Normal and anomalous tobermorites

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SUMMARY. Tobermorite minerals vary in some properties, notably in whether or not unidimensional lattice shrinkage occurs by about 300 °C to give a 9.3 Å form; specimens that do this are called normal, and ones that do not, anomalous. Data are compared for thirteen natural tobermorites and the extent to which normal or anomalous character is related to other properties is examined. The most definite correlations found are with chemical composition and morphology. The conditions of formation of normal and anomalous tobermorites are discussed in the light of synthetic evidence.

TOBERMORITE minerals vary in some properties. most notably in whether loss of molecular water is accompanied by unidimensional lattice shrinkage in the *c*-direction. Such shrinkage has been observed with specimens from Crestmore, California (Taylor, 1953; Farmer et al., 1966), Ballycraigy, Northern Ireland (McConnell, 1954), and Fuka, Japan (Mitsuda et al., 1972), but not with those from Loch Eynort, Scotland (Gard and Taylor, 1957) or Heguri, Japan (Mitsuda, 1973). Tobermorites that show this lattice shrinkage have come to be called 'normal' and ones that do not, 'anomalous'. In this paper, data are compared for thirteen natural tobermorites, and the extent to which normal or anomalous character is related to other properties is discussed.

Specimens. These are described as 14 Å or 11 Å tobermorite according to the approximate value of the layer thickness. All the specimens mentioned in this paper are 11 Å tobermorites unless otherwise stated. Of the specimens listed below, all were examined in the present work except numbers 4 and 12. Table I gives analyses for most of them.

(1) Crestmore, California: the 14 Å tobermorite originally described by Murdoch (1961) as 'Mineral Z' and further studied by Farmer *et al.* (1966).

(2) Bingham, Utah (USNM 127132): the 14 Å tobermorite described by Stephens and Bray (1973).

(3) Fuka, Japan: the intergrowth of 14 Å and 11 Å tobermorites described by Mitsuda et al. (1972).

(4) Ballycraigy, Northern Ireland: the 11 Å tobermorite, some of which was mixed with 14 Å material, studied by McConnell (1954).

(5) Noche Buena, Zacatecas, Mexico (USNM 119450): radial aggregates associated with pyrite.

(6) Fuka, Japan: the purely 11 Å tobermorite associated with no. 3 (Mitsuda et al., 1972).

(7) Heguri, Japan: a new, Sr-bearing tobermorite from the same locality as no. 11.

(8) Portree, Scotland: a new specimen from the locality described by Sweet (1961).

(9) Syke, Scotland (BM 1959, 551).

(10) Pra de la Stua, Italy: a specimen from the locality described by Gottardi and Passaglia (1966).

(11) Heguri, Japan: the specimen described by Mitsuda (1973).

(12) Loch Eynort, Scotland (BM 1937, 1490): the specimen examined by Claringbull and Hey (1952) and by Gard and Taylor (1957).

(13) Noche Buena, Zacatecas, Mexico (USNM 119368): radial aggregates associated with pyrite and apophyllite.

X-ray examination. Powder patterns were obtained using Cu radiation with either a Guinier camera or a diffractometer for unheated specimens and for ones that had been heated at various temperatures, usually for 24-48 h. Either an external (Si, a = 5.4309 Å) or an internal (calcite, a =4.989, c = 17.062 Å) standard was used. The 11 Å tobermorites formed by heating 14 Å tobermorites were relatively poorly crystalline; other differences in pattern between the various 11 Å tobermorites were minimal, as were those between the various 14 Å tobermorites. Single-crystal patterns were also obtained for specimen 5 and intensities measured with sufficient precision to permit unequivocal indexing of the powder patterns of the 11 Å tobermorites and thus least-squares refinement of the pseudocell parameters. Table II gives results. Unless otherwise stated the estimated standard deviations were in the third decimal place for a and b and in the second place for c. Atomic pseudocell

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Specimen	I	3	4	6	7	8	10	II	12
SiO ₂	43.17	45.55	44 [.] 86	45.12	43.82	48·95	45.39	45.24	46.17
Al_2O_3	tr.	2.23	n.d.	3.31	3.11	2.70	6.35	3.81	4.56
Fe ₂ O ₃	0.05	0.10	n.d.	0.23	0.85	tr.	0.13	0.02	0.12
MgO	0.02	0.03	n.d.	0.04	0.06	0.04	4.38	0.05	tr.
CaO	36.43	35.48	36.02	35.24	33.23	33.69	24.53	34.64	35.15
SrO	n.d.	n.d.	n.d.	n.d.	1.65	n.d.	n.d.	n.d.	n.d.
Na ₂ O	nil	0.50	0.02	0.54	0.22	0.55	1.52	0.44	0.26
K ₂ O	nil	0.10	0.02	0.23	0.32	0.02	0.71	0.15	0.52
B_2O_3	0.79	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CO ₂	0.67	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	1.45	n.d.
H ₂ O	19.13	16.01	19 [.] 42	15.52	15.85	13.85	17.94	14.12	13.42
Total	100-26	99.89	100.40	99 [.] 93	99 [.] 79	99.85	100.78	99.91	100.01
Analyst	a	b		b	c	ь	_	ь	
Notes	(1)	(2, 3)	(2)	(1)	(1)	(1)	(2, 4)	(2, 5)	(2)

TABLE I. Chemical analyses of tobermorites

Notes: a, J. Ito; b, Y. Hikichi; c, K. Nagashima. (1) New data. (2) From original paper. (3) EPMA showed that the part of this specimen consisting of intergrown 14 Å and 11 Å tobermorites was very low in Al (Mitsuda et al., 1972). The sample analysed could have been a mixture of nos. 3 and 6. (4) Also TiO₂, 0 10 %. Specimen mixed with a talc-like phase. (5) Specimen contained calcite.

	Unheated				90 °C	300 °C	700 °C	Notes	
Specimer	Pseudocell							 T	
	n a	b	с	d ₀₀₂	d ₀₀₂	d ₀₀₂	d ₀₀₂	Types	
I 2	5·62 5·62	3·67 3·68	27·97 27·99	13·99 14·00	11.35	9.35 s 9.35 s	10·1 w (900 °C) 10·2 w		
3	5·62 5·62	3·68 3·68	28·03 22·72	14·02 11·36	11.36	11·33 w, 9·39 s	11.2 vw/b, 9.8 m/vb	a, b, c	
4 5	5·62 5·61	3·69 3·69	22·6 22·82	11·3 11·41	11·3 11·4	9·35 s 9·36 s	9 [.] 35 vw 9 [.] 4 w	d	Normal
6 7 8	5·63 5·62 5·61	3·69 3·69 3·69	22·70 22·73 22·70	11·35 11·37 11·35		11·1 s-9·5 vs/b 11·35 vs, 9·47 w 11·3 vs, 9·6 m	11·2 vw/b 11·29 s, 9·8 vvw/b 11·2 m	b, e b	Mixed
9 10 11 12	5·62 5·60 5·60 5·63	3-69 3-66 3-69 3-69	22·74 22·80 22·68 22·64	11·37 11·40 11·34 11·32		11-3 vs 11-3 m 11-3 vs 11-3 vs	11-3 vs 11-3 w 11-2 s 11-3 vs	b, f a	Anomalous

TABLE II. X-ray results

Notes: Spacings and pseudocell parameters in Å; intensity symbols, s = strong, m = moderate, w = weak, v = very, b = broad.

a. Pseudocells calculated from powder data in original papers.

b. Partly altered to wollastonite by 700 °C.

c. Also, $d_{002} = 10 \cdot I$ Å after 24 h at 800 °C.

d. Pseudocell for unheated mineral from Megaw and Kelsey (1959), who found for another crystal c = 22.9 Å, and for heated products from Taylor (1959), all from single-crystal data.

e. Also, $d_{002} = 10.2$ Å (s/vb) after 7 days at 500 °C and 11.1 Å (s/vb) after 8 days at 650 °C. f. Less precise data; e.s.d.'s 002 Å on a, 001 Å on b, 005 Å on c.

contents were calculated where the data existed, using densities determined by suspension or, for specimens 4 and 12, taken from the literature (Table III).

Specimens I and 2 are 14 Å tobermorites; both show 'normal' thermal behaviour, with the successive changes in layer thickness to about 11.35, 9.35, and 10.1 Å previously noted for specimen I by Farmer *et al.* (1966). Specimen 3 also consisted largely of 14 Å tobermorite, and this component of it behaved in the same way. The 11 Å stage for specimen I showed small changes in cell parameters with increase in temperature (a 5.59, b 3.67, c 22.85 Å after I h at 66 °C; a 5.59, b 3.67, c 22.69 Å after 3 days at 95 °C). Specimens 4 and 5 are typically normal 11 Å tobermorites, their layer thicknesses changing to 9.35 Å at 300 °C.

Specimens 9-13 show typically anomalous behaviour. The patterns do not change essentially until 700-800 °C, when wollastonite is formed, but with increasing temperature they become weaker and more diffuse, and there are small changes in pseudocell parameters (e.g. for no. 11, a 5.57, b 3.67, c 22.62 Å after heating at 500 °C). Specimen 3 contained a minor proportion of anomalous 11 Å tobermorite. Specimen 10 was found to be mixed with a poorly crystalline Mg hydro-silicate, as with Mg-containing material from Heguri (Mitsuda, 1973); this indicates that tobermorite cannot accommodate appreciable Mg.

Specimens 6-8 show varying types of behaviour intermediate between normal and anomalous, and will be called 'mixed' tobermorites. Specimens 6 and 7 behaved as mixtures consisting mainly of anomalous 11 Å tobermorite with smaller proportions of normal 11 Å tobermorite. Specimen 8 behaves in a more complex way; for samples heated at 500-700 °C, the 002 reflection was a single, broad peak, which shifted gradually from 10-2 Å at 500 °C to 11-2 Å at 700 °C. This specimen probably contained normal and anomalous layers, randomly interstratified.

There is a notable morphological difference between the 14 Å and normal 11 Å tobermorites on the one hand, and the mixed and anomalous 11 Å tobermorites on the other. The specimens of the first group (nos. 1-5) form relatively large platy crystals, up to 50 μ m long in their largest dimension, and having (001) cleavage. Those of the second group (nos. 6-13) mostly form submicroscopic crystals, which occur as dense aggregates. Specimen 13 was exceptional in forming larger crystals, comparable in size with those of the first group.

	Normal		Mixed			Anomalous		Theoretical
Specimen	I	4 2 [.] 44 469	6 2·40 472	7 2·48 471	8 2·46 470	11 2·43 469	12 2·46 470	lor 11 Å tobermorite
Sp. gr.	2.20							
Pseudocell volume (Å ³)	577							
Notes	а	b		с		d		
Si	5.48	5.40	5.12	5.14	5.68	5:34	5.36	6
Al			0.44	0.43	0.37	0.53	0.58	
Fe		_	0.02	0.07		0.01	0.01	
Mg	0.01	_	0.01	0.01	0.01	_		
Ca	4.95	4.65	4.59	4.22	4.19	4.12	4.37	5
Na		0.01	0.02	0.12	0.15	0.10	0.13	
K		0.01	0.03	0.06	0.01	0.05	0.04	
Н	16.19	11.42	11.75	12.41	10.72	11.14	10.42	10
0	24.51	21.12	21.15	21.66	21.54	21.27	21.29	22
X = (Si + Al)	5.48	5.40	5.26	5.57	6.05	5.87	5.94	6
M = (Ca + Sr +								
Mg + Na + K)	4.96	4.67	4.38	4.25	4.33	4.52	4.54	5
M/X	0.91	o·86	0.79	0.81	0.72	0.73	0.76	0.83
Al/(Si + Al)	0.00	0.00	0.08	0.08	0.06	0.09	0.10	0

TABLE III. Atomic pseudocell contents (11 Å tobermorites unless otherwise stated)

Notes: a. 14 Å tobermorite; also C = 0.12, B = 0.17. Theoretical pseudocell contents $Ca_5Si_6O_{26}H_{18}$.

b. H_2O contents assumed 15.0% from weight-loss curve.

c. Also, Sr = 0.11.

d. CO₂ deducted as calcite.

Electron microscopy and diffraction. The first anomalous tobermorite to be studied (no. 12; Gard and Taylor, 1957) differed from other tobermorites then known not only in its thermal behaviour, but also in two other ways. First, it formed, predominantly, lath-shaped crystals with (100) cleavage rather than platy crystals with (001) cleavage. Second, for those crystals that had (001) cleavage. the pattern of systematically weak electron-diffraction reflections not indexable on the pseudocell was abnormal. Scanning and transmission electron micrographs of another anomalous tobermorite (no. 11; Mitsuda, 1973) also showed the crystals to be thick laths. To find whether these characteristics apply to anomalous and mixed tobermorites in general, Dr. J. A. Gard and Mr. H. Hayashi kindly made TEM and SED studies of specimens 3, 6, 7, 8, and II.

With specimen 3, which was largely normal, all the crystals examined were essentially platy with (001) cleavage, and gave SED patterns almost wholly indexable on the *c*-centred orthorhombic true cell with doubled a and b found by McConnell (1954) for specimen 4, which is normal. Some crystals showed weak streaking of reflections parallel to a^* , sometimes with distinct satellite maxima. With the other specimens, all of which were mixed or anomalous, the crystals tended to be elongated parallel to b and to lie either on (001), or on (100), or in intermediate orientations. Because of sampling difficulties one cannot be certain of the relative frequencies of the different orientations, but the (001) cleavage seemed always to be commoner than (100); e.g. for specimen 11, seven crystals were seen to have (001) cleavage and only one to have (100). The SED patterns of crystals lying on (001) all showed considerable streaking parallel to a^* and the weak reflections unindexable on the pseudocell tended to show maxima in non-integral positions similar to those found for the Loch Eynort material. Some crystals showed both these maxima and ones corresponding to the c-centred cell mentioned above. Once again, it is impossible to be certain of the relative frequencies of these effects.

These results suggest that other mixed and anomalous tobermorites tend in varying degrees to show the varied cleavages and pattern of weak reflections found for the Loch Eynort mineral, but that this tendency is slight, and that the (001)cleavage and true cell with doubled *a* and *b* normally predominate, as with normal tobermorites. The Loch Eynort mineral seems to have been an extreme case.

Infrared absorption spectra. Spectra reported in the literature for 11 Å tobermorite are all very much alike. The specimens that have been examined include, among others, synthetic normal tobermorite (Kalousek and Roy, 1957; Diamond *et al.*, 1966), natural anomalous tobermorite (no. 12; Hunt, 1962), and a normal tobermorite formed by heating the natural 14 Å mineral (Farmer *et al.*, 1966). We have confirmed this lack of marked variability. Fig. 1 gives spectra recorded using



FIG. 1. Infrared spectra obtained using Nujol mulls for (a) specimen 3 and (b) specimen 11.

Nuiol mulls for specimens 3 and 11, unheated and after heating at various temperatures. Specimen 3 was mainly 14 Å, which after heating at 90 °C gave mainly normal 11 Å tobermorite, while specimen 11 was anomalous. Specimens 6-9, which were all mixed or anomalous, were also examined and gave results similar to specimen 11. Normal and anomalous tobermorites do, however, differ in the spectra that they give after being heated at 300-700 °C. Specimen 3 showed changes broadly similar to those found for specimen 1 (Farmer et al., 1966), which can be related to the successive changes in layer thickness to 9.3 and 9.7 Å. The anomalous and mixed tobermorites, in contrast, showed relatively slight changes, consisting largely of a general broadening of the Si-O bands and disappearance of some of the weaker peaks. These changes can probably be related to the deterioration in crystallinity that can be observed with X-ray diffraction.

Differential thermal analysis and thermogravimetry. DTA curves were obtained at 10 °C min⁻¹ for specimens 1, 6, 7, 8, and 11. Fig. 2 gives those for specimens 1 and 8, for specimen 3 (from Mitsuda *et al.*, 1973), and for a synthetic 11 Å tobermorite (Ca/(Si+Al) = 0.8, Al₂O₃ 0.5%) prepared at 180 °C and showing mixed thermal behaviour. The curves for specimens 6, 7, and 11 resembled that for specimen 8.

The endotherms at 100-150 °C given by the 14 Å tobermorites (nos. 1 and 3) are due to conversion into the 11 Å form. Those at 150-300 °C are due to



FIG. 2. DTA curves for specimens 1, 3, 8, and a synthetic tobermorite (S).

loss of molecular water and are given by all 11 Å tobermorites, whether normal or anomalous. The exotherms at 800-850 °C, which vary much in intensity and sharpness, are associated with crystallization of wollastonite. In the main, the results support the view that tobermorites with below about 1% Al₂O₃ give only very weak, diffuse exotherms, whereas those with much Al_2O_3 give strong and sharp exotherms at slightly higher temperatures, though specimen 3 gave a stronger peak than might have been expected. The correlation seems to be with Al content rather than with normal or anomalous behaviour, since synthetic tobermorites containing Al and showing normal behaviour give curves similar to that of specimen 8 (Diamond et al., 1966).

Fig. 3 gives TG curves, obtained in N2 at 10 °C min⁻¹, and recalculated as molecules of H₂O retained per pseudocell. Specimen 1 (14 Å) was converted into the 11 Å form by evacuation at room temperature before obtaining the TG curve, which was corrected for the presence of CO_2 , assumed to be lost above 600 °C. The curves for specimens I (normal), 7 and 8 (mixed), and II (anomalous) are all very similar to each other and to the static weight-loss curve for specimen 12 (Gard and Taylor, 1957); all show about one molecule of H₂O to be retained at 400 °C. Previous work (Farmer et al., 1966) suggested that water lost below about 400 °C occurred as molecules and that lost above 400 °C as hydroxyl groups. The similarity of the results for normal, mixed, and anomalous tobermorite suggests that these do not differ

markedly in constitution. No explanation can be found for the very different curve given by specimen 6.

Discussion. The most significant correlations found between normal or anomalous character and other properties are:

Normal 11 Å tobermorites have several features in common with 14 Å tobermorites that are not shared with anomalous 11 Å tobermorites. They tend to occur together, and are similar in morphology and, apart from water content, in composition. In all known cases in nature, the 11 Å tobermorites formed by heating 14 Å tobermorites are normal. However, Hara and Inoue (1976) reported the synthesis of a 14 Å tobermorite that on heating seems to have yielded an anomalous 11 Å form.

The 14 Å and normal 11 Å tobermorites found in nature form relatively large, platy crystals with good (001) cleavage and relatively slight tendency to elongation parallel to b. Mixed and anomalous tobermorites usually form only submicroscopic crystals, which occur as compact aggregates and tend towards a more lath-like morphology. Compared with those of normal and 14 Å tobermorites the (001) cleavage is less pronounced and the tendency to elongation parallel to b is greater.

The known 14 Å and normal 11 Å tobermorites contain no Al and little or no alkali; the mixed and anomalous 11 Å tobermorites contain significant amounts of both Al and alkalis (Tables II and III). These cannot be accommodated purely by replacement of Si with Al plus Na or K, as the amounts of alkali are too small. If it is assumed that Al replaces Si, the substitution must be largely balanced in some other way, such as incorporation of additional H.



FIG. 3. TG curves for specimens 1, 6, 7, 8, and 11.

For normal, mixed, and anomalous tobermorites alike, the contents of both Ca and Si are always well below the theoretical values of 5 and 6 respectively that are indicated by Megaw and Kelsey's (1956, 1959) structure determination (Table III). This nearly always remains true if Al is counted with Si, and Sr and alkalis with Ca. For normal tobermorites the Si contents are particularly low (5.48 and 5.40 and the cation contents less so (4.96 and 4.67). For the mixed and anomalous tobermorites, the opposite is true, the cation contents being particularly low (4.27-4.54) and the (Si + Al) contents less so (5.56-6.05). As a result, the ratios of cations to (Si + Al) are above the theoretical value of 0.83 for normal tobermorites and below it for mixed and anomalous tobermorites.

Other differences between normal and anomalous 11 Å tobermorites are minor or of doubtful significance. The infrared spectra and DTA and TG curves show few differences of any sort and none that can be correlated with normal or anomalous character. The X-ray powder patterns show minor variations in cell parameters, but these, too, appear to be unrelated to normal or anomalous character. Such variations in the c-axial length as exist are not correlated with Al content. This lack of dependence on Al content may be compared with the conflicting results for synthetic specimens, for which some workers have found marked variation (Kalousek, 1957; Diamond et al., 1966) and others little or none (Mitsuda and Taylor, 1975). There is only a weak correlation between the thermal behaviour and the pattern of weak electron-diffraction reflections, of a type suggesting a greater tendency to stacking disorder in the mixed and anomalous tobermorites.

The present results may be compared with those of synthetic studies. El-Hemaly, Mitsuda, and Taylor (1977) showed that reaction of lime, quartz, and water at 105-180 °C in appropriate proportions and under saturated steam pressures gives in succession semi-crystalline calcium silicate hydrate ('C-S-H'), normal, mixed, and anomalous II Å tobermorite, and, above 140 °C, xonotlite. High Ca/Si ratio (1.0), short time, low temperature, stirring, presence of Al, and small quartz particle size all tended to cause the reaction to stop with formation of normal tobermorite. It was suspected that some, at least, of these factors operated through promotion of crystal growth; if the crystals grow sufficiently large while the product is in this stage, conversion into mixed or anomalous tobermorite is retarded. In contrast, low Ca/Si ratio (0.8), long time, high temperature, absence of stirring, presence of both Al and alkali, and large quartz particle size all tended to give anomalous tobermorite. At Ca/Si 0.9-1.0 and 180 °C, this changed rapidly into xonotlite. Both normal and anomalous tobermorites could be obtained from mixes free from Al and from ones containing Al, but if Al and alkali were both present, only anomalous tobermorites were obtained.

Synthesis of 14 Å tobermorite was reported by Kalousek and Roy (1957), Hara and Inoue (1976), and Hara *et al.* (1978); it forms most reproducibly around 60 °C.

The present results agree well with those of these synthetic studies. The characteristic properties of the normal 11 Å tobermorites existing in nature suggest that these were formed at low temperatures, probably around 100 °C, and in environments low in Al and alkalis, relatively high in Ca/(Si + Al) ratio (1.0) and favouring crystal growth. Those of the mixed and anomalous tobermorites suggest that these were formed at higher temperatures, perhaps around 150 °C, and in environments containing Al and alkalis, lower in Ca/(Si + Al) ratio (0.8), and less conducive to crystal growth. The temperatures mentioned assume saturated steam conditions and would have to be substantially increased for higher pressures (Roy and Johnson, 1967).

Wieker (1968, 1976) studied specimen I (a 14 Å tobermorite), and also some II Å tobermorites from Scotland and a synthetic preparation, by a chemical method indicating the degree of anion condensation and by NMR. The degree of anion condensation was estimated from the rate of a reaction with molybdate. He concluded that, in the 14 Å tobermorite, the anions were single chains and that the water occurred partly as SiOH, and partly in molecular form; the single chains persisted if the mineral was heated to yield either the II Å or the 9 Å form. The Scottish and synthetic specimens, in contrast, were considered to contain double chains similar to those in xonotlite.

The structural differences between normal and anomalous tobermorites are unresolved. The only structure in the literature based on experimental evidence is that of Megaw and Kelsey (1956, 1959) for the Ballycraigy mineral, and is not sufficiently exact to lead to any certain explanation. The close similarities in thermal, infrared, and X-ray data suggest that the structural differences are slight, and it is doubtful whether Wieker's (1968, 1976) conclusion that the Crestmore 14 Å tobermorite and the Scottish tobermorites contain single and double chains respectively can be reconciled with them, at least if the chains are as nearly perfect as in typical crystalline calcium silicates such as wollastonite or xonotlite. A more likely hypothesis is: in the 14 Å and normal 11 Å tobermorites, the chains contain many missing tetrahedra, the mean chain length being around 11 Si atoms, and there are no cross-linkages between the chains of adjacent layers; in anomalous 11 Å tobermorites, the mean chain lengths are greater, at least if Al is counted with Si, and there are occasional cross-linkages. This hypothesis appears consistent with all the evidence; the cross-linkages would prevent the lattice shrinkage, and, even if the Si was partly replaced by Al, could produce a degree of condensation in the silicate anion comparable with that of a double chain. The stronger binding of the structure in the *c*-direction might also account for the difference in morphology. Direct experimental proof of the hypothesis is nevertheless lacking.

The present results are of doubtful statistical validity, but suggest that anomalous tobermorites may be at least as common in nature as normal ones. This conclusion, if correct, is compatible with that suggested by the synthetic studies (EI-Hemaly, Mitsuda, and Taylor, 1977) that normal tobermorite is a non-equilibrium product that is only obtainable under a relatively narrow range of conditions.

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