

*The stability of tobermorite in the system CaO-SiO<sub>2</sub>-H<sub>2</sub>O  
at elevated temperatures and pressures*

By K. SPEAKMAN, Ph.D., A.R.I.C.

Building Research Station, Garston, Watford, Herts.

[Taken as read 7 November 1968]

*Summary.* Hydrothermal studies in the silica-rich region of the CaO-SiO<sub>2</sub>-H<sub>2</sub>O system have given information on the stability field of tobermorite. At saturated steam pressures tobermorite is unstable relative to xonotlite (C<sub>6</sub>S<sub>6</sub>H) above 140 °C but between 10 000 and 40 000 lb/in.<sup>2</sup> (69 and 276 N/mm<sup>2</sup>), the decomposition temperature is raised to 285 ± 5 °C. Tobermorite is stable at all compositions between C/S = 0.67 and 1.0 up to this temperature and has a formula close to C<sub>6</sub>S<sub>6</sub>H<sub>5</sub>. Variable compositions reported earlier are thought to be mixtures rather than lime-rich or silica-rich tobermorites.

Data have also been collected on the equilibrium assemblages below C/S = 0.67 and between C/S = 1.0 and 1.5 involving truscottite, gyrolite, xonotlite, foshagite, and hillebrandite.

**T**HE hydrated calcium silicate mineral tobermorite was first described by Heddle (1880). Since then data have been reported on several other closely related minerals that differ only in the amounts of constitutional water they contain. They are all similar in structure to the clay minerals (Taylor and Howison, 1956) and are characterized by the value of the 002 interlayer spacing. This increases with increasing H<sub>2</sub>O:SiO<sub>2</sub> ratio. At least three definite varieties are known, having basal spacings of 14, 11.3, and 9.3 Å. The most common form is that having the 11.3 Å spacing and it corresponds to the composition<sup>1</sup> C<sub>5</sub>S<sub>6</sub>H<sub>5</sub>.

Synthetic analogues of tobermorite have been prepared hydrothermally from lime/silica mixes and the 11.3 Å variety has been identified in commercial autoclaved sand-lime bricks (Taylor, 1952). The badly crystallized products of the hydration of certain Portland cement components have also been shown to be closely related to the tobermorite minerals.

Although the term 'tobermorite' strictly refers only to the natural

<sup>1</sup> Cement chemical nomenclature: C = CaO, S = SiO<sub>2</sub>, H = H<sub>2</sub>O, C/S = CaO:SiO<sub>2</sub>. The 9.3 Å tobermorite is also known by the name riversideite, and the 14 Å form is sometimes wrongly termed plombierite; the latter is a gelatinous material closely resembling C-S-H-(1) (J. D. C. McConnell, *Min. Mag.*, 1954, vol. 30, p. 293), while 14 Å tobermorite from Crestmore, California, has been shown to be a well-crystallized mineral (J. Murdoch, *Amer. Min.*, 1961, vol. 16, p. 245).

minerals, it has also been used in a loose sense to cover a whole range of hydrated calcium silicates from the almost amorphous synthetic materials formed during the room-temperature hydration of cement to the well-crystallized autoclaved products. A study of the conditions of formation and stability of the natural minerals has, therefore, practical industrial value as well as geological interest.

*Previous work.* Heller and Taylor (1951) found that at saturated steam pressures tobermorite was formed hydrothermally from C/S = 1.0 mixtures between 110 and 150 °C; above 160 °C xonotlite was produced. During their study of equilibria in the system  $\text{CaSiO}_3\text{-H}_2\text{O}$ , Buckner and Roy (1955) and Buckner, Roy, and Roy (1960) examined the stability of tobermorite up to 30 000 lb/in.<sup>2</sup> (207 N/mm<sup>2</sup>).<sup>1</sup> Sealed noble metal tubes, which prevent the removal of volatile components from the reaction mixes and so maintain the correct bulk composition, were not used in all cases. The authors found that tobermorite was stable up to 285 °C between 15 000 and 30 000 lb/in.<sup>2</sup> (103–207 N/mm<sup>2</sup>) over the range of compositions C/S = 0.8–1.0. The tobermorite was always in the 11.3 Å form. Above 285 °C, xonotlite was found to be the stable phase. Scawtite (CSH(A)) resulting from carbon dioxide contamination was frequently encountered.

Volkonskii *et al.* (1964) reported on a limited high-pressure hydrothermal study in the  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  system. They investigated the products formed from C/S = 1.0, 0.8, and 0.43 compositions by reaction at 250 °C for short times up to 12 hours using pressures of 11 700 lb/in.<sup>2</sup> and 13 200 lb/in.<sup>2</sup> (81 and 91 N/mm<sup>2</sup>). Tobermorite was found to increase with time at the C/S ratio of 0.8 while xonotlite replaced it at C/S 1.0.

In his paper on the subsystem  $\text{CaSiO}_3\text{-SiO}_2\text{-H}_2\text{O}$  Harker (1964) reported few runs in the accepted composition range of tobermorite, C/S 0.8–1.0. Pressures in excess of 10 000 lb/in.<sup>2</sup> (69 N/mm<sup>2</sup>) were not investigated and all but one run used the same starting material. The resulting P-T stability curve for the reaction tobermorite  $\rightarrow$  xonotlite +  $\text{H}_2\text{O}$  shows a gradual rise from (an estimated) 230 °C at 5000 lb/in.<sup>2</sup> to over 300 °C at 40 000 lb/in.<sup>2</sup> in contrast to the curve of Buckner, Roy, and Roy (1960), which is parallel to the pressure axis.

Roy and Johnson (1965) confirmed earlier work that tobermorite of composition  $5\text{CaO}:6\text{SiO}_2:5\text{H}_2\text{O}$  decomposes at 285 °C under pressures of 20 000–45 000 lb/in.<sup>2</sup> (138–310 N/mm<sup>2</sup>) to give xonotlite and truscottite.

<sup>1</sup> Newton (N) = the force that when applied to a mass of 1 kg produces an acceleration of 1 m.sec<sup>-2</sup>; 1 N/mm<sup>2</sup> = 145.04 lb/in.<sup>2</sup>.

The authors mention 'silica-rich' and 'lime-rich tobermorite' and suggest that xonotlite can coexist with the latter over a wide temperature range. A series of compatibility diagrams was presented to summarize their findings.

Reviews by Taylor (1960) and by Roy and Harker (1960) cover much of the previous knowledge on composition, synthesis, and properties of the many compounds formed in the system under investigation.

*Experimental.* Equilibrium studies in this system are complicated by the slowness of reactions at these temperatures and by the ease of nucleation of high-temperature, metastable phases. These metastable products are often well crystallized and convert to the equilibrium assemblage very slowly. In order to minimize the chances of drawing misleading conclusions from the results of such effects, reaction times were made as long as was practicable and equilibria were approached from as many directions as possible. This was achieved by the use of a large variety of starting materials (see Table I).

Experiments at saturated steam pressures were carried out in stainless steel tubes, closed by means of a threaded stopper and copper gasket, similar in design to that described by Barrer (1948). A silver liner was used to contain the starting material and CO<sub>2</sub>-free water required to generate the pressure. These vessels were heated either in an oven, fitted with fan circulation and controlled to  $\pm 2$  °C, or in vertical tube furnaces regulated to within 5 °C of the desired temperature. Cold seal vessels were used for high-pressure runs, the specimens being contained in sealed gold capsules. Every attempt was made to exclude carbon dioxide from all reactants and freshly de-ionized CO<sub>2</sub>-free water was used throughout.

Quenching of all reaction vessels ensured that atmospheric temperature and pressure were attained within seconds of removal from the furnace. The suspensions from the low-pressure runs were filtered in CO<sub>2</sub>-free air, washed with acetone and quickly transferred to a desiccator for drying under vacuum. Anhydrous magnesium perchlorate was used as the desiccant and the drying times were between two and three days. With the specimens treated in the cold seal apparatus the filtration and washing stages were unnecessary.

Identification of the phase assemblages was carried out by means of X-ray diffraction and, to a lesser extent, optical microscopy. A 114.6-mm diameter quadruple focusing Guinier powder camera and Cu-K $\alpha$  radiation were used to record the X-ray patterns. In almost every case the patterns were readily resolved and resort to other methods of

identification was virtually unnecessary. Most of the products were found to consist of masses of anhedral grains less than  $10\ \mu$  in any dimension. They were too small for any optical properties to be measured except mean refractive indices.

*Results.* Table I gives the results of the more important and significant runs from a total of more than 160 carried out over a wide range of temperatures, pressures, and compositions.

TABLE I. Hydrothermal syntheses in the system  $\text{CaO-SiO}_2\text{-H}_2\text{O}$ . S.M., starting materials (see key below)

Run	S.M.	Temp. (°C)	Pressure lb/in. <sup>2</sup>	N/mm <sup>2</sup>	Time (days)	Products <sup>‡</sup>
CaO:SiO <sub>2</sub> = 0.80 (4:5)						
5	1	90	10	0.1	164	Qtz + CSH (1)
6	2	90	10	0.1	164	CSH (1)
2	2	110	21	0.2	180	Tob
14	1	140	53	0.4	196	Tob + tr xon
12	5	160	90	0.6	196	Tob + gyr + tr xon + scaw
124	8	204	17 200	119	32	Tob
144	5	211	24 300	167	28	Tob
145	5	231	22 500	155	39	Tob
189	3	248	8 800	61	7	Gyr + xon + tr tob
143	5	258	26 500	183	17	Tob + scaw
214	3	272	35 700	246	7	Gyr + xon + l. scaw + tr tob
146	5	275	26 900	185	28	Tob + scaw + trus ?
216	3	280	7 900	54	14	Gyr + trus + xon + scaw
222	5	282	7 500	52	7	Tob + l. xon + scaw + trus ?
178	5	283	19 000	131	13	Tob + scaw + trus ?
223	5	284	39 600	273	14	Tob + scaw
157	5	284	30 000	207	10	Tob + scaw + trus ?
174	5	286	12 500	86	8	Tob + trus ? + tr scaw
154	5	287	22 600	156	10	Tob + xon + scaw + trus ?
240	5	290	40 900	282	7	Tob + xon + scaw + trus ?
215	3	292	8 700	60	7	Trus + xon + scaw
163	5	294	23 500	162	9	Tob + xon + scaw + trus
179	5	300	31 700	219	13	Tob + xon + trus + scaw
188	3	300	21 100	145	7	Trus + xon + scaw
177	5	306	5 500	38	17	Tob + xon + trus + scaw
166	5	314	25 500	176	8	Tob + xon + trus + tr scaw
169	5	324	4 400	30	10	Trus + xon + scaw + tr tob
167	5	334	21 500	148	11	Tob + xon + tr trus + scaw
168	5	347	24 200	167	11	Tob + xon + trus + scaw
175	5	367	23 800	164	7	Xon + trus + tr scaw
180	5	368	8 700	60	7	Xon + $\alpha$ -wol
172	5	380	17 700	122	10	Xon + cris + $\alpha$ -wol
171	5	398	25 500	176	10	Xon + $\alpha$ -wol
CaO:SiO <sub>2</sub> = 0.83 (5:6)						
15	1	140	53	0.4	196	Tob + gyr + qtz + l. xon.
16	3	150	79	0.5	133	Gyr + tob.
18	7	150	79	0.5	133	Gyr + tob.
11	1	160	90	0.6	196	Tob + xon + l. qtz.
17	3	170	115	0.8	133	Gyr + tob.
160	8	200	15 000	103	21	Tob + tr gyr.
149	1	225	25 000	172	38	Xon + qtz + l. tob + tr scaw.

TABLE I (cont.)

<i>Run</i>	<i>S.M.</i>	<i>Temp.</i> (°C)	<i>Pressure</i>		<i>Time</i> (days)	<i>Products</i> ‡
			<i>lb/in.<sup>2</sup></i>	<i>N/mm<sup>2</sup></i>		
CaO:SiO <sub>2</sub> = 0.83 (5:6)						
129	8	231	28 100	194	5	Gyr + xon + tr tob.
141	2	240	18 500	128	8	Gyr + tob + xon.
193	3	248	24 500	169	8	Gyr + tob + xon.
126	8	250	26 700	184	7	Gyr + xon + tob.
194	3	250	8 400	58	8	Gyr + xon + tr tob.
192	3	254	25 200	174	7	Tob + gyr + xon.
138	2	262	29 500	203	14	Gyr + tob + seaw + tr xon.
209	4	265	36 000	248	7	Scaw + gyr + l. tob.
210	4	269	7 500	52	10	Trus + seaw.
128	8	269	23 700	163	5	Gyr + xon + tr tob.
182	4	272	22 000	152	17	Xon + gyr + tob.
233	3	276	7 000	48	14	Gyr-trus + xon + tr seaw ?
185	3	276	26 800	185	7	Tob + gyr + xon.
205	3	281	20 900	144	7	Gyr-trus + xon + tr seaw.
208	4	282	34 000	234	7	Gyr + seaw + gyr-trus + tr xon.
225	7	285	8 300	57	7	Tob + gyr + seaw + xon.
183	4	287	20 000	138	16	Xon + trus + tr tob + tr seaw.
224	7	292	23 000	159	7	Tob + gyr + seaw + tr xon.
234	3	292	8 000	55	10	Trus + xon.
181	4	302	29 400	203	17	Xon + trus + tr seaw.
186	3	316	18 800	130	13	Xon + trus + tr seaw ?
184	4	320	21 500	148	16	Xon + trus + seaw.
CaO:SiO <sub>2</sub> = 1.00 (1:1)						
7	8	90	10	0.1	164	Gel.
8	8	140	53	0.4	149	CSH(I).
19	3	150	79	0.5	133	Xon.
21	4	150	79	0.5	133	Xon + seaw + tr tob.
9	2	160	90	0.6	149	Xon.
20	3	170	115	0.8	133	Xon.
202	3	149	17 500	121	7	Tob + xon.
212	4	152	11 200	77	7	Tob + tr xon.
211	4	161	20 800	143	7	Xon + l. tob.
203	3	202	21 800	150	7	Xon.
116	6	206	29 900	206	28	Xon.
120	2	208	28 100	194	28	Xon.
101	8	226	16 300	112	7	Xon.
117	6	246	22 900	158	18	Xon.
196	3	246	18 400	127	7	Xon.
199	4	248	8 000	55	7	Xon.
200	4	252	15 700	108	7	Xon.
121	2	256	27 300	188	8	Xon.
105	8	260	23 200	160	7	Xon.
122	2	273	26 000	179	13	Xon.
102	8	275	30 400	210	7	Xon.
195	3	291	21 000	145	10	Xon.
104	8	295	5 000	35	8	Xon.
103	8	300	17 000	117	7	Xon.
112	8	305	9 800	68	11	Xon.
CaO:SiO <sub>2</sub> 0.5 (1:2)						
113	1	210	23 500	162	21	Tob + qtz + xon.
226	4	259	18 000	124	11	Trus + qtz.
114	1	306	27 900	192	29	Qtz + xon.

TABLE I (cont.)

Run	S.M.	Temp. (°C)	Pressure		Time (days)	Products‡
			lb/in. <sup>2</sup>	N/mm <sup>2</sup>		
CaO:SiO <sub>2</sub> 0.6 (3:5)						
229	4	233	29 200	201	7	Gyr + trus + qtz.
230	4	244	20 500	141	10	Gyr + trus + scaw + qtz.
CaO:SiO <sub>2</sub> 0.67 (2:3)						
153	1	200	15 000	103	19	Tob + qtz + l. xon.
110	1	213	22 900	158	22	Tob + xon + qtz.
227	4	235	19 900	137	11	Gyr + scaw.
228	4	256	22 800	157	7	Gyr + trus + qtz.
109	1	264	27 000	186	26	Xon + qtz.
CaO:SiO <sub>2</sub> 0.917 (11:12)						
218	3	228	26 000	179	7	Xon + tob.
217	3	271	22 000	152	7	Xon + tob.
236	3	275	6 400	44	7	Xon.
221	3	278	35 600	245	10	Tob + xon.
220	3	285	7 300	50	7	Xon + trus.
237	3	285	36 400	251	7	Xon + tr tob.
219	3	304	33 100	228	7	Xon + tr trus.
CaO:SiO <sub>2</sub> 1.33 (4:3)						
232	4	158	20 600	142	7	Gel.
108	1	193	29 500	203	34	Xon + hil.
107	1	205	19 100	132	14	Xon + hil.
106	1	246	23 200	160	14	Xon + hil.
239	4	259	25 100	173	7	Fosh + U.P. + l. xon.
238	4	275	21 100	145	7	Fosh + U.P. + l. xon.
235	4	285	29 100	201	7	Fosh + U.P. + l. xon.
231	4	304	18 500	128	7	Fosh + U.P. + l. xon.

## Key to Table I

## Starting materials (S.M.)

1. Calcium hydroxide + finely ground quartz.
2. Calcium hydroxide + silica gel.
3. Gels made from Ca(OH)<sub>2</sub> and colloidal silica.\*
4. Gels prepared by hydrolysis of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> in the presence of Ca(NO<sub>3</sub>)<sub>2</sub>.
5. Synthetic tobermorite prepared from a C/S 0.8 glass.
6. Synthetic xonolite prepared from a C/S 1.0 glass.
7. C-S-H(1) prepared from a C/S 0.83 lime; 'Syton' gel.
8. Glass.

## Products

CSH(1):	C-S-H(1) of Taylor, 1950.	Qtz:	Quartz
Cris:	Cristobalite	Scaw:	Scawtite
Fosh:	Foshagite	Tob:	Tobermorite
Gel:	Tobermorite (?) gel†	Trus:	Truscottite
Gyr:	Gyrolite	α-Wol:	Pseudowollastonite
Gyr-trus:	Gyrolite-truscottite mixed layer phase	Xon:	Xonolite
Hil:	Hillebrandite	U.P.:	Unidentified phase
		l.:	Little

\* 'Syton 2X', from Monsanto Chemicals Ltd.

† Material resembling a tobermorite gel, showing only three broad X-ray lines.

‡ Phases listed in order of decreasing abundance.

*Discussion*

*General.* Before discussing the phase relations in the system, a brief mention must be made of the criteria used to assess the stability of the various phases in a particular assemblage.

Harker (1964) has listed the conditions under which stable equilibria in hydrothermal systems can be assumed. However, the rate of reaction with certain starting materials used in the present study was such that complete equilibrium was not always attained after considerable periods of time. The formation of new phases in the presence of large quantities of unchanged reactants were only taken as indications of the probable equilibrium products. With crystalline starting materials (tobermorite, xonotlite, etc.) the presence of the smallest amount of a second phase after reaction indicates that the original material is unstable. On the other hand, the development of crystalline phases from amorphous starting materials (gels, glass, etc.) does not necessarily mean that they are equilibrium products. Experience has shown that metastable products are often formed preferentially from certain reactants and that they can persist for long periods. Only by the use of the maximum variety of starting materials can these effects be minimized and the true equilibrium products be identified.

*Phase stability and equilibria: Tobermorite.* The results of runs carried out at saturated steam pressures indicate that tobermorite is formed over a very narrow temperature range. Below 100 °C the products from compositions between C/S 0.8 and 1.0 were either C-S-H (1) or near amorphous gels, which showed only the three strongest  $hk0$  reflections of tobermorite. Well-crystallized tobermorite was formed at 110 °C after reaction times of 4 to 6 months, but at temperatures above 140 °C it gave way to xonotlite and occasionally gyrolite. In all cases the tobermorite was in the 11.3 Å form and none of the other hydration states were detected. The slowness of reactions at these low temperatures and pressures makes it impossible to obtain any information on the equilibrium products, but it is clear that above 140° C xonotlite is more stable than tobermorite.

Although the exact relationship between C-S-H (1) and tobermorite is not yet known it is evident that they are closely related. The readiness with which the former is converted into tobermorite suggests that it differs only in the degree of crystallinity. Since C-S-H (1) can be prepared at room temperature (Taylor, 1950) it is possible that tobermorite itself would form at much lower temperatures than 110 °C after very long periods of time.

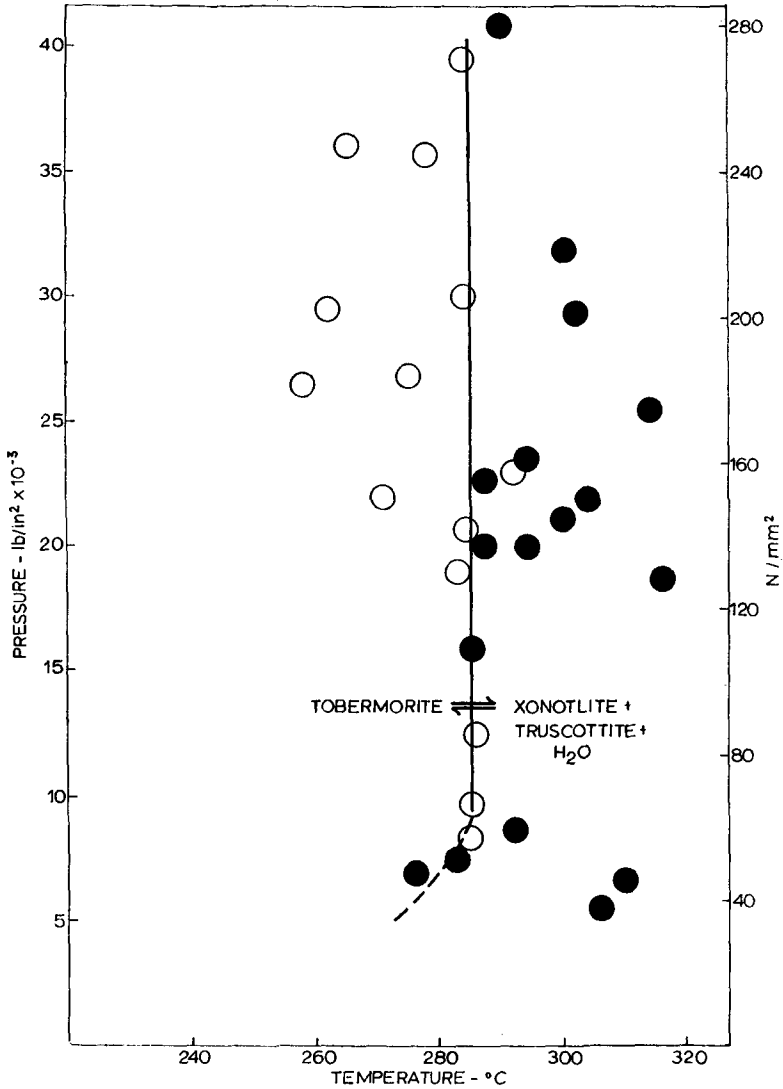


FIG. 1. Pressure-temperature curve for the reaction tobermorite  $\rightleftharpoons$  xonotlite + truscottite + H<sub>2</sub>O.

At higher temperatures and pressures the position is much clearer. An increase in pressure from that of saturated steam to 5000–40 000  $\text{lb/in}^2$  (35–280  $\text{N/mm}^2$ ) causes the decomposition temperature of



tobermorite to be raised considerably. The pressure-temperature curve representing this decomposition is shown in fig. 1. Over the pressure range quoted above, tobermorite is stable up to  $285 \pm 5^\circ\text{C}$ , the curve being essentially parallel to the pressure axis. At pressures below 10 000 lb/in.<sup>2</sup> (69 N/mm<sup>2</sup>) there is some evidence that the curve tails off to slightly lower temperatures. Both the decomposition temperature and the nature of the curve agree well with the results of Buckner, Roy, and Roy (1960) but do not support the findings of Harker (1964) that pressure has a marked effect on the reaction temperature in this range. As with the low-pressure runs and in common with the observations of previous workers, only the 11.3 Å form of tobermorite was encountered.

Data on the composition of tobermorite was obtained from a study of the phase assemblages recorded in table I. At the C/S molar ratio of 1.0 xonotlite was formed at all temperatures above 140 °C over the whole pressure range and is undoubtedly the stable phase, although at the lower temperatures tobermorite was formed initially as an intermediate. Using starting mixtures with a C/S ratio of 11:12, tobermorite and xonotlite were formed together in approximately equal amounts over a wide range of temperature and pressure conditions. This confirmed that xonotlite is an equilibrium phase at much lower temperatures than was previously thought and not solely a product of the decomposition of tobermorite above 285 °C. Comparison of runs 236 and 221 at this composition shows that at lower pressures xonotlite replaces tobermorite at temperatures a little below the 285 °C that applies to the higher pressure range.

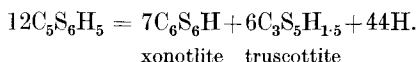
The results of runs at the C/S ratio of 0.8 can be expressed in terms of two assemblages:

Below 285 °C: tobermorite + gyrolite (or truscottite)

Above 285 °C but below the decomposition temperature of truscottite: xonotlite + truscottite (or gyrolite)

Both gyrolite and truscottite have compositions below C/S 0.8, so their formation from this mix requires tobermorite to have C/S ratio greater than 0.8. If the C/S 11:12 composition is midway between those of tobermorite and xonotlite as suggested above, the former would have the same composition as the natural mineral (C/S 0.833 or 5CaO:6SiO<sub>2</sub>) or close to it. Two preparations that contained tobermorite as the only detectable phase were analysed for water and gave values of 11.0 and 10.4 %. On the basis of the above lime/silica composition these figures lead to the formulae C<sub>5</sub>S<sub>6</sub>H<sub>4.4</sub> and C<sub>5</sub>S<sub>6</sub>H<sub>4.1</sub> respectively. If it is assumed

that a small amount of unreacted starting material remained in these preparations, as is often the case, the proportion of water would approach even closer to the five moles per formula weight found in the mineral. The evidence, therefore, points to the complete identity of the natural and synthetic materials, so that equilibria involving tobermorite can best be expressed in terms of the formula  $C_5S_6H_5$ . The decomposition can be represented thus:



Hence, the terms 'lime-rich' and 'silica-rich tobermorite', and the formulae  $C_4S_5H_4$  and  $C_5S_5H_5$  used by previous authors appear to have no relevance. They probably refer to intimate mixtures of tobermorite with amorphous silica or lime that have the over-all compositions indicated by the above formulae.

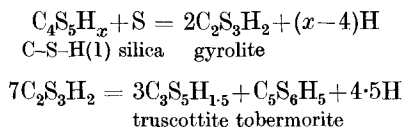
Up to 285 °C and between C/S 0.67 (or 0.6) and C/S 0.83 tobermorite and gyrolite or tobermorite and truscottite can coexist, depending on the temperature. At higher C/S molar ratios up to 1.0 tobermorite and xonotlite form the stable equilibrium assemblage. Between 285 and 360 °C xonotlite and truscottite are the stable phases over the whole composition range.

*Gyrolite and truscottite.* Both gyrolite and truscottite were frequently and readily prepared in the course of this work at compositions below C/S 1.0, more particularly between C/S 0.5 and 0.8.

Since natural gyrolite was first reported by Anderson (1851) both it and synthetic preparations have been investigated by several workers. In recent years Mackay and Taylor (1953), Strunz and Micheelsen (1958), Meyer and Jaunarajs (1961), and Harker (1960, 1964) have discussed its crystallography, composition, and equilibrium relationships to the other hydrated calcium silicates. Meyer and Jaunarajs were unable to determine the composition by synthesis because sufficiently pure specimens could not be prepared, but from structural considerations assigned to it the formula  $Ca_2Si_4O_9(OH)_2 \cdot 3H_2O$ . However, the latest synthetic work of Harker (1964) and analysis of the mineral quoted by Mackay and Taylor (1953) indicate that the composition  $2CaO \cdot 3SiO_2 \cdot 2H_2O$  is substantially correct. Both Meyer and Jaunarajs (1961) and Harker (1960, 1964) synthesized gyrolite at temperatures as low as 145–150 °C and the latter author found that it was replaced by truscottite above 220 °C. Harker also found gyrolite to be very persistent at much higher temperatures when the composition of the starting material was above a

C/S ratio of 0.67. The present results agree well with those of Harker. Gyrolite was formed as low as 140 °C at saturated steam pressures (run 15) and in short runs, as high as 290 °C (runs 224, 225). It slowly decomposed to truscottite via mixed-layer intermediate materials, which have basal spacings between those of the two component phases. This mixed layering, which is due to the close structural relationship of gyrolite and truscottite, has been detected by several previous workers. Due to the persistence of gyrolite for long periods above its decomposition temperature, it is difficult to determine the conditions under which truscottite begins to form. It was prepared reproducibly above 250 °C but also as low as 233 °C (run 229), which supports the 220 °C obtained by Harker from longer runs.

The reactions involved in the formation and decomposition of gyrolite can be expressed as:



Below 220 °C, tobermorite + gyrolite is the stable assemblage at C/S ratios between 0.67 and 0.83; this is replaced by truscottite + tobermorite between 220 and 285 °C.

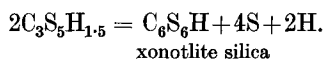
No definite information on the composition of gyrolite was obtained from the results of runs at the C/S 0.67 ratio. Run 227 indicates a C/S lower than 0.67 and run 228 suggests that it is higher.

Like gyrolite, truscottite has been the subject of extensive investigations since its discovery in Sumatra by Hövig (1914). Until recently truscottite was thought to be identical with the mineral reyerite, but Chalmers *et al.* (1964) have shown that the two almost certainly differ in both structure and composition. Analyses of natural and synthetic truscottites have resulted in a range of compositions being reported between C/S 0.5 and 0.75, all except one between C/S 0.5 and 0.67. A thorough analytical examination of synthetic preparations by Harker (1960, 1964) led to the proposal that the composition should be represented as  $\text{C}_3\text{S}_5\text{H}_{1.5}$ . The most recent analysis of the mineral from a new source in Japan (Minato and Kato, 1967) gives a formula of  $\text{Ca}_2\text{Si}_4\text{O}_9(\text{OH})_2$ , in good agreement with the results of Mackay and Taylor (1954) and Meyer and Jaunarajs (1961).

In the present study run 226 indicates that truscottite has a C/S ratio above 0.5 while run 229 suggests a value close to 0.6. These findings are

not conclusive, but in view of their agreement with the results of Harker, the formula  $C_3S_5H_{1.5}$  is favoured here.

Meyer and Jaunarajs found that truscottite was unstable relative to xonotlite + cristobalite above 300 °C at saturated steam pressures. At pressures up to 50 000 lb/in.<sup>2</sup> (345 N/mm<sup>2</sup>), however, Harker found that it only decomposed to xonotlite + silica above 350 °C. He added that the slope of the P-T curve should be negative, from volume considerations, although extremely steep. Present results show that truscottite is not formed above 367 °C. The phase assemblages formed from a C/S 0.8 mix at higher temperatures were, xonotlite + pseudowollastonite, and xonotlite + cristobalite + pseudowollastonite. It seems reasonable to assume from considerations of composition that silica was also present in the first assemblage but remained undetected because of its poor crystallinity. Muan and Osborn (1952) and Buckner and Roy (1955) have shown that pseudowollastonite is unstable below 1125 °C, yet Mackay and Taylor (1953), Meyer and Jaunarajs (1961), and Chalmers *et al.* (1964) have found that it is formed by the dry heating of gyrolite, truscottite, or reyerite at temperatures between 700 and 800 °C. It is thought that a close structural similarity exists between all the above minerals and pseudowollastonite and that the latter is formed preferentially by an oriented transformation. The same reaction would be expected to take place at lower temperatures under hydrothermal conditions. Previous equilibrium studies (Buckner, Roy, and Roy (1960)) have shown that wollastonite is not formed much below 400 °C at pressures between 5000 and 30 000 lb/in.<sup>2</sup> (35–207 N/mm<sup>2</sup>) and when formed is in the low-temperature  $\beta$ -modification. Clearly, pseudowollastonite from the decomposition of truscottite is a non-equilibrium phase, so that the most probable reaction representing the breakdown of truscottite under equilibrium conditions is:



*Foshagite and hillebrandite.* Several runs were carried out at a C/S ratio of 1.33, the results of which can be seen in table I. At temperatures between 190 and 250 °C, xonotlite + hillebrandite was the only assemblage found. This is in good agreement with earlier work as summarized by Roy and Harker (1960) and reinforces the above mentioned evidence on the stability of xonotlite at low temperatures. Above 260 °C, foshagite was formed reproducibly at pressures between 18 000 and 30 000 lb/in.<sup>2</sup> (124–207 N/mm<sup>2</sup>), along with a little xonotlite and an

unidentified phase that gave the following X-ray diffraction lines: 6.5 Å vw, 3.43 Å w, 3.31 Å mw, 3.19 Å mw, 2.89 Å m, 2.46 Å mw, 2.44 Å w and 1.72 Å mw. There was no evidence of the formation of kilchoanite in any of the preparations at this composition.

Little information has been reported on the stability range of foshagite, but Roy and Johnson (1965) placed its lowest equilibrium formation temperature at 295 °C. The present results, however, indicate that foshagite is formed at temperatures some 30 or 40 °C lower than this.

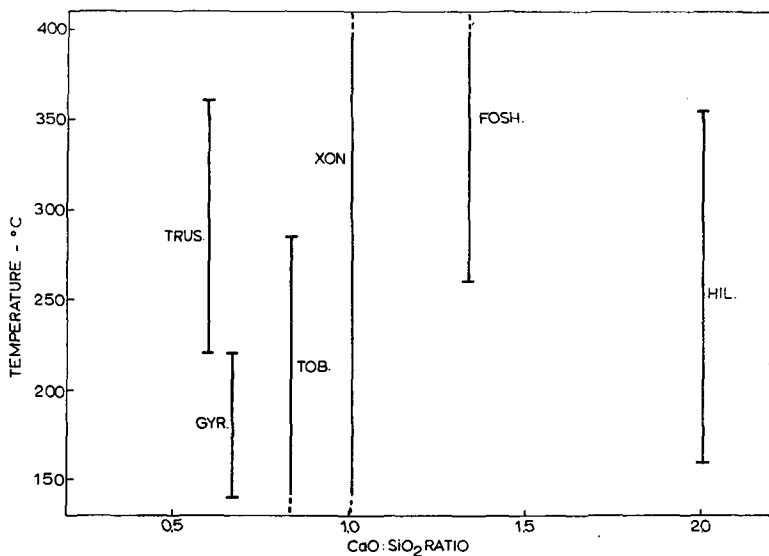


FIG. 2. Approximate temperature-stability ranges of compounds in the low-lime region of the CaO-SiO<sub>2</sub>-H<sub>2</sub>O system, up to 400° C at pressures between 5000 and 40 000 lb/in<sup>2</sup>.

*Silica-rich phases.* All runs from compositions below C/S 0.67 contained silica as one of the equilibrium phases, usually with gyrolite or truscottite. Phases more silica-rich than truscottite were not found, which confirms previous observations that, in the temperature and pressure range studied, all equilibria below C/S 1.0 can be expressed only in terms of truscottite, gyrolite, tobermorite, xonotlite, silica, and water.

The results of the whole study together with the findings of earlier workers are presented in fig. 2 in the form of composition *v.* stability range plots of the phases encountered.

*Acknowledgements.* I thank the Trustees of the British Museum for specimens of tobermorite, gyrolite, and truscottite and Mr. L. J. Larner for the chemical analysis of the gel starting materials.

*References*

- ANDERSON (T.), 1851. *Phil. Mag.*, ser. 4, vol. 1, p. 111.  
BARRER (R. M.), 1948. *Journ. Chem. Soc.*, p. 127.  
BUCKNER (D. A.) and ROY (R.), 1955. *Bull. Geol. Soc. Amer.*, vol. 66, p. 1536.  
— ROY (D. M.), and ROY (R.), 1960. *Amer. Journ. Sci.*, vol. 258, p. 132.  
CHALMERS (R. A.), FARMER (V. C.), HARKER (R. I.), KELLY (S.), and TAYLOR (H. F. W.), 1964. *Min. Mag.*, vol. 33, p. 821.  
HARKER (R. I.), 1960. *Bull. Geol. Soc. Amer.*, vol. 71, p. 1881.  
— 1964. *Journ. Amer. Ceram. Soc.*, vol. 47, p. 521.  
HEDDLE (M. F.), 1880. *Min. Mag.*, vol. 4, p. 119.  
HELLER (L.) and TAYLOR (H. F. W.), 1951. *Journ. Chem. Soc.*, p. 2397.  
HÖVIG (P.), 1914. *Jaarb. Mijnwezen Nederland. Oost-Indië, Batavia*, 1914, vol. 41 (for 1912), p. 202.  
MACKAY (A. L.) and TAYLOR (H. F. W.), 1953. *Min. Mag.*, vol. 30, p. 80.  
— — 1954. *Ibid.*, vol. 30, p. 450.  
MEYER (J. W.) and JAUNARAJA (K. L.), 1961. *Amer. Min.*, vol. 46, p. 913.  
MINATO (H.) and KATO (A.), 1967. *Min. Journ. (Japan)*, vol. 5, p. 144.  
MUAN (A.) and OSBORN (E. F.), 1952. *Industrial Heating*, vol. 19, p. 1293.  
ROY (D. M.) and HARKER (R. I.), 1960. *Proc. 4th Internat. Symp. Chem. Cements*, vol. 1, p. 196. Published 1962.  
— and JOHNSON (A. M.), 1965. *Proc. Internat. Symp. Autoclaved Calcium Silicate Building Products*, p. 114. Published 1967.  
STRUNZ (H.) and MICHEESEN (H.), 1958. *Naturwiss.*, vol. 45, p. 515.  
TAYLOR (H. F. W.), 1950. *Journ. Chem. Soc.*, p. 3682.  
— 1962. *Journ. Appl. Chem.*, vol. 2, p. 3.  
— and HOWISON (J. W.), 1956. *Clay Min. Bull.*, vol. 3, p. 98.  
— 1960. *Proc. Internat. Symp. Chem. Cements*, vol. 1, p. 167. Published 1962.  
[VOLKONSKIИ (B. V.), KOHOBABOB (П. Ф.), and TOLMACHEB (G. П.)] Волконский (Б. В.), Коновалов (П. Ф.) и Толмачев (Г. П.), 1964. Эксперимент в Техн. Минералог. и петрогр. по материалам Совещ. 7, Львов, стр. 79.

[*Manuscript received 29 March 1968*]

---