
86   occupies the other apical site. Wollastonite-like chains decorate the calcium polyhedra layer
87   on both sides. Using the terminology of the cement chemists, the chains are formed by
88   'paired' tetrahedra connected by 'bridging' tetrahedra. Silicate chains are connected to the
89   calcium polyhedra layers with the paired tetrahedra sharing the 'dome' edges and the bridging
90   tetrahedra sharing the apical oxygen or hydroxyl-hosting apex.

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

102   Two distinct kinds of 'complex module' exist, differing each other in the ways to
103   place the bridging tetrahedron with respect to the paired tetrahedra on the two sides of the
104   calcium polyhedra layers (Fig. 3):

105   *i*) 'complex module' of type A (Fig. 3a): the bridging tetrahedra are placed at right on
106   one side and at left on the other side (or *vice versa*) with respect to the paired tetrahedra of the
107   corresponding chains. This kind of complex layer occurs in phases with monoclinic sub-cell
108   (or family cell, in agreement with the OD terminology) symmetry;

109   *ii*) 'complex module' of type B (Fig. 3b): the bridging tetrahedra on both sides are all
110   placed at left (or at right) with respect to the corresponding paired tetrahedra. This kind of
111   complex layer occurs in the phases presenting an orthorhombic sub-cell symmetry.

112   In the crystal structure of the 11 Å phases (*i.e.* tobermorite and clinotobermorite), the
113   stacking of the complex modules gives rise to the condensation of wollastonite-like chains,
114   with the formation of double chains. In the resulting framework, structural cavities occur,
115   hosting additional water molecules and cations (usually calcium). In the crystal structure of
116   the '14 Å tobermorite', the complex modules are separated by a layer containing additional
117   calcium cations and a larger amounts of water molecules with respect to the 11 Å phases, *i.e.*
118   5 water molecules with respect to 3 water molecules. Finally, in the '9 Å tobermorite',
119   adjacent complex modules are wedged together, the ridges of one fitting in the hollows of the
120   other. No water molecules occur, being the apical sites occupied only by hydroxyl groups; the
121   additional calcium cation is six-fold coordinated by the oxygen atoms of the framework. The
122   crystal structure of these different 'tobermorites' are shown in Figure 4.

123

Chemical composition and recalculation of the crystal-chemical formulae

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

129

130   Two possible strategies for the recalculation of the chemical formulae of
131 'tobermorites' can be followed:

132   *i*) recalculation based on the number of anions. This method is sensitive to the
133 difficulty in the accurate determination of the water content, related to the usual low amount
134 of homogeneous available material;

135   *ii*) recalculation based on the number of cations. Considering this strategy, there are
136 some possibilities (*e.g.*, considering the total number of cations) but, owing to the wide
137 chemical variability of the 'tobermorites', related to the possible occurrence of additional
138 cations within the structural cavities or in the interlayers, a recalculation based on the number
139 of tetrahedral cations seems the most reliable. It should be taken into account that some
140 structural data indicate the possibility of defects in the tetrahedral chains, with the local
141 omission of the bridging tetrahedra (*e.g.*, Taylor, 1986). However, natural samples usually
142 have a good crystallinity and, as a first approximation, we can neglect the possible defects of
143 the tetrahedral chains, recalculating the chemical analyses on the basis of 6 tetrahedral atoms
144 per formula unit (*apfu*), assuming the possible substitution of Si^{4+} by Al^{3+}, in agreement with
145 several authors (*e.g.*, Diamond, 1964; Komarneni *et al.*, 1985; Richardson *et al.*, 1993;
146 Faucon *et al.*, 1999; Andersen *et al.*, 2003).

147

148 **'Tobermorites': state of the art**

149   Table 1 shows the nomenclature schemes of 'tobermorites' reported in literature and
150 the accepted species given in the IMA list (March 2014).

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

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

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

165

166 *Plombièrite*

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

170   McConnell (1954, 1955) studied a natural gelatinous material from Ballycraigy,
171 Larne, County Antrim, Ireland. On the basis of X-ray powder diffraction data, he attributed
172 the phase to the C-S-H (I) group. Moreover, taking into account its chemical composition, he

173 identified the material as plombièrite. The author attributed this name indifferently to the
174 gelatinous phase and to the most hydrated member of the C-S-H (I) compounds, *i.e.*
175 crystalline '14 Å tobermorite'. Actually, the X-ray powder diffraction pattern collected on the
176 specimen from Ballycraigy did not show the 14 Å basal reflection.

177 Consequently, according to Taylor (1964), the name plombièrite should indicate only
178 the poorly crystalline phases, in agreement with the first description given by Daubrée (1858).
179 According to Taylor (1964), the crystalline phase, characterized by a basal spacing of 14 Å,
180 should deserve a new name. Unfortunately, since the first natural descriptions of a crystalline
181 '14 Å tobermorite' (Heller and Taylor, 1956; Mitsuda *et al.*, 1972), this phase has been
182 usually referred as plombièrite in the mineralogical literature. Bonaccorsi *et al.* (2005), using
183 a specimen from Crestmore, Riverside County, California, USA, solved and refined the
184 crystal structure of plombièrite (natural '14 Å tobermorite'). The ideal crystal-chemical
185 formula of plombièrite is $Ca_5Si_6O_{16}(OH)_2 \cdot 7H_2O$. The chemical variability is limited to small
186 changes in the calcium content (usually between 4.5 and 5 *apfu*) and to minor Al-for-Si
187 substitution (Biagioni, 2011).

188
189 *Tobermorite*

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

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

198 The crystal structure determinations by Merlino *et al.* (1999, 2000, 2001) allowed a
199 deeper understanding of the crystal-chemistry of this phase and the interpretation of its
200 thermal behavior. The examination of chemical data reported in literature (Biagioni, 2011)
201 confirms the wide chemical variability of calcium content, generally ranging between 4 and 5
202 *apfu*, in agreement with the crystal structure of tobermorite. Some analyses show low Ca
203 content, less than 4 *apfu*; this is usually due to the analysis of inhomogeneous material, with
204 the admixture of Ca-poor phases. Analyses showing a Ca content higher than 5 *apfu* could be
205 explained as the result of the close association of tobermorite with phases having a higher
206 Ca:Si ratio (*e.g.*, xonotlite, $Ca_6(Si_6O_{17})(OH)_2$) and/or calcite.

207 Al^{3+}-for-Si^{4+} substitution in the tetrahedral chains is widespread, with a maximum
208 possible Al content of 1 Al *apfu*. Owing to a maximum Al content of 1/6 of the tetrahedral
209 sites, it is worth noting that Al-rich samples should not deserve any new name. Al-free
210 tobermorite is very rare, *e.g.*, Kalahari Manganese Field, Republic of South Africa (Merlino *et*
211 *al.*, 2001).

212 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 $0 \le x \le 1$ and $0 \le y \le 1$.
213

214 The variable x represents the amount of additional calcium hosted in the structural
215 cavities ('zeolitic' calcium, in agreement with Bonaccorsi and Merlino, 2005). Consequently,
216 tobermorite is actually a series between two endmembers, $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$ and

217 $Ca_5Si_6O_{17}·5H_2O$. As illustrated by Merlino *et al*. (2001), this chemical difference guides the
218 thermal behavior ("normal" or "anomalous", according to the definition given by Mitsuda and
219 Taylor, 1978) of tobermorite: the phases having $x \sim 0$ show an "anomalous" behavior,
220 whereas the increasing Ca content favors a "normal" behavior.
221
222   *Clinotobermorite*
223   Clinotobermorite has been first found in Fuka, Okayama Prefecture, Japan, by Henmi
224 and Kusachi (1992). It is the monoclinic dimorph of tobermorite, characterized by the
225 'complex module' of type A (according to Bonaccorsi and Merlino, 2005).
226   The sub-cell structure of clinotobermorite was solved by Hoffmann and Armbruster
227 (1997), whereas its real structure was determined by Merlino *et al*. (2000).
228   The natural occurrences of clinotobermorite are very rare and its genetic relationships
229 with tobermorite are still unknown. According to Henmi and Kusachi (1992),
230 clinotobermorite could be a low-temperature polymorph of tobermorite, whereas Biagioni *et*
231 *al*. (2012) observed a clinotobermorite-like phase as the product of the thermal treatment of an
232 "anomalous" tobermorite.
233   Chemically, clinotobermorite shows usually *ca*. 5 Ca *apfu*; however, Biagioni (2011),
234 using X-ray single-crystal techniques, observed the coexistence of tobermorite and
235 clinotobermorite in a crystal from Gambellara quarry, Veneto, Italy, having a calcium content
236 of 4.2 *apfu*. In addition, clinotobermorite and tobermorite coexist in a specimen from San Vito
237 di Leguzzano, Veneto, Italy; in this specimen, crystals are unsuitable for single-crystal studies
238 and were used for the collection of X-ray powder patterns. The refinement of their relative
239 abundance with the Rietveld method indicated a *ca*. 50:50 ratio of these two phases. Owing to
240 the fact the average content of calcium is 4.1 *apfu*, it is possible that clinotobermorite of this
241 sample is Ca-poor (Biagioni, 2011).
242
243   *Riversideite*
244   Eakle (1917) described two new minerals from Crestmore, Riverside County,
245 California, USA, and named them crestmoreite and riversideite. The latter would differ from
246 the former only in the lower water content. Flint *et al*. (1938) concluded that crestmoreite and
247 riversideite are the same phase and proposed to drop out the name riversideite. Subsequently,
248 Taylor (1953a) demonstrated that crestmoreite (and riversideite as well) is an association, at
249 submicroscopic scale, of tobermorite "with different hydration states" and wilkeite, a
250 discredited phase corresponding to a phosphatian ellestadite (Rouse and Dunn, 1982; Pasero
251 *et al*., 2010). In particular, he observed basal reflections at 14.0 and 11.2 Å, indicating the
252 coexistence of plombièrite and tobermorite. No 9.3 Å basal reflection was observed.
253   McConnell (1954) assumed that the phase studied by Eakle (1917) was actually the 9
254 Å phase, transformed into the more hydrated terms due to the lack of proper preservation. As
255 a matter of fact, a '9 Å tobermorite' has been easily obtained through heating of "normal"
256 tobermorite by several authors (*e.g*, McConnell, 1954; Biagioni, 2011). None of the
257 specimens so obtained expands its basal spacing if kept at room conditions. According to our
258 knowledge, only two possible natural occurrences of '9 Å tobermorite' have been described:
259   *i*) Gross (1977) reported the occurrence of riversideite from the Hatrurim Formation,
260 Israel, associated with other 'tobermorites'. Unfortunately, no analytical data are given;

261   *ii*) Marincea *et al.* (2001) described the occurrence of a 9 Å phase, in fibers up to 50

262 μm in length, strictly associated with plombièrite. They reported only a chemical analysis,

263 recalculated on the basis of the formula of riversideite proposed by Mandarino (1999), *i.e.*

264 $Ca_5Si_6O_{16}(OH)_2 \cdot 2H_2O$.

265   Merlino *et al.* (2000) determined the crystal structure of 'clinotobermorite-9 Å',

266 obtained through thermal treatment of clinotobermorite at 300°C. According to these authors,

267 the chemical formula of the 9 Å phase with monoclinic sub-cell should be $Ca_5Si_6O_{16}(OH)_2$;

268 the species with orthorhombic sub-cell should have the same ideal composition.

269

Potentially new mineral species

271   The examination of literature data and our researches on 'tobermorites' point to the

272 potential existence of other members belonging to the 'tobermorite group':

273   *i*) Biagioni (2011) described the coexistence of a Ca-poor clinotobermorite, closely

274 associated with tobermorite, from Gambellara quarry and San Vito di Leguzzano, Veneto,

275 Italy. If confirmed, its ideal chemical composition could be $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$.

276   *ii*) K-Al tobermorite was synthesized by Mitsuda (1970). Some natural phases

277 containing K and Al have been described by Organova *et al.* (2002) and Biagioni (2011). In

278 those cases, K^+ ions occupy less than 50% of the site within the structural cavities, but the

279 possible existence of 'tobermorites' having a K^+ occupancy larger than 50% should be taken

280 into account.

281

Revision of the nomenclature of the tobermorite supergroup

283   The increasing knowledge of the crystal-chemistry of 'tobermorites' allows the

284 introduction of a new nomenclature scheme.

285   Following Mills *et al.* (2009), we define the tobermorite supergroup, from the name of

286 the most common phase within it. Tobermorite supergroup is formed by the tobermorite

287 group, and the unclassified minerals plombièrite, clinotobermorite, and riversideite. The new

288 nomenclature for the 'tobermorites' is summarized in Table 2. In the table, the structural

289 chemical formula is expressed separating the content of the structural cavities or the

290 interlayers (within round brackets) from the chemical composition of the 'complex modules'

291 (within square brackets).

292   In agreement with the structural and chemical data outlined above, we can state:

293   *i*) plombièrite – notwithstanding the recommendation given by Taylor (1964), who

294 suggested the use of the name plombièrite to indicate an amorphous C-S-H gel and the

295 introduction of a new name to indicate the crystalline '14 Å tobermorite', the consolidated use

296 of the term 'plombièrite' to describe the latter phase suggests its maintenance. Consequently,

297 plombièrite should be defined as the crystalline '14 Å tobermorite', with type-locality

298 Crestmore, Riverside County, California, USA. Neotype material is represented by the

299 specimen studied by Bonaccorsi *et al.* (2005) and kept in the mineralogical collection of the

300 Museo di Storia Naturale, Università di Pisa, under catalog number 19690.

301   *ii*) Tobermorite group – this group is composed by two mineral species,

302 kenotobermorite, $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$, and tobermorite, $Ca_5Si_6O_{17} \cdot 5H_2O$. The prefix 'keno'

303 indicates the Ca-free nature of the structural cavities of this member of the tobermorite group.

304 The name tobermorite is in agreement with the Ca-rich nature of the formula given in the
305 IMA list. Tobermorite and kenotobermorite form a continuous solid solution. As regards the
306 type material, it should be noted that a more accurate characterization of type tobermorite
307 described by Heddle (1880) is mandatory in order to define the type specimens for the two
308 new endmembers in the tobermorite group. If a re-study of the type material described by
309 Heddle (1880) proves impossible, neotype specimens may be defined. In particular, we
310 suggest that the type specimen of tobermorite could be that studied by Henmi and Kusachi
311 (1992), who reported chemical analysis, unit-cell parameters, and X-ray powder diffraction
312 data of tobermorite from Fuka, corresponding to the chemical composition, on the basis of
313 (Si+Al) = 6 *apfu*, $(Ca_{4.85}Mg_{0.01})_{\Sigma4.86}(Al_{0.15}Si_{5.85})_{\Sigma6}O_{16.57}(OH)_{0.43}\cdot4.35H_2O$. Type material of
314 kenotobermorite is represented by the specimen studied by Merlino *et al.* (2001) from the
315 N'Chwaning II mine (and not the Wessels mine, as erroneously reported in that paper),
316 Kalahari Manganese Field, South Africa; the type specimen is kept in the mineralogical
317 collection of the Museo di Storia Naturale, Università di Pisa, catalogue number 19691.
318 Finally, it should be considered the possible existence of other members of the tobermorite
319 group, having different 'zeolitic' cations (*e.g.*, K^+ ion); in this case a prefix (*e.g.*, kali-) should
320 be used.

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

326   *iv*) Riversideite – its description is very incomplete and its natural occurrence is not
327 unequivocally demonstrated. There is the possibility that natural '9 Å tobermorite' will never
328 be found at its type locality (Crestmore, Riverside County, California) neither in other
329 localities. However, owing to the consolidated use of the name 'riversideite' to indicate
330 natural '9 Å tobermorite', the name should be maintained and the species should be indicated
331 as 'questionable'.

332   *v*) Owing to the OD nature of 'tobermorites', several natural polytypes are known. Their
333 nomenclature is given in Table 3.

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340

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Table captions

Table 1. Nomenclature scheme for the 'tobermorite group' proposed by McConnell (1954) and Taylor (1964), compared with the mineral species reported in the IMA list (March 2014).

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

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

Figure captions

Fig. 1. The fundamental building unit in the crystal structure of 'tobermorites', the so-called 'complex module'. The sheet of seven-fold Ca-centered 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 site of Ca-centered polyhedra.

Fig. 2. Column of Ca-centered polyhedra running along **b**. The polyhedra can be described as formed by a pyramidal part on one side and a domatic part on the other site. 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].

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

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

473 **Table 1**. Nomenclature scheme for the 'tobermorite group' proposed by McConnell (1954)
474 and Taylor (1964), compared with the mineral species reported in the IMA list (March 2014).
475

	d_{002} (Å)	McConnell (1954)	H₂O:SiO₂ molar ratio	Taylor (1964)* Mineralogical name	Chemical formula	IMA list Name	Chemical formula
Crystalline tobermorites	9.6	**Riversideite**	0.5	9.3 Å tobermorite **Riversideite**	$C_5S_6H_{0-2}$	**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		

476 *Taylor (1964) attributed to the 'tobermorite group' phases with a basal spacing of 12 and 10 Å, corresponding
477 to the mineral species tacharanite and oyelite, respectively. Owing to the lack of structural data, their
478 relationships with the 'tobermorite group' is only speculative.
479

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

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 group	Clinotobermorite	$Ca_5Si_6O_{17} \cdot 5H_2O$	$[Ca_4Si_6O_{17} \cdot 2H_2O] \cdot (Ca \cdot 3H_2O)$
		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)	$Ca_5Si_6O_{16}(OH)_2$	$[Ca_4Si_6O_{16}(OH)_2] \cdot Ca$

485 **Table 3**. Nomenclature scheme for natural polytypes in the tobermorite supergroup.

486

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	s.g.	Ref.
Plombièrite-4O	11.2	7.3	56	90	90	90	$F2dd$	[1]
Plombièrite-2M	6.735	7.425	27.987	90	90	123.25	$B11b$	[1]
Kenotobermorite-4O	11.265	7.385	44.970	90	90	90	$F2dd$	[2]
Kenotobermorite-2M	6.735	7.385	22.487	90	90	123.25	$B11m$	[2]
Tobermorite-2M	6.732	7.369	22.680	90	90	123.18	$B11m$	[2]
Clinotobermorite-2M	11.276	7.343	22.642	90	97.28	90	Cc	[3]
Clinotobermorite-1A	11.274	7.344	11.468	99.18	97.19	90.02	$C1$	[3]

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

487 **Fig. 1**. The fundamental building unit in the crystal structure of 'tobermorites', the so-called
488 'complex module'. The sheet of seven-fold Ca-centered polyhedra is shown in blue, whereas
489 wollastonite-like silicate chains are shown in yellow. (a) An oblique projection of the
490 'complex module'; the 'complex module' is seen down [010] and [100] in (b) and (c),
491 respectively. The two fundamental repeat units of the 'complex module' are shown. Circles
492 represent water molecules (light blue) and oxygen atoms or hydroxyl groups (red) bonded to
493 the apical site of Ca-centered polyhedra.
494
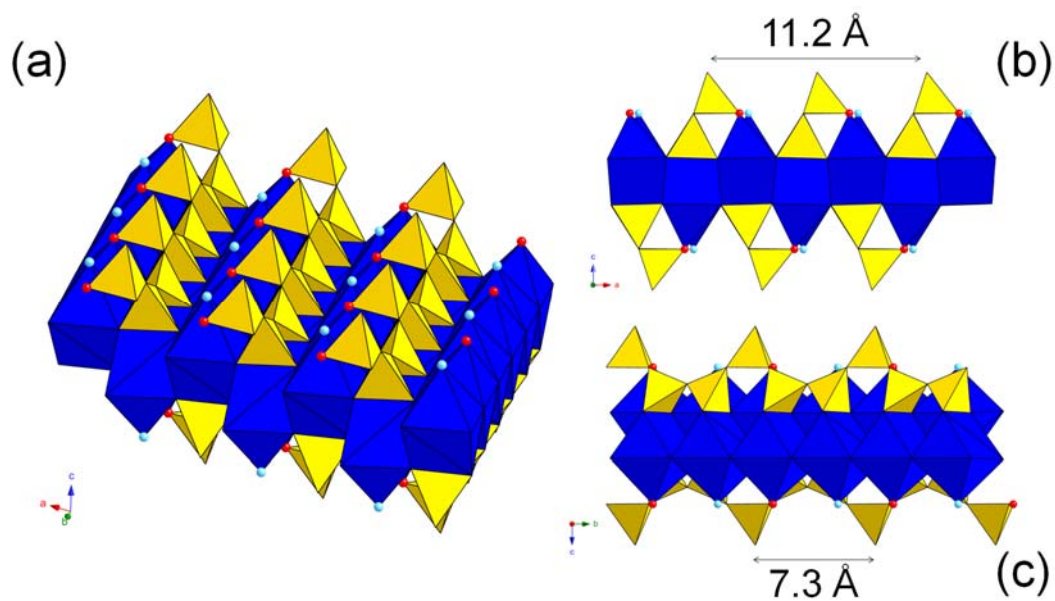
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499   formed by a pyramidal part on one side and a domatic part on the other site. The apical
500   ligands, on the pyramidal parts, are represented by H_2O molecules (in light blue) and (O^{2-},OH^-)
501   anions (in red), alternating along [010].
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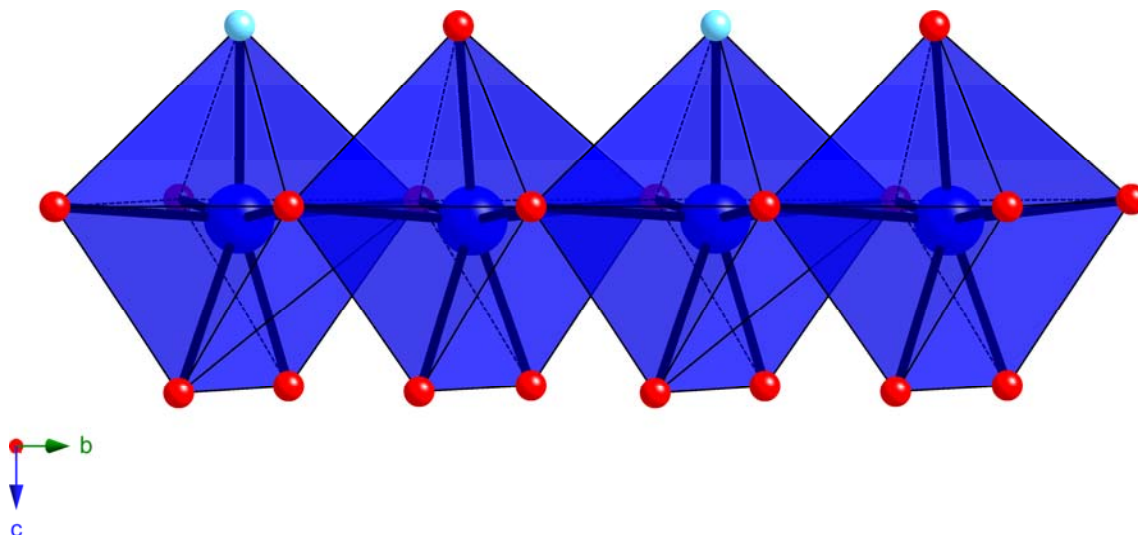
505 **Fig. 3**. 'Complex modules' of type A (a) and B (b). Polyhedra: blue = Ca-centered polyhedra;
506 yellow = Si-centered tetrahedra.
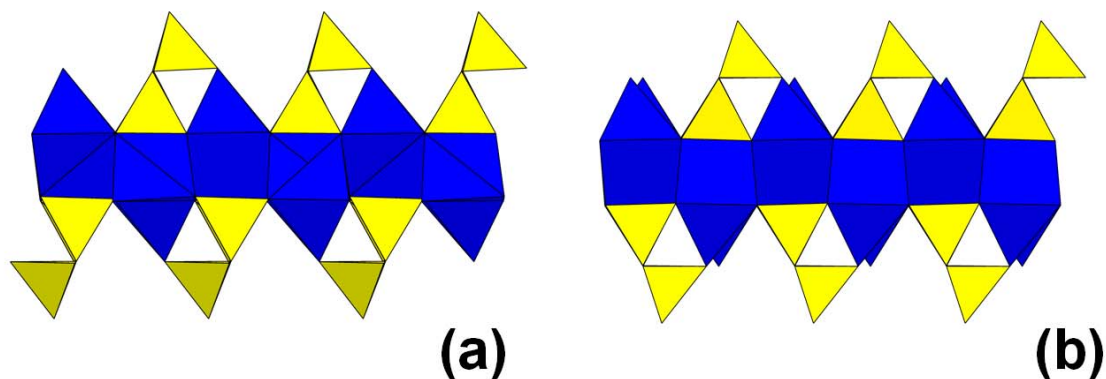
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511 **Fig. 4**. Crystal structure of 'tobermorites', as seen down **b**. For polyhedra, colors as in Fig. 1.
512 Circles: light blue = water molecules; blue = fifth calcium cations (not shown in the crystal
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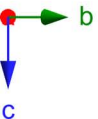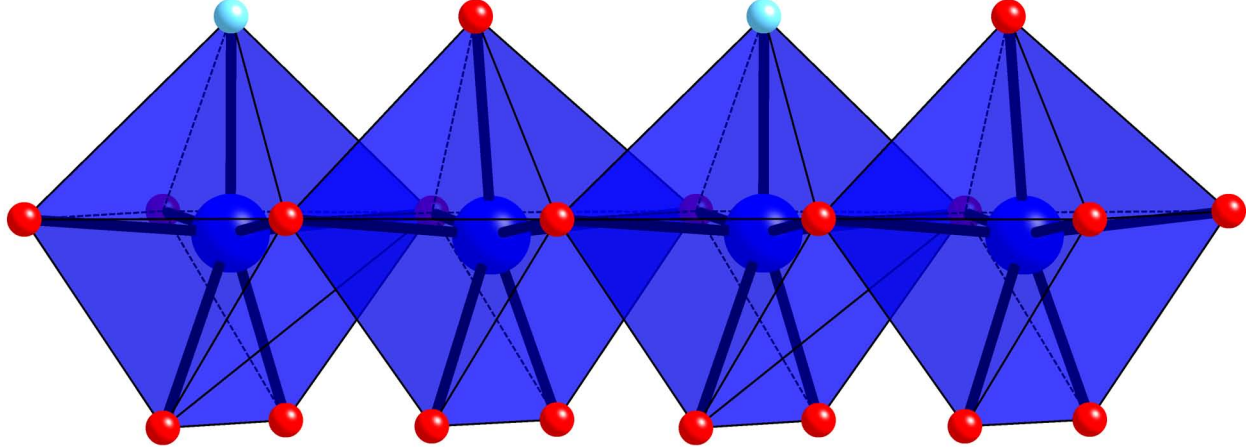

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(a)

(b) 11.2 Å

(c) 7.3 Å

(a)   (b)

14 Å

11 Å
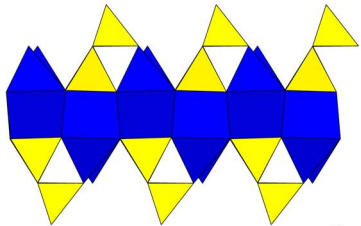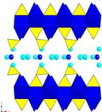
9 Å
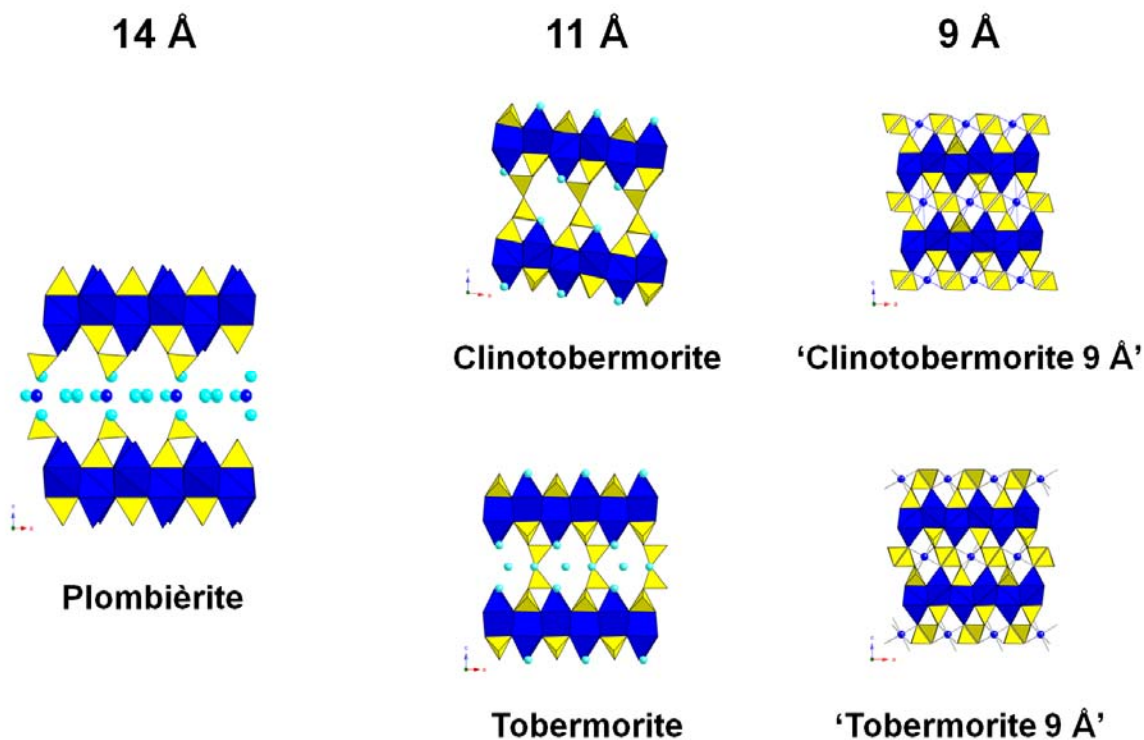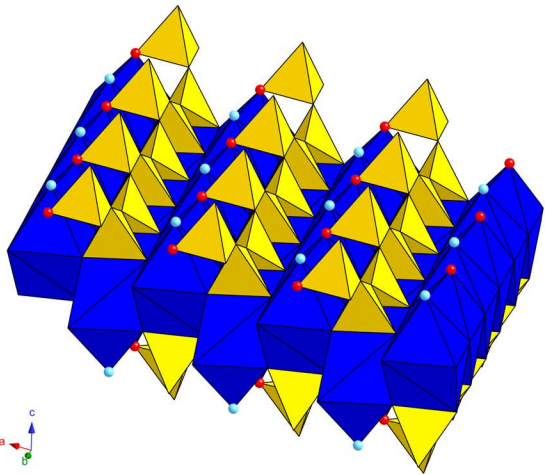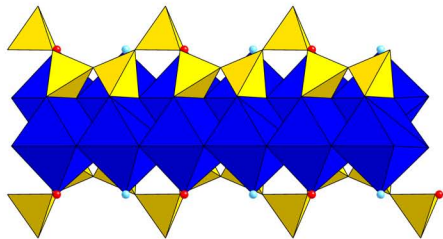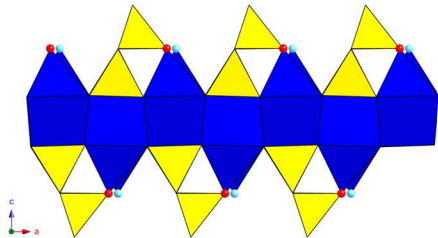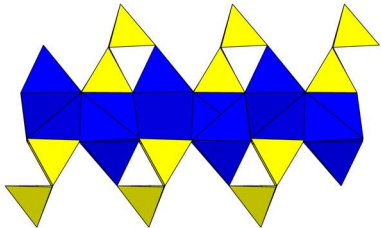
Plombièrite

Clinotobermorite

Clinotobermorite 9 Å

Tobermorite

Riversideite