

# Reactions in the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ . Hydrothermal treatment of some compositions on the joins $\text{Ca}_3\text{Si}_2\text{O}_7\text{-Mg}_3\text{Si}_2\text{O}_7$ and $\text{Ca}_2\text{SiO}_4\text{-Mg}_2\text{SiO}_4$

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**SUMMARY.** The effects of hydrothermal treatments on gel mixtures and synthetic minerals in the  $\text{C}_3\text{S}_2\text{-M}_3\text{S}_2$  and  $\text{C}_2\text{S-M}_2\text{S}$  regions of the  $\text{CaO-MgO-SiO}_2$  system have been investigated. The products formed in the temperature range 180–350 °C at pressures up to 220 N/mm<sup>2</sup> were identified.<sup>1</sup> The reactants generally behaved as simple mixtures of binary silicates and their products agreed well with existing data for reactions in the  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  and  $\text{MgO-SiO}_2\text{-H}_2\text{O}$  systems. An unidentified phase that resulted from the hydration of åkermanite could be a new compound in the quaternary  $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$  system. There was no evidence to indicate that a magnesium analogue of kilchoanite can be formed from materials that are isostructural with  $\gamma\text{-Ca}_2\text{SiO}_4$ .

**RESULTS** of earlier studies in the  $\text{Ca}_2\text{SiO}_4\text{-SiO}_2\text{-H}_2\text{O}$  region of the  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  system by Speakman and Taylor (1965, 1967) and Speakman (1968) showed that a material consisting largely of kilchoanite was formed when a mixture of  $\gamma\text{-Ca}_2\text{SiO}_4$  and quartz, having an over-all  $\text{CaO/SiO}_2$  ratio of 1.5, was treated hydrothermally at 180 °C. The thermodynamic stability of kilchoanite formed at low temperatures and pressures has been the subject of much discussion (Speakman and Taylor, 1967; Roy and Harker, 1960; Roy and Johnson, 1965) and although the point has not been finally settled, current opinion favours the view that it is a non-equilibrium phase under these conditions. The explanation for the readiness with which  $\gamma\text{-Ca}_2\text{SiO}_4$  can form kilchoanite is almost certainly connected with the structural and chemical similarities that exist between them. The equilibrium products xonotlite and hillebrandite, on the other hand, have very different crystal structures.

The present work was undertaken to investigate the possible formation of a magnesium substituted kilchoanite from forsterite and monticellite, which are isostructural with  $\gamma\text{-Ca}_2\text{SiO}_4$ . The study was later extended to include an examination of the products formed from several other compositions on the join  $\text{Ca}_3\text{Si}_2\text{O}_7\text{-Mg}_3\text{Si}_2\text{O}_7$ . Four compositions were thought to be sufficient to give all the information required to detect and characterize a magnesium analogue of kilchoanite and any other new phases formed in this particular region. More emphasis was placed on the nature of the starting materials and on their influence on the type of products formed than on the number of compositions examined, since the formation of kilchoanite is believed to be a structure-dependent phenomenon and the starting material all important.

<sup>1</sup> 1 N/mm<sup>2</sup> = 10 bars = 9.869 atm.

The published literature dealing with hydrothermal reactions in both the CaO-SiO<sub>2</sub>-H<sub>2</sub>O and MgO-SiO<sub>2</sub>-H<sub>2</sub>O systems is very extensive, particularly concerning equilibrium products (Taylor, 1960; Bowen and Tuttle, 1949; Kitahara, Takenouchi, and Kennedy, 1966). However, experiments were still carried out on mixes with compositions representing the end-members of the two joins because of the possibility of formation of new non-equilibrium products.

Data on reactions in the CaO-MgO-SiO<sub>2</sub>-H<sub>2</sub>O system are very scant and appear to be confined to reports on the hydration reactions of particular calcium magnesium silicates that occur in slags, that is monticellite and åkermanite (Budnikov, Gorshkov, and Khmelevskaya, 1960; Gorshkov and Khmelevskaya, 1960), and to the observations made in certain subsystems containing CaO, MgO, SiO<sub>2</sub>, and H<sub>2</sub>O that have been encountered during more comprehensive studies in genetic geology (Nolan and Edgar, 1963; Nolan, 1966).

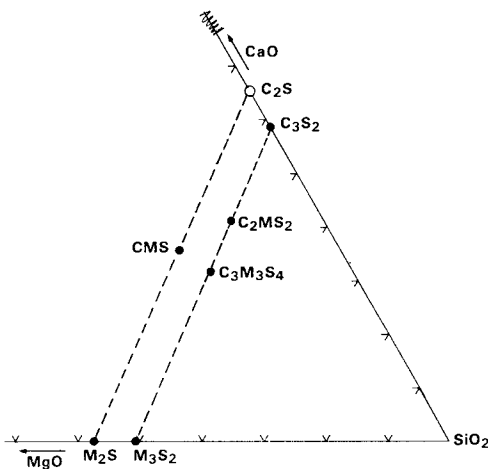


FIG. 1. Full circles represent compositions studied.

that have been encountered during more comprehensive studies in genetic geology (Nolan and Edgar, 1963; Nolan, 1966).

*Experimental.* The region of the CaO-MgO-SiO<sub>2</sub> system that includes the compositions studied is shown in fig. 1 and the types of starting materials used were:

$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2}$	Synthetic minerals	Crystalline mixes	Gels
1.5	{ rankinite åkermanite	monticellite + SiO <sub>2</sub> forsterite + SiO <sub>2</sub>	{ 3CaO . 2SiO <sub>2</sub> 2CaO . MgO . 2SiO <sub>2</sub> 3CaO . 3MgO . 4SiO <sub>2</sub> 3MgO . 2SiO <sub>2</sub>
2.0	{ monticellite forsterite		2MgO . SiO <sub>2</sub>

The synthetic magnesia-containing silicate minerals were prepared from A.R. grade CaCO<sub>3</sub> and MgCO<sub>3</sub> and quartz sand (99.8 % SiO<sub>2</sub>) ground to pass a 300-mesh sieve. For åkermanite, the oxide mix was melted at 1500 °C and cooled to a glass, which, after grinding, was annealed at 1400 °C. Several cooling, grinding, and annealing cycles were required before pure åkermanite was obtained. For monticellite, after heating the oxide components at 1420 °C for three days, with daily grinding to pass a 300-mesh sieve, the product was found to be monticellite without any traces of contaminants. For forsterite, the components were sintered at 1550 °C for 48 hours, cooled, crushed, and reheated at the same temperature for a further 48 hours. The process was repeated until only forsterite could be detected in the X-ray powder pattern.

Rankinite,  $3\text{CaO} \cdot 2\text{SiO}_2$ , was prepared by heating synthetic kilchoanite at  $1200^\circ\text{C}$  for 24 hours, the kilchoanite having been synthesized as described earlier from  $\gamma\text{-Ca}_2\text{SiO}_4$  and quartz.

Gel starting materials were prepared by first decomposing  $\text{CaCO}_3$  (when required) in nitric acid, dissolving magnesium nitrate in the resulting solution, then adding the required amount of colloidal silica (Syton 2X).<sup>1</sup> After evaporating the mixtures to dryness the crushed powders were heated to  $680^\circ\text{C}$  for three hours, during which time the nitrates were removed.

Once prepared, the starting materials were treated hydrothermally by one of the two following standard methods: About 0.5 g of the material was placed in a covered silver tube and, along with a measured amount of water, enclosed in a simple steel bomb of the type developed by Barrer (1948) from the earlier descriptions of Morey and Ingerson (1937). Sufficient water was added to develop saturated steam pressures at the temperatures used. The bombs were either stood in an electric oven or placed in vertical muffle furnaces for the required reaction times. They were then rapidly quenched in water and the contents filtered and washed with acetone in carbon-dioxide-free air.

High-pressure experiments were carried out by enclosing the specimens in sealed gold tubes and subjecting them to externally applied hydrostatic pressures in a cold-seal apparatus (Roy and Osborn, 1952). After reaction the pressure vessels were *P-T* quenched and the products removed from the gold tubes.

Samples prepared by both methods were placed in a desiccator and dried over anhydrous magnesium perchlorate under vacuum for 48 hours. X-ray powder diffraction patterns of all specimens were obtained using a 114.6-mm quadruple focusing Guinier camera and  $\text{Cu-K}\alpha$  radiation. Optical examination of the specimens gave very little additional information because of the extremely small particle size.

*Discussion.* The reaction conditions and products detected by X-rays for all the materials used in this study are presented in table I. It will be noted that serpentine ( $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) was formed over a wide range of conditions from almost all compositions containing MgO. It occurred in all degrees of crystallinity from materials showing only three broad, diffuse X-ray bands at  $5.2\text{--}4.4 \text{ \AA}$ ,  $2.6\text{--}2.45 \text{ \AA}$ , and  $1.55\text{--}1.52 \text{ \AA}$  in preparation 48, to well-ordered products having 10 or 11 of the strongest lines of natural serpentine in preparation 63. However, it was not possible to ascertain which member of the serpentine group was present in any of the preparations by X-ray methods alone. Microscopic examination did not reveal any appreciable amounts of fibrous crystals and the mean refractive index of 1.55 was not sufficiently specific to differentiate between chrysotile and antigorite. Further evidence obtained from DTA traces indicated that the magnesium silicate hydrate phase in those specimens examined was chrysotile; an observation which is in agreement with results of earlier studies in this ternary system (Bowen and Tuttle, 1949).

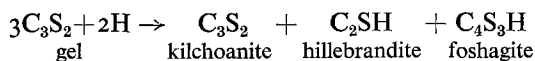
In several cases the X-ray powder data were difficult to resolve unequivocally because of the presence of five or even six phases, some of which were in a poor state

<sup>1</sup> Monsanto Chemical Co.

of crystallinity. A gel-like nature is typical of some of the reaction products in this system and they often remain badly crystallized even after autoclaving at saturated steam pressures for many months. The rates of reaction under the saturated steam conditions used were often very slow particularly in the case of the well-crystallized starting materials. However, these difficulties were only encountered in the identification of minor phases and it is believed that the over-all reaction processes discussed below are substantially correct.

The results can best be discussed in terms of the particular starting material compositions and the effects of time, temperature, and water vapour pressure on them.

*C<sub>3</sub>S<sub>2</sub> composition.*<sup>1</sup> Kilchoanite was found to be the major phase formed in all preparations in which gels were used and in fact was almost the sole product at 300 °C. In preparations 1 and 2 foshagite (C<sub>4</sub>S<sub>3</sub>H) and hillebrandite (C<sub>2</sub>SH) were also formed, probably in accordance with the reaction:



Scawtite (7CaO·6SiO<sub>2</sub>·CO<sub>2</sub>·2H<sub>2</sub>O), which results from a small amount of almost unavoidable carbonation, is a common contaminant in hydrothermal reactions involving lime and silica.

Rankinite was extremely slow to react under saturated steam conditions and produced only two very weak powder lines at 3·33 Å and 3·04 Å after 90 days at 180 °C. Even after 92 days at 300 °C just a trace of a second phase (hillebrandite) could be detected: hillebrandite was possibly formed from a small amount of C<sub>2</sub>S impurity in the rankinite. High pressure and temperature served to break up rankinite to kilchoanite, foshagite, and a third unidentified phase (A) the X-ray pattern of which is recorded in table II.

The formation of kilchoanite both from gel and from rankinite is remarkable since, particularly at temperatures below 350 °C, it is regarded as a non-equilibrium phase and has previously only been prepared under these conditions from  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> to which it has a close structural resemblance. It is possible that the well-established effect of the formation of metastable products from gel starting materials may explain the persistence of kilchoanite for such long periods at 180 °C, but its independent synthesis from  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub>, rankinite, and gels indicates that the position regarding the equilibrium assemblages hillebrandite+xonotlite or kilchoanite+H<sub>2</sub>O at CaO/SiO<sub>2</sub> = 3/2 is far from resolved.

*M<sub>3</sub>S<sub>2</sub> composition.* The only detectable product from reactions carried out at this composition using gels and forsterite+quartz mixes was serpentine. The degree of crystallinity increased with both time and temperature, but after 56 days at 300 °C showed only six bands on the X-ray pattern. Bowen and Tuttle (1949) and Kitahara *et al.* (1966) have shown that serpentine is the equilibrium product for temperatures up to ~ 500 °C at this composition.

Forsterite reacted very slowly with silica and was apparently still the major phase

<sup>1</sup> C = CaO, S = SiO<sub>2</sub>, M = MgO, H = H<sub>2</sub>O; i.e. C<sub>3</sub>S<sub>2</sub> = 3CaO·2SiO<sub>2</sub>.

TABLE I. *Details of hydrothermal preparations.* 1 N/mm<sup>2</sup> = 10 bars = 9.869 atm.

No.	Composition	Starting material]	Preparation conditions			Phases detected by X-rays
			Temp. °C	Pressure N/mm <sup>2</sup>	Time days	
1	3CaO.2SiO <sub>2</sub>	gel	180	1.0	15	Kil+fosh+hill?+tr. scaw
2	"	"	180	1.0	56	" " " " "
3	"	"	300	8.6	16	Kil+tr. xon+tr. fosh?
4	"	"	300	8.6	56	" " " "
5	"	Rankinite	180	1.0	15	Rank+tr. hill "
6	"	"	180	1.0	42	" "
7	"	"	180	1.0	90	" "
8	"	"	300	8.6	16	" "
9	"	"	180	1.0	42	" "
			300	8.6	47	" "
10	"	"	300	8.6	92	" "
11	"	"	202	149.6	14	" "
12	"	"	250	182.0	14	" "
13	"	"	357	221.3	21	Kil+fosh+A
14	2CaO.MgO.2SiO <sub>2</sub>	gel	180	1.0	14	Kil+serp+fosh+l. scaw+l. bruc?
15	"	"	180	1.0	56	" "
16	"	"	300	8.6	14	Kil+xon+serp+fosh+l. scaw+l. bruc
17	"	"	300	8.6	56	Kil+xon+serp+fosh+tr. scaw+l. bruc?
18	"	Åkermanite	180	1.0	3	Åkerm
19	"	"	180	1.0	7	"
20	"	"	180	1.0	35	Hill+serp+B+åkerm+tr. scaw
21	"	"	180	1.0	91	Hill+serp+B+tr. scaw
22	"	"	300	8.6	35	Åkerm
23	"	"	300	8.6	88	Åkerm+C+l. serp+l. fosh?
24	"	"	243	183.4	41	Mont+xon+fosh+scaw
25	"	"	355	173.1	41	Fosh+serp+hill.
26	CaO.MgO.SiO <sub>2</sub>	Monticellite	180	1.0	3	Mont
27	"	"	180	1.0	7	"
28	"	"	180	1.0	35	Mont+tr. serp.
29	"	"	180	1.0	91	Mont+l. serp+tr. hill
30	"	"	300	8.6	49	Serp+mont+bruc+tr. hill?
31	3CaO.3MgO.4SiO <sub>2</sub>	gel	180	1.0	15	Serp+kil+xon+scaw+tr. hill?
32	"	"	180	1.0	56	Kil+serp+fosh+l. scaw
33	"	gel*	180	1.0	15	Fosh+xon+l. serp+l. scaw
34	"	gel*	180	1.0	44	Fosh+xon+l. scaw+l. serp.
35	"	gel	300	8.6	15	Xon+serp+l. kil+tr. scaw+tr. hill?
36	"	"	300	8.6	56	Serp+xon+tr. kil+tr. hill
37	"	gel*	300	8.6	15	Serp+xon+l. kil+tr. scaw+tr. hill.

No.	Composition	Starting material	Preparation conditions			Phases detected by X-rays
			Temp. °C	Pressure N/mm <sup>2</sup>	Time days	
38	3CaO.3MgO.4SiO <sub>2</sub>	gel*	300	8.6	44	Serp+xon+fosh+l. kil+l. scaw
39	"	gel	249	99.3	29	Serp+xon+scaw+l. kil+tr. hill?
40	"	Monticellite + quartz	180	1.0	3	Mont+Q+tr. gy
41	"	"	180	1.0	7	Mont+Q+gy
42	"	"	180	1.0	35	Mont+xon+gy+l. serp+tr. scaw
43	"	"	180	1.0	72	Mont+xon+serp+l. scaw
44	"	"	180	1.0	128	Mont+xon+serp
45	"	"	300	8.6	35	" " "
46	"	"	275	139.3	34	Xon+mont+scaw+serp
47			290	206.2	25	Scaw+serp+hill+fosh?
48	3MgO.2SiO <sub>2</sub>	gel	180	1.0	14	Serp
49	"	"	180	1.0	56	"
50	"	"	300	8.6	18	"
51	"	"	300	8.6	56	"
52	"	Forsterite + quartz	180	1.0	6	Forst+Q+tr. serp
53	"	"	180	1.0	42	Forst+l. Q+tr. serp
54	"	"	300	8.6	16	Forst+serp
55	"	"	180	1.0	90	" "
56	"	"	300	8.6	52	" "
57	"	"	251	180.6	14	" "
58	"	"	304	199.9	21	" "
59	"	"	349	199.3	21	" "
60	2MgO.SiO <sub>2</sub>	gel	180	1.0	18	Serp+bruc
61	"	"	180	1.0	56	" "
62	"	"	300	8.6	16	" "
63	"	"	300	8.6	56	" "
64	"	Forsterite	180	1.0	6	Forst
65	"	"	180	1.0	42	"
66	"	"	180	1.0	90	"
67	"	"	300	8.6	64	Serp+forst+bruc

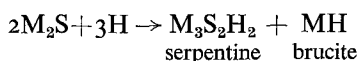
\* Equi-weight mixture of C<sub>3</sub>S<sub>2</sub> and M<sub>3</sub>S<sub>2</sub> gels.

Key to phases (l. = little; tr. = trace).

Åkerm	Åkermanite	Kil	Kilchoanite	Serp	Serpentine
Bruc	Brucite	Mont	Monticellite	Xon	Xonotlite
Forst	Forsterite	Q	Quartz	A	} unidentified phases (see text)
Fosh	Foshagite	Rank	Rankinite	B	
Gy	Gyrolite	Scaw	Scawtite	C	
Hill	Hillebrandite				

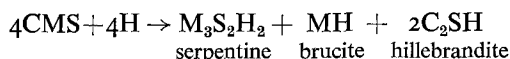
after all the quartz had disappeared. It seems that due to the greater reactivity of the quartz a 'high-silica serpentine' was first formed with a composition probably approaching that of talc (there was an indication of the 9.5 Å talc line in one or two preparations) and this by reaction with more forsterite was slowly reaching the true stoichiometric serpentine composition. Such materials having compositions between talc and serpentine yet showing the powder pattern of the latter have been described by Kalousek and Mui (1954).

*M<sub>2</sub>S composition.* When both gels of this composition and forsterite were treated hydrothermally between 180 and 300 °C for times up to 90 days the only detectable reaction products were serpentine and brucite (Mg(OH)<sub>2</sub>):

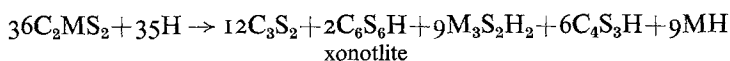
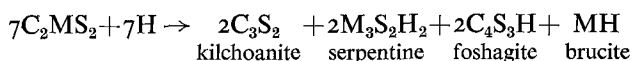


This is in complete agreement with the equilibrium data cited above, which indicates that no ternary phases more magnesia-rich than serpentine are formed in the system.

*CMS composition.* Monticellite, like forsterite, reacted very slowly at 180 °C, forming only small amounts of serpentine and hillebrandite after 91 days. After 49 days at 300 °C however, hydration had proceeded to an advanced stage, which resulted in the formation of appreciable quantities of brucite. The hydration of monticellite over this temperature range can be represented as:



*C<sub>2</sub>MS<sub>2</sub> composition.* Gels and synthetic åkermanite were used as the starting materials in this part of the work. Kilchoanite was the major product at both 180 and 300 °C, while serpentine, foshagite, xonotlite, and possibly brucite could be identified in varying minor amounts. Xonotlite was only found in preparations 16 and 17 made at 300 °C. Two possible reaction schemes can be suggested to explain these assemblages, one for 180 °C the other for 300 °C:



The hydrothermal reactions of åkermanite are quite varied and depend on the temperatures and pressures used. Under saturated steam pressures at 180 °C hillebrandite, serpentine, and an unidentified phase (B) result. The X-ray powder pattern of B, which can be seen in table II, does not correspond to that of any known calcium silicate hydrate, magnesium silicate hydrate, or any common binary compound of CaO or MgO. It is possible that it is due to a quaternary calcium magnesium silicate hydrate compound, only one of which (tremolite) has so far been characterized in the literature. However, the fact that neither the gel of this composition nor any of the other ternary starting materials used in this work gave rise to similar patterns would seem

to indicate that it would be a non-equilibrium product possibly related in structure to åkermanite. It is impossible to speculate further on the identity of this product without carrying out a much more detailed examination of preparations containing it.

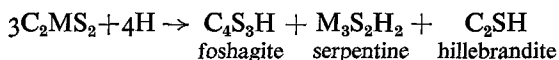
At 300 °C and saturated steam pressure åkermanite appears to react more slowly and forms serpentine and another unidentified phase (C)—see table II. In the absence of more detailed information it is not possible to draw any definite conclusions about

TABLE II. *X-ray powder spacings for unidentified phases A, B, and C*

A		B		C		A		B		C	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
4.08 Å	mw	—	—	—	—	2.38	w	2.37	w	2.35	w
—	—	—	—	3.84 Å	w	—	—	2.29	vw	2.28	vw
3.40	m	3.37 Å	vw	3.30	vw	—	—	2.22	vw	2.22	mw
3.21	vs	3.20	vw	3.19	w	—	—	2.17	vw	—	—
3.04	w	3.05	w	3.01	vw	2.11	vw	—	—	—	—
2.99	vw	—	—	—	—	1.995	ms	—	—	—	—
2.95	w	2.95	m	—	—	—	—	1.955	w	—	—
2.84	mw	2.84	mw	2.85	vw	1.840	vw	1.860	vw	1.860	w
2.80	s	—	—	—	—	—	—	1.840	m	—	—
2.71	vw	—	—	2.75	w	1.825	mw/d	1.820	vw	—	—
2.65	vw	—	—	—	—	1.748	vw	—	—	—	—
—	—	2.59	vw	—	—	1.720	w	—	—	—	—
2.54	vw	2.55	vw	2.56	mw	—	—	—	—	1.680	vw
2.46	mw	2.45	w	2.45	w	—	—	—	—	1.670	w
2.44	vw	—	—	—	—	—	—	1.600	w	—	—

this material, except that it is not an established binary or ternary phase in either the CaO-SiO<sub>2</sub>-H<sub>2</sub>O or MgO-SiO<sub>2</sub>-H<sub>2</sub>O systems. It could therefore be a quaternary calcium magnesium silicate hydrate compound, and might have some relationship to 'phase B'.

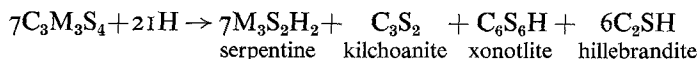
At higher pressures the behaviour of åkermanite again depends on the temperature. At 243 °C monticellite, xonotlite, and foshagite are formed whereas at 355 °C the products are foshagite, serpentine, and hillebrandite. The latter of these reactions can be represented by the equation:



*C<sub>3</sub>M<sub>3</sub>S<sub>4</sub> composition.* Three types of starting material were used: homogeneous lime-magnesia-silica gel, an equi-weight mixture of C<sub>3</sub>S<sub>2</sub> and M<sub>3</sub>S<sub>2</sub> gels, and monticellite+quartz. Assemblages involving serpentine, xonotlite, kilchoanite, foshagite, and hillebrandite were obtained with kilchoanite being formed preferentially from the homogeneous gel at 180 °C as against foshagite or xonotlite from the mixed gel. Increase in pressure to 99.3 N/mm<sup>2</sup> (preparation 39) has no effect on the identity of the products at this composition. The following equation illustrates the formation of

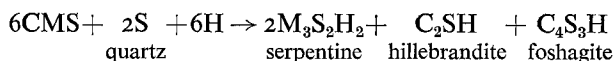


the reaction products found in preparations 31, 35, 36, 37, and 39 and seems to be typical of the group as a whole:



The apparent deviations from stoichiometry shown by certain assemblages (e.g. preparations 32–4) are possibly due to a certain amount of substitution of  $\text{Ca}^{2+}$  for  $\text{Mg}^{2+}$  and vice versa, to slight compositional variability in the phases detected, or to non-identification of minor products of poor crystallinity.

In mixtures with silica, monticellite reacted very slowly at saturated steam pressures. Raising the pressure to 206 N/mm<sup>2</sup>, however, brought about its complete decomposition within 25 days. The course of the reaction is governed by the rapid dissolution of quartz, which initially causes the formation of the silica-rich calcium silicate hydrate gyrolite ( $\text{C}_2\text{S}_3\text{H}_2$ ). As more lime and magnesia are liberated from the hydrating monticellite, serpentine is formed and gyrolite gives way to the more lime-rich xonotlite. All gyrolite disappears between 35 and 72 days at 180 °C and in less than 35 days at 300 °C. At high pressures (preparation 47) hillebrandite and foshagite, which with serpentine probably constitute the final equilibrium assemblage at 290 °C, form within 25 days. This can be represented as:



Previous work on the hydration of slag minerals has been mainly concerned with reactions at ambient temperatures and the effects of various activators, such as lime and gypsum, on the hardening of set pastes. In this connection there seems to have been little effort devoted to the identification of phases formed under autoclave conditions. However, Budnikov *et al.* (1960) state that åkermanite and a glass of the same composition form  $\gamma$ - $\text{C}_2\text{S}$  hydrate ( $\text{C}_2\text{SH}(\text{C})$ ) and serpentine on autoclaving at 185 °C for 8 hours. Since  $\gamma$ - $\text{C}_2\text{S}$  hydrate has recently been shown to be a mixture of  $\text{Ca}_8\text{Si}_5\text{O}_{18}$  and calcio-chondrodite,  $\text{Ca}_5\text{Si}_2\text{O}_8(\text{OH})_2$  (Speakman and Taylor, 1967) it appears that these phases along with serpentine are the main products under these short-duration reaction conditions. In the present study neither of these two compounds nor the closely related kilchoanite could be detected in any of the åkermanite hydration products.

As a result of a similar study to that carried out by the above authors Butt *et al.* (1960) concluded that they had prepared 'åkermanite hydrate' from the mineral and a glass of the same composition, but no further data on characterizing the material were reported.

*Conclusions.* The hydrothermal reactions of materials with compositions in the range  $\text{C}_3\text{S}_2$ – $\text{M}_3\text{S}_2$  and  $\text{C}_2\text{S}$ – $\text{M}_2\text{S}$  have been studied in the range 180–350 °C and the products defined. In almost all cases the ternary lime–magnesia–silica compositions behave as simple mixtures of calcium and magnesium silicates. The phases encountered include xonotlite, foshagite, kilchoanite, hillebrandite, and serpentine, all of which are either equilibrium phases under these conditions in their respective ternary systems or are

frequently encountered metastable compounds. The formation of kilchoanite from rankinite and from all the lime-containing gels is of considerable interest and could help to throw more light on its standing as an equilibrium phase at temperatures below 350 °C.

The results obtained from reactions of forsterite and quartz show conclusively that at least in suspensions no magnesium analogue of kilchoanite is formed. This is probably partly due to the rapid dissolution of the quartz, which facilitates the extraction of magnesia from the forsterite and results in the formation of serpentine.

There is some evidence to support the belief that a quaternary calcium magnesium silicate hydrate phase can be prepared from åkermanite at 180–300 °C, although its existence has by no means been confirmed. It is worthy of note that the only other reported preparation of such a compound (except those for tremolite) also resulted from a reaction of åkermanite.

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